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Reactions of Hydrosilanes with Transition-Metal Complexes: Formation of Stable Transition-Metal Silyl Compounds

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Contents

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I. Introduction

Transition-metal silyl chemistry has grown immensely over the past two decades and research continues to prosper in this area. The field of silylmetal chemistry began with the synthesis of the iron complex, $Cp(OC)_2FeSiMe_3$, by Wilkinson in 1956 but development lagged during the next decade and was ignited in the 1970s. Since that time a number of novel complexes have been prepared and industrial

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applications such as hydrosilation of olefins have been developed. Silylmetal complexes are now known for nearly all of the transition metals and a variety of ligands at the metal center and silicon have been utilized. A number of reviews are available covering earlier work in this area.[1−5]

There are a variety of synthetic methods available for the preparation of complexes containing a metal−silicon bond and these are described in more detail in section II (Background). The most common and versatile method involves the oxidative addition of a Si−H bond in a hydrosilane to a transition-metal center. The intent of this review is to cover reports from 1981 through 1997 on the reaction of hydrosilanes with metal complexes. In the majority of cases, complexes that were isolated and characterized are emphasized. Thus, the vast literature on hydrosilation reactions is not included unless silylmetal complexes were separated from the reaction mixtures. In several cases the complexes were only sufficiently stable to be characterized in solution and these complexes are also included. About 400 references reported stable silylmetal complexes prepared from hydrosilanes during this 16-year period.

The goal of this review is to provide a comprehensive study of the types of metal precursors used in the oxidative addition reactions and to give a detailed description of the products formed including techniques used to characterize the complexes. The review is divided into several sections starting with the Background (section II). Section II is intended to provide the reader with a brief overview of the major synthetic methods available for the preparation of silylmetal complexes as well as relevant information regarding oxidative addition reactions of hydrosilanes. The synthesis section (section III) describes in detail the stable products from oxidative addition of silanes (SiH_4, I°, II°, and III°) to transition-metal complexes. Tables 1−4 provide characterization data for each compound entry according to the type of silane and are organized according to triad starting with the early transition metals. At the end of each triad there is a section containing di- or polynuclear complexes.

Following the synthesis section is a discussion on the solid-state structures of a number of silylmetal complexes (section IV) and Table 5 summarizes structural information (TM−H, Si−H, and TM−Si bond distances) for complexes reported in this review. Thus, all of the complexes shown in Tables 1−4 that were structurally characterized by X-ray crystallography are listed in Table 5. Additional data for TM−Si bond distances for complexes prepared by other routes are reported in the footnotes for Table 5.

A discussion of NMR spectroscopic data is given in section V, and complexes that show fluxional behavior are discussed in some detail in this section. Section VI is an overview of nonclassical silane metal complexes (σ-type, η^2-$HSiR_3$) first describing the spectroscopic characterization (Table 7) and then X-ray structural data for these complexes (Table 8). A subsection then describes β-agostic (M−X−*Si*−*H*) systems (Tables 10 and 11). Structures for selected complexes will appear at the end of Tables 1−5, 7, 8, and 11. Section VII describes theoretical calculations that have been reported relating to silane oxidative addition reactions to metal centers. The generality of oxidative addition for other Si−X bonds is demonstrated briefly in section VIII.

This is a fascinating and active area of chemistry but many questions remain unsolved. The conclusion to this review addresses some of the general observations found with silane oxidative addition reactions and some possible future pathways that investigators could explore. This review is intended to further stimulate interest in this area and provide the reader with an idea of the type of research that has been performed and to provide a starting point for future studies.

II. Background

Hydrosilanes are useful synthetic precursors for the preparation of a number of silicon containing compounds including silylmetal complexes.[6] Oxidative addition or metathesis of a Si−H bond in a hydrosilane (including SiH_4, $RSiH_3$, R_2SiH_2, and R_3SiH) to a metal center is known for nearly all of the transition-metal elements and provides stable complexes containing a TM−Si bond.

Oxidative addition reactions to a metal center increase the formal oxidation state and coordination number of the metal.[7] The reaction may be reversible resulting in reductive elimination of the previously added species. These are an important class of reactions for organometallic chemists since many catalytic and stoichiometric reactions involve oxidative addition and/or reductive elimination steps. The oxidative addition of H_2 is thermodynamically favorable but addition of a C−H bond is generally restricted to intramolecular reactions with activated C−H bonds. Intramolecular addition of arene C−H bonds (orthometalation) has been known for two decades.[8] On the other hand, the interaction of hydrosilanes with transition metals is quite facile and generally occurs under mild conditions. Comparison of the relative bond energies involved in C−H and Si−H activation to Pt shows that the driving force for addition of Si−H bonds to the metal is due to the formation of a strong Pt−Si bond compared to a weaker Pt−C bond and the breaking of a weaker sp^3-Si−H bond compared to a slightly stronger sp^3-C−H bond.[9] The addition was found to be exothermic with a small activation barrier. However, it must be recognized that Si−H bond strengths vary with substituents.[10] For example, the following values have been reported for $HSiR_3$: 74.6 kcal/mol for R = Me, 96.8 kcal/mol for R = OEt, and 100 kcal/mol for R = F.[10b] Later, Ding and Marshall summarized seven *different* values obtained from the literature for Me_3SiH with their measurement being the highest at 95.1 ± 1.4 kcal/mol.[10c] Little experimental data have been reported for TM−Si bond energies. Recently, Puddephatt and co-workers reported a Pt−Si bond strength of 55.7 ± 3.3 kcal/mol for $[PtIMe_2(SiMe_3)(bpy)]$ (bpy = 2,2′-bipyridyl), nearly 24 kcal/mol stronger than the $Pt-CH_3$ bond![11] The bond energies for early TM−Si bonds are expected to be

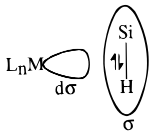


Figure 1. M−(η^2-HSi) σ-bonding interaction.

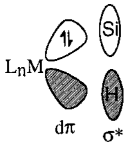
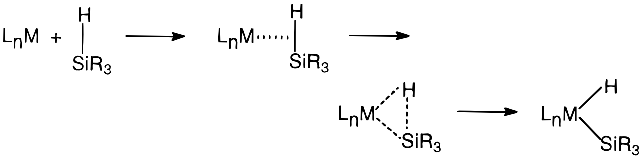


Figure 2. M−(η^2-HSi) π-back-bonding interaction.

lower than late transition metals. Although no experimental bond energy data exist, significantly longer TM−Si bond lengths are found for early transition metals supporting a weaker interaction.

The reaction of a hydrosilane with a metal center can proceed to give a “classical” (two-center, two-electron) or a “nonclassical” (three-center, two-electron) interaction along an oxidative addition pathway (Scheme 1).[1d,5] The “nonclassical” interaction involves a partial or arrested addition of the Si−H bond to the metal center. Other descriptive terms have been used to describe the “nonclassical” interaction such as σ-complex or agostic interaction. A σ-complex can be an intermediate or a transition state in an oxidative addition reaction or as in many cases an isolated complex. Schubert has proposed that the oxidative addition pathway is initated when the H atom in the Si−H unit approaches the metal center. The Si−H component then pivots to place the Si atom near the metal increasing the TM−Si interaction and weakening the Si−H bond.[5] A number of these complexes have been characterized and are described in detail in section VI.

Scheme 1



The orbital interactions that occur between the Si−H unit and the metal center can reveal the extent of oxidative addition for nonclassical complexes. A σ-interaction can exist between a metal d-orbital and the Si−H σ-bonding orbital as shown in Figure 1. A π-component may arise when a metal dπ-orbital interacts with the Si−H σ*-antibonding orbital (Figure 2). If sufficient π-back-bonding occurs then weakening of the Si−H bond ensues and can result in full oxidative addition of the Si−H bond. The greater basicity of the Si−H bond relative to the H−H or C−H bond makes the Si−H unit a better σ-donor.[7a] In addition, the greater accessibility of the σ*-orbital allows the Si−H unit to be a better π-acceptor. The nature of the σ-donor or σ*-acceptor ability of the Si−H unit potentially may be tuned by the substituents on silicon.

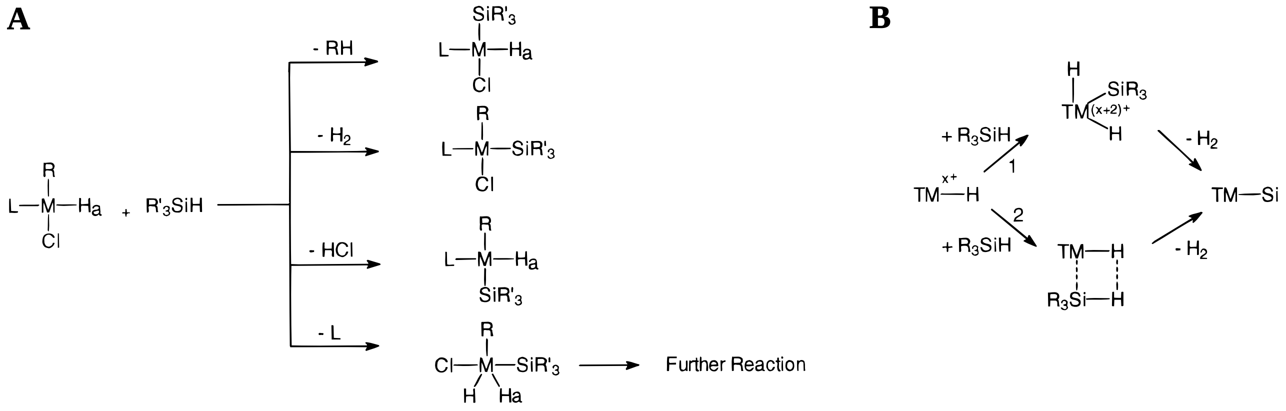
The substituents at either silicon or the metal center can have an impact on the oxidative addition pathway. Although silanes bearing either electronegative or electron-donating groups have been reported to react with transition-metal centers it is generally observed that electron-rich late-transition-metal centers (groups 9 and 10) or electron-withdrawing groups at silicon (such as $SiCl_3$) tend to result in full oxidative addition of the silane. In general, sterically undemanding and electronegative groups bound to silicon favor an oxidative addition reaction. Increased electron density at the metal center or electrophilic behavior at silicon increases the d-back-bonding and leads to full oxidative addition. Although reports are limited, other Si−X bonds are known to add to metal centers including Si−C, Si−Si, and Si−Y (Y = halogen).[1d,12a,b] Reactions involving Si−X bonds will be introduced briefly in section VII.

A number of calculations and experiments to probe the nature of the TM−Si bond have been reported and generally employ simple model systems to provide a basis for understanding the TM−Si interaction. Section VII addresses the nature of bonding in TM−Si complexes and relative bond energies from calculations.

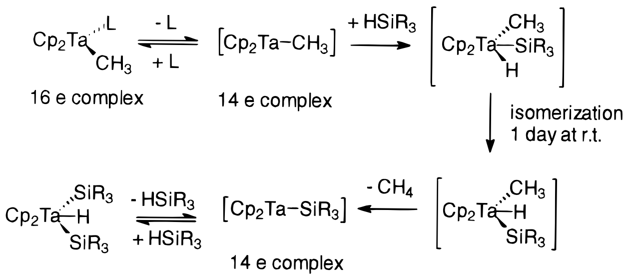
Addition of a hydrosilane to a metal center is often accompanied by elimination of a small molecule such as RH (hydrocarbon), H_2, HX, and L (ligand such as PR_3) as illustrated for a generic transition-metal complex in Scheme 2A. The actual process that provides the final complex may involve either an oxidative addition of the Si−H bond to the metal center (path 1 in Scheme 2B) or through a metathesis transition state (path 2, Scheme 2B). In either case an open coordination site is required at the metal center, thus common transition metal precursors contain ligands such as CO or PR_3, loss of which may be promoted by thermolysis or photolysis. Since oxidative addition commonly involves an increase in the oxidation state of the metal by 2 units, a 16-electron (or lower) metal center is required. The complexes of early transition metals (particularly groups 3−5) utilized in reactions with hydrosilanes are often in the highest oxidation state allowed for the group. Thus, the most probable pathway in these triads is a metathesis route. However, for electron-rich complexes (particularly groups 9 and 10 where less than an 18-electron count is common) an oxidative addition pathway is assumed. Since precursors in groups 6−8 (and often for group 5) tend to contain metals in low oxidation states, either route is possible although oxidative addition is most often assumed. Other routes may also operate as suggested by recent experiments in alkyl/hydride exchange in the reaction of *erythro*-$Cp_2Zr[CH(D)CH(D)$-*t*-$C_4H_9](Cl)$ with $HB(C_6F_5)_2$. In this case, the observed stereochemistry in the 1,2-d_2-neohexyl product was not consistent with a σ-bond metathesis route but with alkyl abstraction (attack at the back lobe of the Zr−C σ-bonding orbital).[12c] In the following discussion (section III) an oxidative addition pathway is assumed except for the early triads in the group oxidation state.

The sequence shown in Scheme 3 illustrates the reaction of a hydrosilane with a transition-metal complex.[13a] Initial loss of a ligand, L, gives the reactive 14-electron complex, $Cp_2Ta{-}CH_3$. Reaction

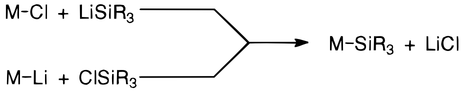
Scheme 2



Scheme 3



Scheme 4



of this complex with the hydrosilane occurs and in this particular example is followed by isomerization. The reaction involving the SiH_3 derivative was monitored by NMR.[14] The next step involves elimination of CH_4 to give another 14-electron complex, $Cp_2Ta-SiR_3$. Oxidative addition of a second molecule of $HSiR_3$ completes the final step (reversible) to the observed product.

Other synthetic methods have been utilized for the preparation of complexes containing a metal−silicon bond. The salt elimination method is fairly common and can involve a combination of a metal halide and a silylmetallic reagent or a metal anionic species and a silicon halide generalized as shown in Scheme 4.[1a,b,2a] The latter route appears to be most efficient with nucleophilic TM anions in combination with sterically undemanding iodosilanes. Both polar and nonpolar solvents have also been utilized but anionic species are generally less soluble in the latter. Tetrahydrofuran should be used with caution since it has been shown to produce significant amounts of siloxane products. The most commonly employed silylmetallic reagents are silyllithium compounds that contain tertiary silyl centers (R_3SiLi) where at least one substituent at silicon is an aromatic group. Stable silyl anions containing H substituents at silicon are rare. Tilley et al. have reported the reaction of Mes_2HSiLi with $Cp^*_2Zr(Me)Br$ which gave the complex $Cp^*_2Zr(Me)(SiHMes_2)$ and reaction with $Cp^*_2ZrCl_2$ afforded a Zr−Si metallacycle.[15a] Tessier-Youngs and co-workers prepared dimeric platinum−silyl complexes, $[(Et_3P)_2Pt]_2(\mu\text{-}SiXPh)(\mu\text{-}SiYPh)$ ($X = Y = H$; $X = Y = Cl$; $X = H$, $Y = Cl$), from Ph_2HSiLi and $(Et_3P)_2PtCl_2$. These complexes were also generated by reaction of $PhSiH_3$ with $(Et_3P)_2PtCl_2$ and Na (see Table 2).[15b] More recently a number of functionalized silyllithium reagents containing amino $[(R_2N)R'_2SiLi]$ or alkoxy groups $[(RO)R'_2SiLi]$ have been prepared[15c] but have not yet been utilized for prepartion of silyl−transition-metal complexes.

The first silylmetal complex (reported by Wilkinson) was prepared by reaction of a transition-metal anionic species with a chlorosilane (eq 1).[16] Tilley and co-workers have used silylaluminum and -mercury reagents as the active organometallic species[17] and an example is shown in eq 2.[17a]

$$Na[Fe(CO)_2Cp] + ClSiMe_3 \longrightarrow Cp(CO)_2Fe\text{-}SiMe_3 + NaCl \tag{1}$$

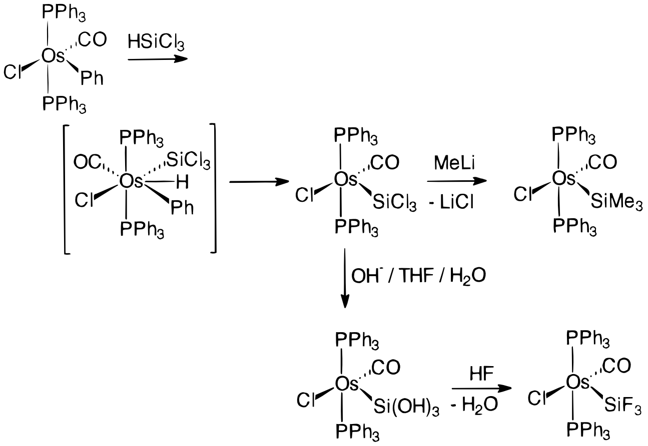
$$Cp_2ZrCl_2 + Al(SiMe_3)_3{\cdot}OEt_2 \longrightarrow Cp_2Zr(SiMe_3)Cl \tag{2}$$

Other miscellaneous methods are known for the formation of complexes containing a TM−Si bond, a few of which will be mentioned here. Berry et al. have reported the preparation of some early transition-metal−silyl complexes by a formal silylene insertion into a metal−hydride bond (eq 3).[18] The reaction is believed to involve a free silylene species generated thermally from hexamethylsilirane, however, a related reaction involving Mo was found to proceed by a radical chain mechanism.[19]

$$Cp_2TaH_3 + \text{":}SiMe_2\text{"} \longrightarrow Cp_2Ta(H)_2SiMe_2H \tag{3}$$

Metal-bound silyl ligands can be modified by substitution with a number of nucleophilic or electrophilic reagents with the metal−silicon bond remaining intact. This approach provides a notable route to introduce functionality at silicon. An example for an osmium complex is given in Scheme 5.[20] Substitution reactions at silicon can provide numerous new silyl complexes when preparations by other routes may be unavailable. $TM-SiCl_3$ complexes are practical starting compounds for substitution reactions of this type and can generally be prepared by oxidative addition of $HSiCl_3$ (commercially available at low cost) to an appropriate metal species. Other silanes such as $HSiF_3$ would require special equipment for handling and $HSiX_3$ ($X = Br, I$) are generally unstable. Substitution of metal bound ligands [(Y)-

Scheme 5



$(L)_nTM-SiR_3 + Z \rightarrow (Z)(L)_nTM-SiR_3 + Y]$ can also provide new complexes containing a TM−Si moiety.

The current review provides an extensive listing of stable silylmetal complexes that were formed by oxidative addition or metathesis of a hydrosilane with a transition-metal precursor. The sections following will address aspects of synthesis, structural analysis, and NMR observations for both "classical" and "nonclassical" complexes. Theoretical calculations and a miscellaneous section covering lanthanide complexes and other Si−X additions are found near the end of the review article. Tables are provided to list characterization information (see below).

Section III describes in detail the formation and characterization of "classical" TM−Si complexes prepared from hydrosilanes. The section is subdivided according to the type of hydrosilane used (SiH_4, $RSiH_3$, R_2SiH_2, and R_3SiH) and progresses from early to late transition metals with Tables 1−4 listing characterization data. Structural and NMR spectroscopic data for the "classical" complexes are discussed in sections IV and V, respectively. The syntheses and characterization of "nonclassical" complexes are discussed in section VI. Within each Table (1−4, 7, and 9) each compound is numbered according to the sequence of appearance within a given table (i.e. **2−25**, **4−100**, etc.) and this number is used to identify an individual compound in the text of the review. Within a triad, complexes are listed in sequential order starting with mononuclear complexes of the first row metals proceeding down through the heavier elements in that triad. The ligands bound to the metal center are written first followed by the metal then the silyl group. The ligand sequence for the groups bound to the metal center for the compound entries was arbitrarily chosen with the following order regardless of oxidation state of the metal: η^5-Cp > η^5-Cp* > η^6-C_6R_6 > CO > PR_3 > PP > other > H. For a given type of ligand such as a phosphine, the order is given on the basis of increasing complexity of the R groups. The silyl groups are subdivided according to the type of silane used for the reaction (i.e., primary, secondary, etc.) and for derivatives with identical metals and ligands the groups on silicon are placed in order of increasing complexity (alkyl > aryl > halide> alkoxy). In cases where the structure of the molecule is not evident from the formula, a representation of the structure is provided although this mainly applies to the di- and polynuclear complexes. Abbreviations are given for ligands when required and a listing of the abbreviations is provided at the end of each characterization table.

The characterization tables (Tables 1−4, 7, and 11) provide the following information (when provided by the original authors): preparative route, yield, color, melting point, if elemental analyses were obtained, NMR solvents and temperature used for the NMR experiment if other than room temperature was used, ^1H chemical shifts (and coupling constants relating to M−H and Si−H resonances when relevant), ^{29}Si chemical shifts (and coupling constants to metals when relevant), and a listing of other techniques used to characterize the complex. Each unique preparative route is given a letter designation, which is described at the end the table. The description includes the metal precursor and any other reagents used in the reaction. When the reacting silane is not obvious from the given product the silane is identified in a footnote to the table. In a number of references several derivatives were prepared by the same general synthetic route and may differ only by groups attached to silicon (i.e., Ph_3Si vs Ph_2MeSi) or by a phosphine ligand (i.e., Ph_3P vs Et_3P). In cases such as this, due to the sheer volume of entries reported in the review, one representative example is generally provided for that reference and additional complexes are provided in footnotes to the table. Footnotes are also provided to convey any pertinent information regarding the synthesis of the compound of interest.

Compounds in Table 5 (structural data for classical complexes) appear with their identification number as reported in Tables 1−4. Additional examples are included for compounds that involved reaction of a hydrosilane and reported before 1980 where the only characterization involved X-ray crystallography; or the derivative appears in a footnote to Tables 1−4. In footnotes to Table 5 are summarized TM−Si distances for all compounds reported in the Cambridge Structural Database for silylmetal complexes prepared by other routes and a reference is provided for all these bond distances.

III. Silyl−Transition-Metal Complexes Formed from Hydrosilane Reactants

A. SiH_4

Complexes containing a SiH_3 substituent are rare and the early examples were prepared by salt elimination between H_3SiX and L_nM^-.[2a,b] Silyl complexes derived from SiH_4 or a precursor that generates SiH_4 are shown in Table 1.[21−29] Probably the difficulty of handling SiH_4 discourages many investigators from studying its reactivity. However, problems also arise due to additional transformations that occur at Si−H bonds in the initially formed $TM-SiH_3$ complex which lead to product mixtures or insoluble materials that are difficult to characterize. A novel way to

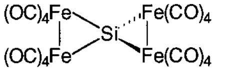
Table 1. Reactions of SiH_4 with Metal Complexes*,†

Complex	Prep.[1a] (% Yd)	Color m.p.	Anal.	NMR				Other	Ref.
				solvent (temp)[1b]	^{1}H[1c] M-H	^{1}H[1c] Si-H	^{29}Si[1c]		
Titanium Triad									
1-1 $CpCp^*(Cl)HfSiH_3$[1d]	A (—)	lt. yellow —	N	S	—	3.90 (s)	-46.5 $^{1}J_{SiH} = 156$	IR	21a
Vanadium Triad									
1-2 $Cp_2(H)_2TaSiH_3$ (sym. isomer)	B (80)[1e]	white —	HRMS	S	-3.99 (b)	4.21 (t) $^{3}J_{HH} = 1.5$	-74.1	IR	13
1-3 $Cp_2(H)TaSiH_3(H)$[1f] (unsym. isomer)	B (—)	—	—	S	-3.01 (d) -4.32 (d) $^{2}J_{HH} = 6.1$	4.46 (d) $^{3}J_{HH} = 2.5$	-40.1	—	13
Chromium Triad									
1-4 $(OC)(depe)_2(H)MoSiH_3$[1g]	C (—)	yellow —	Y	T (-5)	-7.57 (s)[1h]	3.48 (s)[1h] $^{1}J_{SiH} = 143$	—	VT-NMR	22
Manganese Triad									
1-5 $[Cp^*(OC)_2(H)Mn]_2SiH_2$	D (15)	yellow 130° (d)	Y	X (25)	-11.55 (s)	4.59 (s)	—	^{13}C IR, MS X-ray	23
Iron Triad									
1-6* $[(OC)_8Fe_2]_2Si$	E (61)[1i]	orange —	N	—			—	IR, MS Raman X-ray	24a
1-7* $(OC)_9Fe_3[\mu_3\text{-}Si\{Fe(CO)_2Cp\}]_2$	E (67)	red —	N	X			[1j]	^{13}C IR X-ray	25
Cobalt Triad									
1-8* $[(OC)_7Co_2]_2Si$	F (45)	deep red —	—	—	—	—	—	IR, MS X-ray	26, 27
1-9 $(OC)(Ph_3P)_2(H)_2IrSiH_3$[1k]	G (—)	—	N	T	-10.42 (m) - 9.67 (m) $^{2}J_{HH} = 4.0$	3.76 (m) $^{3}J_{HH} = 1.8$, 3.1	—	^{31}P	28
Nickel Triad									
1-10 *trans*-$(Cy_3P)_2(H)PtSiH_3$	H (—)	colorless 178-180 (d)	Y[1l]	S (50)	-0.75[1m] $^{1}J_{PtH} = 528$ $^{3}J_{HH} = 0$	3.76[1m] $^{2}J_{PtH} = 20$	—	^{31}P IR X-ray	29

* Structural formulas for compound numbers marked with an asterisk may be found at the end of the table. † A dash (—) in an entry (and in subsequent tables) indicates that the information was not provided in the reference cited. Abbreviations: d, decomposes; Cp, η^5-C_5H_5; Cp*, η^5-C_5Me_5; Et, C_2H_5; Cy, c-C_6H_{11}; depe, $Et_2PCH_2CH_2PEt_2$; lt., light.

Footnotes: [1a] Reactant Key: A, $CpCp^*Hf[Si(SiMe_3)_3]Cl$. B, Cp_2TaH_3; C, $(depe)_2MoCO$; D, $Cp^*Mn(CO)_3$; E, $Fe_2(CO)_9$; F, $Co_2(CO)_8$; G, $IrH(CO)(PPh_3)_3$; H, *trans*-$(Cy_3P)_2PtH_2$. [1b] Solvent key: S, C_6D_6; T, C_7D_8; X, $CDCl_3$. Data are for ambient temperature (in °C) unless specified otherwise. [1c] In ppm. Coupling constants are in Hz. Assignments: s, singlet; d, doublet; t, triplet. Heteroatom spectra are normally proton decoupled. Coupling constants are reported with respect to the nucleus measured. [1d] Mixed with $CpCp^*Hf(OMe)Cl$ (15%) and $CpCp^*HfCl_2$ (25%). **1**−**1** is unstable in solution. [1e] Yield is for mixture of isomers. **1**−**2** was isolated by recrystallization of isomer mixture. [1f] Not isolated. [1g] In equilibrium with (η^2-$HSiH_3$) isomer (see Table 7). [1h] $^{1}H\{^{31}P\}$ NMR. [1i] Also prepared from $Fe_2CO)_9$ and $HSiCl_3$ in the presence of Et_3N.[24b] [1j] Not detected with available instrument. [1k] Main isomer formed has phosphines in cis arrangement. Ratio of isomers cis/trans 92:8. Data given for major isomer. [1l] Analysis is outside of ±0.5% of calculated percentage value for carbon. [1m] Multiplicities consistent with trans configuration.

Compound structures for Table 1.



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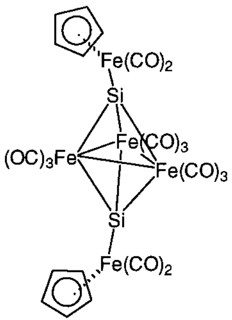

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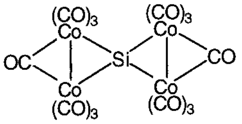
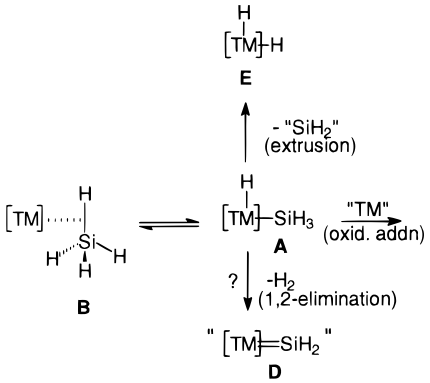


1-8

Scheme 6



bypass the problem of handling SiH_4 has been suggested by Tilley and co-workers[21] who demonstrated that $HSi(OMe)_3$ and $HRSi(OMe)_2$ may be the synthetic equivalents of SiH_4 and $RSiH_3$. The disproportionation or redistribution of alkoxysilanes is promoted by a range of Zr and Hf complexes but particularly by $[CpCp^*ZrH_2]_2$ and $CpCp^*Zr(OMe)_2$. In this case, the metal complexes may be functioning as Lewis acids which are known to promote redistribution reactions of alkoxysilanes.[30] Alternatively, [TM] and $HSi(OMe)_3$ may form $H[TM]Si(OMe)_3$ followed by disproportionation with excess $HSi(OMe)_3$ to give $H[TM]SiH_3$. Although disproportionation also occurs with electron-rich metal centers a more complex process involving metal−silylene intermediates probably takes place.[31]

After oxidative addition of SiH_4 to [TM] to give $H[TM]SiH_3$, **A**, additional reactions may occur which are summarized in Scheme 6. Extrusion of "SiH_2" from $CpCp^*ClHfSiH_3$ occurs at room temperature[21] and tautomers of $Mo(CO)(LL)_2(H)SiH_3$ (LL = $Et_2PCH_2CH_2PEt_2$; **A** = **B**) have been identified.[22] Such examples will be described in more detail in sections V and VI. Condensation of $Cp^*Mn(H)(CO)_2SiH_3$ occurs with another $Cp^*Mn(CO)_2$ unit to give $[Cp^*(OC)_2(H)Mn]_2SiH_2$ (**1−5**, X-ray; an example of **C** in Scheme 6).[23] A similar, although more complex process, occurs in the reaction of SiH_4 with a mixture of $[CpFe(CO)_2]_2$ and $Fe(CO)_5$ to give the product $(OC)_9Fe_3[\mu_3\text{-}Si\{Fe(CO)_2Cp\}]_2$ (**1−7**, X-ray).[25] Attempts to thermally induce a 1,2-elimination of dihydrogen from **1−5** failed[23] although other complexes prepared from organosilanes exhibit conversions related to A→D (see section III.B) as well as A→E[3d].

Examples of late-transition-metal−silyl complexes are also scarce. Only three complexes were found from 1978 to the present. Complete condensation of silane with $Co_2(CO)_8$ afforded the cluster complex, $[(OC)_7Co_2]_2Si$ (**1−8**,[26] X-ray[27]). This complex readily decarbonylates at $T \geq 20$ °C to give the known cluster, $[(OC)_4CoSiCo_3(CO)_9]$.[32]

A six coordinate Ir(III) complex, $(OC)(Ph_3P)_2(H)_2IrSiH_3$ (**1−9**) was isolated (as a mixture of isomers) and the air-stable Pt(II) complex, *trans*-$(Cy_3P)_2(H)PtSiH_3$ (**1−10**) were prepared from silane and $IrH(CO)(PPh_3)_3$[28] and $(Cy_3P)_2PtH_2$,[29] respectively. The latter was characterized crystallographically.[29] Similar complexes were also reported from the reaction of germane in both cases.

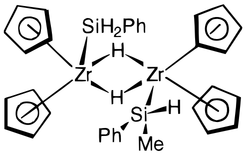


Figure 3. Structure of Zr dimer, **2−8**.

B. Primary Silanes

Table 2[33−81] summarizes the products isolated from reactions of primary silanes, $RSiH_3$, with transition-metal complexes. Most investigations with primary silanes involve R = aryl, since the low molecular weight alkyl compounds (R = Me, Et, Pr) are gases at 25 °C and thus require more specialized handling. Several studies of reactions of $RSiH_3$ with metal complexes involve a metallocene fragment (Cp_2M, M = Ti, V, and Cr triads) although the synthetic strategies vary with each triad.

Several products have been isolated from the reaction of Cp_2TiMe_2 and hydrosilanes. When the reaction was conducted in the presence of a phosphine, a titanium(III) derivative, $Cp_2TiSiH_2Ph(PR_3)$ [R = Me, Et (**2−2**)] was isolated in high yield.[33] Secondary silanes also formed Ti(III) adducts.[33] The related reaction of Cp_2ZrBu_2 [through a presumed Cp_2Zr(butene) intermediate] with a secondary silane resulted in the isolation of the Zr(IV) complex, $Cp_2Zr(H)(SiHPh_2)(PMe_3)$[82,83] (**3−5** and **3−6**) in equally high yield.

In the absence of a phosphine, hydride-bridged metal dimers were obtained as illustrated in Figure 3 for the Zr dimer, **2−8**. More complex dimers that contain a lower oxidation state for the metal (described in section VI.C) have also been reported.[35,36] When $MeSiH_3$ is mixed with Cp_2TiMe_2 (in the absence of phosphines) the dimeric product contains Ti(III) as a mixture of cis and trans isomers of $[Cp_2Ti(\mu\text{-}HSiMeH)]_2$ and such products are described further in section VI.C. The same Ti(III) dimer is generated when $(EtO)_2MeSiH$ is mixed with Cp_2TiMe_2. In this case, the titanocene causes the disproportionation of the ethoxysilane to $(EtO)_3SiMe$ and $MeSiH_3$ and the latter reacts with Cp_2TiMe_2.[30b]

Tilley has utilized the removal of the bulky $Si(SiMe_3)_3$ group in $Cp_2M[Si(SiMe_3)_3]Cl$ (M = Zr, Hf) by reaction with hydrosilanes as a synthetic method for the formation of metal hydrosilyl complexes. The method is particularly useful in the hafnium case. Derivatives of $CpCp^*Hf(SiH_2Ar)Cl$ [Ar = Ph (**2−5**), *p*-Tol, *p*-$MeOC_6H_4$, *p*-FC_6H_4, and Mes] are stable enough to be isolated.[21] However, $Cp_2M(SiH_2Ph)Cl$ (M = Zr, Hf) tends to be unstable and exhibits the equivalent of extrusion of the silylene, "SiHPh", to give $[Cp_2MHCl]_n$ and silicon oligomers.

Although $PhSiH_3$ reacts (>100 °C) with Cp_2V and Cp_2VMe_2, the metal-containing products were not identified although silicon oliogmers $H(PhSiH)_xH$ (x = 2, 3) were produced.[84] Berry and co-workers were was able to show that Cp_2TaH_3 reacted with $MeSiH_3$ (>100 °C) to give two isomers of $Cp_2Ta(H)_2SiH_2Me$ (**2−11** and **2−12**) in nearly quantitative yield if the H_2 liberated was removed periodically from the reaction mixture.[13] In a similar reaction of $PhSiH_3$

Table 2. Reactions of $RSiH_3$ with Metal Complexes*,†

Complex	Prep.[1a] (%Yd)	Color m.p. ,°C	Anal.	NMR solvent[1b] (temp)	^1H[1c] M-H	^1H[1c] Si-H	^{29}Si[1c]	Other	Ref.
Titanium Triad									
2-1 $Cp_2(Me_3P)TiSiH_2Ph$	A (—)	purple —	Y[1d]	—		—	—	X-ray EPR MM Calc.	33, 34
2-2 $Cp_2(Et_3P)TiSiH_2Ph$ [1e]	A (88)	dk. violet —	Y [1d]	—		—	—	X-ray EPR	33
2-3 $Cp_2(Cl)HfSiH_2Cy$ [1f]	B (—)	yellow —	N	S		4.43 (d)	14.8 (t) $^1J_{SiH} = 145$	^{13}C IR	21a
2-4 $CpCp^*(Cl)Hf\text{-}SiH_2Me$	B (65) [1g]	yellow 108-110	Y	S (22)		4.34 (q) 4.59 (q)	-7.36 (t)	^{13}C IR	21a
2-5 $CpCp^*(Cl)Hf\text{-}SiH_2Ph$ [1h]	B (70)	yellow 123-125	Y	S (22)		4.68 (d) $^2J_{HH} = 1.2$ 5.14 (d) $^2J_{HH} = 1.2$	-14.3 $^1J_{SiH} = 144$	^{13}C IR UV-vis X-ray	21a
2-6 $1,4\text{-}[CpCp^*(Cl)Hf\text{-}SiH_2]_2C_6H_4$	B (39)	yellow >300	Y	S (22)		4.78 (s) 5.26 (s)	—	^{13}C IR	21a
2-7 $2,5\text{-}[CpCp^*(Cl)Hf\text{-}SiH_2]_2C_4H_2S$	B (40)	yellow 185-187	Y	S (22)		5.00 (s) 5.42 (s)	-14.1 $^1J_{SiH} = 158$	^{13}C IR	21a
Titanium Triad: M_2									
2-8* $Cp_2Zr(SiH^1{}_2Ph)(\mu\text{-}H)_2(SiH^2MePh)\text{-}ZrCp_2$	A (58)	yellow —	Y	S	-5.02 (q) $J_{HH} = 11$	4.78 (m, H^1) 4.87 (s, H^2)	15.8 [1i] $^1J_{SiH} = 168$ -7.9 (td) $^1J_{SiH} = 147, 15$		35, 36
2-9 $[Cp_2Zr(\mu\text{-}H)\text{-}\{SiH(Ph)^+\}]_2$ $[Bu_n(C_6F_5)_{4\text{-}n}B]_2$ $(n = 0,2)$ [1j]	C (57)	yellow —	Y	V (-40) S (25)	-2.93 (s) -3.39 (s)	6.17 (br s) 5.78 (br s)	108.0 105.9	^{11}B, ^{13}C, ^{19}F UV-vis	37, 38
2-10 $[CpCp^*Zr(\mu\text{-}H)\{SiH(Ph)^+\}]_2$ $[Bu_n(C_6F_5)_{4\text{-}n}B]_2$ $(n = 0,2)$ [1k]	C (70)	—	N	S	-2.85 (q) -1.82 (q) $J_{HH} = 1.7, 15$	5.53 (br s)	106.0	^{11}B,^{13}C ^{19}F	37, 38
Vanadium Triad									
2-11 $Cp_2(H)_2TaSiH_2Me$ (sym isomer)	D (99)[1l]	white —	HRMS	S	-4.35 (br)	4.93 (m)	-33.5	IR	13a
2-12 $Cp_2(H)Ta\text{-}SiMeH_2(H)$ (unsym. isomer)	D (—)	—	—	S	-4.51 (d) -3.22 (d) $^2J_{HH} = 6.7$	5.33 (q) $^3J_{HH} = 4.3$	-7.0	—	13a
2-13 $Cp_2(H)Ta\text{-}(SiMeH_2)_2$ (sym. isomer) [1m]	E (82)[1l]	yellow —	Y HRMS	S	-3.85 (s)	4.78 (q) $^3J_{HH} = 3.9$	-11.7	—	13a
2-14 $Cp_2(H)Ta\text{-}(SiMeH_2)_2$ (unsym. isomer) [1m]	E (—)	—	—	S	-6.15 (s)	4.45 (q) 4.18 (q)	-23.4 -5.9	—	13a
2-15 $(C_5H_4SiMe_3)_2(H)_2\text{-}NbSiPhH_2$	F (92)	white —	Y	S	-4.90 (br s)	5.24	—	^{13}C IR	39
Chromium Triad									
2-16 $(OC)_5Cr{=}SiH\text{-}[C_6H_4CH_2NMe_2\text{-}2]$	G (87)	yellow 163-164	Y	S	—	5.68 (s)	110.9 $^1J_{SiH} = 162$	^{13}C IR, MS	40
2-17 $(OC)_5Cr{=}SiH\text{-}C_{10}H_6CH_2NMe_2\text{-}8]$	G (73)	— 171-72 (d)	Y	S	—	5.95 (s)	102.1 $^1J_{SiH} = 165$	^{13}C IR, MS	40

Table 2 (Continued)

Complex	Prep.[1a] (%Yd)	Color m.p., °C	Anal.	NMR				Other	Ref.
				solvent [1b] (temp)	^{1}H [1c] M-H	^{1}H [1c] Si-H	^{29}Si [1c]		
2-18 $(OC)_5Cr{=}SiH[C_{10}H_6NMe_2\text{-}8]$	G (51)	—	Y	T	—	—	120.4 $^{1}J_{SiH} = 165$	IR, MS	40
2-19a $Cp_2(H)MoSiH_2Ph$	H (—)	yellow 121-123	—	T	-8.17	5.06	—	IR, MS	41
2-19b $\{H_2Mo(SiH_2Ph)SiPh[(C_6H_4)PhPCH_2CH_2PPh_2]_2\}$	[1n] (78)	yellow	Y [1n]	S	-4.5 (br m) -5.4 (br quint)	4.2 (s)	—	IR X-ray	42
Chromium Triad: M_x or $M_xM'_y$									
2-20* $\{[Cp(OC)_2Mo][Co_2(CO)_6]\}SiMe$	I (14)	black ~100 (d)	Y	S			—	IR	43
2-21* $\{[Cp(OC)_2W][Co_2(CO)_6]\}SiMe$	I (12)	black ~100 (d)	Y	S			—	IR	43
Manganese Triad									
2-22 $Cp(OC)_2Mn{=}SiH[C_6H_4CH_2NMe_2\text{-}2]$	J (76)	— 136 (d)	Y	S: (^{1}H) S/T': (^{29}Si)		6.18 (s)	131 $^{1}J_{SiH} = 157$	^{13}C IR, MS	44
2-23 $Cp(OC)_2Mn{=}SiH[C_{10}H_6CH_2NMe_2\text{-}8]$	J (63)	— 210-211 (d)	Y	S		6.25 (s)	120 $^{1}J_{SiH} = 165$	^{13}C IR, MS	44
2-24 $Cp'(OC)_2Mn{=}SiH[C_6H_4CH_2NMe_2\text{-}2]$	J (63)	—	Y	S/T': (^{29}Si)		—	132 $^{1}J_{SiH} = 149$	^{13}C IR, MS	44
2-25 $Cp'(OC)_2Mn{=}SiH[C_{10}H_6CH_2NMe_2\text{-}8]$	J (68)	— 215-216 (d)	—	S: (^{29}Si)		—	124 $^{1}J_{SiH} = 166$	^{13}C IR, MS	44
2-26 $Cp'(OC)_2Mn{=}SiH[C_{10}H_6NMe_2\text{-}8]$	J (60)	—	Y	S		—	142 $^{1}J_{SiH} = 164$	^{13}C IR, MS	44
2-27 $Cp(dmpe)(H)MnSiH_2Ph$	K (58)	green-yellow	Y	Y	-14.14 (dd, br)	4.96 (m)	—	^{13}C, ^{31}P IR	45
2-28 $Cp(dmpp)HMn(SiH_2Ph)$	K (49)	green-yellow	Y	Y	-14.58 (dd)	4.96 (m)	—	^{13}C, ^{31}P IR	45
2-29 $[(c\text{-}C_5H_9)_3P](H)_5Re(SiH_2Ph)_2$	L (—)	transparent	Y	—	—	—	—	X-ray	46
Iron Triad									
2-30 $(OC)_4Fe{=}SiH[C_6H_4CH_2NMe_2\text{-}2]$	M (81)	dk. red oil	Y	T'/S		—	47.1 48.2 $^{1}J_{SiH} = 180$	^{13}C IR, MS	44
2-31 $(OC)_4Fe{=}SiH[C_{10}H_6CH_2NMe_2\text{-}8]$	M (68)	red-black 132-133	Y	T'/S		—	95.5 $^{1}J_{SiH} = 191$	^{13}C IR, MS	44
2-32 $(OC)_4Fe{=}SiHPh(DMI)$	M (61) [1o]	black-red —	Y	T'/S		—	83.5 $^{1}J_{SiH} = 199$	^{13}C IR	44
2-33 $(OC)_4Fe{=}SiH(1\text{-}C_{10}H_7)(DMI)$	M (58) [1o]	—	Y	T'/S		—	81.5 $^{1}J_{SiH} = 219$	^{13}C IR, MS	44
2-34 $Cp(OC)_2FeSiH_2(t\text{-}Bu)$	N (4) (83) [1p]	yellow oil	Y	S		4.49 (s)	21.1	^{13}C IR, MS	47
2-35 $Cp(OC)_2FeSiH_2Tx$	N (5)	yellow oil	HRMS	S		4.53 (s)	—	IR, MS	47
2-36 $Cp^*(OC)_2FeSiH_2(t\text{-}Bu)$	N (54) (81) [1m]	yellow —	Y	S		4.27 (s)	38.2	^{13}C IR, MS	47

Table 2 (Continued)

Complex	Prep.[1a] (%Yd)	Color m.p. ,°C	Anal.	NMR				Other	Ref.
				solvent [1b] (temp)	^{1}H [1c] M-H	^{1}H [1c] Si-H	^{29}Si [1c]		
2-37 Cp*(OC)$_2$Fe-SiH$_2$Tx	N (50)	yellow oil	HRMS	S		4.27 (s)	—	IR, MS	47
2-38 Cp*(OC)$_2$Fe-SiH$_2$(*p*-Tol)	N (7)	lt. yellow	Y[1d]	S		5.05 (s)	43.2	^{13}C, IR	47
2-39 Cp(OC)(H)Fe-[SiH$_2$(*p*-Tol)]SiMe$_3$	N (52)	yellow brown oil	N	S	-13.55 (s)	4.39 [1q] 4.26 [1q] J_{HH} = 6.9	—	IR, MS	47
2-40 Cp*(OC)(H)Fe-[SiH$_2$(*p*-Tol)]$_2$	N (7)	lt. yellow —	N	S	-12.19 (s)	5.24 (s) 5.22 (s)	—	IR	47
2-41a Cp*(OC)(H)Fe-[SiH$_2$(*p*-Tol)]SiMe$_3$	N (39)	lt. yellow —	N	S	-12.68 (s)	5.20 (s) 5.19 (s)	5.1 30.2	^{13}C IR, MS	47
2-41b (η^6-*p*-Tol)Fe(H)$_2$-(SiHCl$_2$)$_2$	[1r] (1-2%)	yellow —	Y[1d]	S Z	-18.66 (t) -18.66 (t) $^2J_{SiH}$ = 17.6	6.07 (t) $^3J_{HH}$ = 5.2 5.86 (t) $^3J_{HH}$ = 4.8	—	X-ray	48
2-42 (Ph$_2$EtP)$_3$(H)$_3$Fe-SiH$_2$Ph	O (88)	yellow — 114 (d)	Y	S (25)	-14.29 (1s)	6.51 (br s)	—	^{31}P IR	49
2-43 Cp*[(*i*-Pr)$_3$P](H)-Ru(SiH$_2$Ph)$_2$ [1t]	P (60)	colorless —	Y	S	-11.40 (d)	4.94 (m) 5.22 (m)	—	^{31}P IR	50
2-44 Cp*[(*i*-Pr)$_3$P](Cl)-(H)RuSiH$_2$Ph	Q (66)	gold-yellow —	Y	R	-10.33 (d)	4.97 5.41	—	IR	51
2-45 [(*i*-Pr)$_3$P]$_2$(OC)-(H)$_3$Os[Si(OMe)$_2$Ph]	[1u] (65)	white —	Y	S	-10.89 (t)	—	—	^{31}P IR	52
Iron Triad: M$_x$									
2-46a* Cp$_2$(OC)$_3$Fe$_2$-[μ-SiH(*t*-Bu)]	R (69)	ruby-red —	Y	[1v] (^{1}H) S: (^{29}Si)		7.23 (s)	254	VT-NMR ^{13}C IR, MS X-ray	47, 53
2-46b Cp$_2$(OC)$_2$(μ-OC)-Fe$_2$[μ-Si(H)CHEt$_2$] [1w]	[1x] (70)	red	Y	S		7.18 (d)	237.2 (s)	^{13}C IR, MS X-ray	54a
2-47 Cp$_2$(OC)$_2$(μ-OC)-Fe$_2$[μ-Si(H)Mes] (3 isomers)	[1y] (57)	brick-red 133	Y	S		8.17 (s) 7.54 (s) 7.01 (s)	—	IR, MS	54b
2-48 *cis*-Cp*$_2$(OC)$_3$Fe$_2$-[μ-SiH(*p*-Tol)] [1z]	R (41)	red —	Y	[2a]: (^{1}H) S: (^{29}Si)		7.44 (s)	250	^{13}C IR, MS UV-vis	47, 55
2-49 *trans*-Cp*$_2$(OC)$_3$-Fe$_2$[μ-SiH(*p*-Tol)]	R (3) [1z]	red —	HRMS	[2a] (^{1}H) S: (^{29}Si)		7.01 (s)	236	^{13}C IR, MS UV-vis	47, 55
2-50* [(OC)$_3$Fe]$_2$(μ-CO)-(μ-SiHPh)	S (14)	yellow —	Y	S		5.8(s)	161.71 161.67 J_{SiH}= 203	^{13}C IR	56
2-51 [(OC)$_{11}$(μ-H)Os$_3$-{2-BrC$_6$H$_4$CH$_2$-SiH$_2$}]	[2b] (—)	—	N	—	-18.93	4.51	—	IR	57
Cobalt Triad									
2-52 Cp(OC)Co=Si(H)[C$_6$H$_4$CH$_2$NMe$_2$-2] [2c]	T (71)	—	Y	S		5.75 (s)	95 $^1J_{SiH}$ = 162	^{13}C IR, MS	40

Table 2 (Continued)

Complex	Prep.[1a] (%Yd)	Color m.p. ,°C	Anal.	NMR				Other	Ref.
				solvent [1b] (temp)	^{1}H [1c] M-H	^{1}H [1c] Si-H	^{29}Si [1c]		
2-53 $Cp(OC)Co{=}Si(H)[C_{10}H_6CH_2NMe_2\text{-}8]$ [2c]	T (65)	—	Y	S		5.98 (s)	86 $^{1}J_{SiH} = 165$	^{13}C IR	40
2-54 $(OC)_2(Cy_3P)(H)Ir\text{-}(SiH_2Ph)_2$ [2d]	U (—)	lt. yellow oil	N	S	-10.6 (d)	4.9-5.2 (m)	—	^{31}P IR	58
2-55 $OC(Et_3P)_2I(H)Ir(SiH_2OSiH_3)$ [2e]	V (—)	—	N	S	-9.83 $^{3}J_{HH} = 3.0$	5.71 (SiH_2) 4.89 (SiH_3)	—	^{31}P	59
2-56 $OC(Et_3P)_2I(H)Ir[SiH_2P(SiH_3)_2]$ [2f]	V (—)	—	N	S	-10.0 (tdt) $^{3}J_{HH} = 2.8$	3.9 (dtd, SiH_2) 4.1 (d, SiH_3)	—	^{31}P IR	59
2-57 $OC(Ph_3P)_2(H)_2Ir\text{-}SiH_2F$ [2g]	W (—)	—	N	T	-10.22 (br dtq) $^{2}J_{HH} = 4.4$ -9.35 (m)	6.64 (m) $^{2}J_{HH} = 15.3$ $^{3}J_{HH} = 4.2, 1.0$ $^{3}J_{HH} = 2.0$	—	^{19}F, ^{31}P	28
2-58 $OC(Ph_3P)_2(H)_2Ir\text{-}SiH_2SiH_3$ [2h]	W (—)	—	N	T	-10.53 $^{2}J_{HH} = 4.0$ -9.46	3.47, 3.20 (SiH_2) $^{3}J_{HH} = 4.4$ 4.06 (SiH_3) $^{3}J_{HH} = 3.8$ $^{4}J_{HH} = 2.8$	—	^{31}P	28
2-59 $OC(dppe)(H)_2Ir\text{-}SiH_2Ph$ [2h]	X (—)	colorless —	N	S	-9.45 (dd) -10.54 (t)	5.39 (m)	—	^{31}P IR	60
2-60a $OC(dppe)(H)Ir\text{-}(SiH_2Et)_2$ [2h]	X (—)	colorless —	N	S	-10.51 (t)	4.39 (m)	—	^{31}P IR	60
2-60b $(Cy_3P)_2(acac)(H)\text{-}IrSiH_2Ph$ [2i]	Y (39)	white —	Y	S	-25.93 (t)	4.22 (t)	—	^{31}P IR	61
Cobalt Triad: M_x									
2-61* $(OC)_{20}Co_6Si_3H_2$	Z (40-50)	yellow —	N	—		—	—	IR X-ray	62a
2-62* $(OC)_{20}Co_6Si_2$	Z (—)	yellow —	N	—			—	IR	62a
2-63* $(OC)_{14}Co_4Si_2S$	Z (43)	yellow-orange —	N	—			—	IR X-ray	62a
2-64a* $\{(OC)_7Co_2\text{-}[(OC)_4Co]Si\}_2O$	Z (~25)	brown —	N	—			—	IR	62a
2-64b $(OC)_6(\mu\text{-}OC)Co_2\text{-}[\mu\text{-}SiH\{Fe(CO)\text{-}(MeNC)Cp\}]$	[2j] (32)	ocher 81	Y[1d]	S'		5.39	—	IR, MS	62b
2-65* $(OC)_8(HC)Co_3\text{-}(\mu\text{-}SiHPh)$	2A (10)	orange —	Y	Q		6.50 (s)	—	IR, MS	63
2-66* $(OC)_9Co_3Si\text{-}FeCp(CO)_2$	Z (62)	violet 110 (dec)	Y [1d]	S			247.8	^{1}H IR, MS	64
2-67 $(OC)_{11}Co_4(\mu_4\text{-}SiR)_2$ $R = Co(CO)_4$ [2k]	Z (30)	dk. orange —	N	—			—	IR, MS X-ray	62a, 65
2-68* $(OC)_{11}Co_4\text{-}(\mu_4\text{-}SiMe)_2$	2B [2l] (100)	red-black —	N	X				^{1}H, ^{13}C IR, MS X-ray	66
2-69* $(OC)_2(\mu\text{-}CO)\text{-}(dppm)_2Rh_2\text{-}(\mu\text{-}SiHPh)$ [2m]	2C (75) [2n]	yellow —	Y	S		5.31 (tt)	—	^{31}P IR	67, 68

Table 2 (Continued)

Complex	Prep.[1a] (%Yd)	Color m.p., °C	Anal.	NMR solvent[1b] (temp)	NMR ^1H[1c] M-H	NMR ^1H[1c] Si-H	NMR ^{29}Si[1c]	Other	Ref.
2-70 $(OC)_2(dpam)_2(H)_2Rh_2(\mu\text{-}SiHEt)(SiH_2Et)$ [2o]	2D (—)	—	N	Y (-60)	-11.92 (m) -12.05 (m) -12.57 (m)	3.29, 3.58 (br m, SiH_2Ph) 5.30 (br m, SiPhH)	—	—	68
2-71* $(OC)_2(dppm)_2(H)_3Rh_2(\mu\text{-}SiHPh)$ [2p]	2E (—) [2q]	yellow-orange —	N	Y (-70)	-9.23 (m)	6.33 (m)	—	VT-NMR ^{31}P IR	67, 68, 69
2-72* $(OC)_2(dppm)_2(H)_3Rh_2(\mu\text{-}SiHEt)$ [2r]	2E (50-60)	—	Y [1d]	S		5.47 (m)	—	^{31}P IR X-ray	67, 68
2-73 $(OC)_2(dppm)_2Rh_2(\mu\text{-}SiHPh)_2$ [2r]	2E (40)	white —	N	Y		5.65 (m)	—	^{31}P IR X-ray	67, 68
2-74* $(dippe)_2Rh_2(\mu\text{-}SiHBu)_2$ [2s]	2F (67)	red —	Y	T		8.07 (br s) 7.58 (br s)	—	^{31}P X-ray	70
2-75* $(OC)_2(dppm)_2(H)_2Ir_2(\mu\text{-}SiHPh)$	2G (84)	lt. yellow —	Y	Y	-11.43 (m)	6.72 (s)		^{31}P IR X-ray	71
Co Triad: M_y [2t]									
2-76* $[(OC)(Et_3P)_2I(H)IrSiH_2]_2O$ [2u]	V (—)	white —	Y	S	-9.80 (tt)	5.78 (td)	-30.1 $^1J_{SiH} = 196$ $^2J_{SiH} = 10.4$	^{31}P IR, MS	59
2-77* $\{(OC)(Et_3P)_2I(H)IrSiH_2\}_2PSiH_3$ [2f]	V (—)	—	N	S	-9.8 (m) $^3J_{HH} = 1.8$	4.1 (m, SiH_2) 4.2 (m, SiH_3)	—	^{31}P	59
2-78* $[(OC)(Et_3P)_2I(H)SiH_2]_3P$ [2v]	V (—)	white —	Y	S	-9.7 (dt) $^3J_{HH} = 1.6$	4.2 (quin)	—	^{31}P IR	59
Ni Triad									
2-79 $(dmpe)Pd(SiH_2C_6H_4SiH_2)_2$	2H (67) [2w]	white 195-220 (d)	Y	S	—	4.7-4.8 (m) 4.83-4.95 (m) 4.98-5.17 (m)	-8.31 (t) -6.58 (dd)	^{13}C, ^{31}P IR X-ray	72
2-80 $(dcpe)Pd(SiH_2Ph)_2$	2I (—) [2x]	[2x] 142	Y	S		5.34 (dd)	—	^{13}C,^{31}P IR, MS	73
2-81 $(Et_3P)_2Pt(SiH_2Ph)_2$ [2y]	2J (—) [2z]	—	—	—		—	—	—	74 [23a]
2-82 $(Et_3P)_2Pt(SiH_2C_6H_4SiH_2)$ [2z]	2J (—)	white —	—	—		—	—	^1H,^{13}C, ^{31}P,^{195}Pt	75 [3a]
2-83 $(Et_3P)_2Pt(SiH_2C_6H_4SiH_2)_2$	2J (—)	—	—	—		—	—	^1H,^{13}C, ^{31}P,^{195}Pt X-ray	75 [3a]
2-84 $(Et_3P)_2(H)Pt(SiH_2C_6H_4SiH_2)(SiH_2C_6H_4SiH_3)$ [3c]	2J (—)	—	—	—	—	—	—	^1H,^{13}C, ^{31}P,^{195}Pt	75 [3a]
2-85 *fac*-$(dmpe)(H)Pt(SiH_2Ph)_3$	2K (100) [3d]	—	—	—	—	—	—	X-ray	74 [3a]
2-86 $(dcpe)Pt(SiH_2SiH_3)_2$	2L (—) [3e]	white	—	—		—	—	X-ray [3f]	76 [3a]
Ni Triad: M_2 [2t]									
2-87* $[(Et_3P)_2Pt]_2[\mu\text{-}SiH(Hex)]_2$	2J (—) [3g]	yellow —	—	S		3.98 (m)	-93 (m) (*trans*) [3h] $^1J_{PtSi} = 659$ -66 (m) (*cis*)	^{13}C, ^{31}P IR	77

Table 2 (Continued)

Complex	Prep.[1a] (%Yd)	Color m.p., °C	Anal.	NMR				Other	Ref.
				solvent [1b] (temp)	^{1}H [1c] M-H	^{1}H [1c] Si-H	^{29}Si [1c]		
2-88 [(Pr$_3$P)$_2$Pt]$_2$-[μ–SiH(Hex)]$_2$	2M (64) [3g]	yellow —	—	S		3.89 (m) $^1J_{SiH}$ = 159 $^2J_{PtH}$ = 26	-94 (m) (*trans*) [3h] $^1J_{PtSi}$ = 661 -75 (m) (*cis*)	^{13}C, ^{31}P ^{195}Pt IR X-ray	77
2-89* *cis*-[(Et$_3$P)$_2$Pt]$_2$-[μ-SiHCy)]$_2$ [3i]	2N (15) [3j]	brown —	—	—		—	—	IR X-ray	78, 79
2-90 *trans*-[(Et$_3$P)$_2$Pt]$_2$-(μ–SiHPh)$_2$ [3k]	2J [31] (100)	—	—	—		—	—	—	74 [3a]
2-91* *trans*-[(Et$_3$P)$_2$Pt]$_2$-[(μ-SiH(*p*-Tol)]$_2$	2N (25)	yellow —	Y	—		[3m]	-93.3	^{1}H,^{13}C ^{29}Si,^{31}P IR X-ray	79
2-92* [(Et$_3$P)$_2$-[(μ-SiHC$_6$H$_4$SiH$_2$)$_2$-Pt(PEt$_3$)$_2$]	2J (—) [3n]	—	—	—		—	—	^{13}C, ^{31}P ^{195}Pt X-ray	75 [3a]
2-93 *trans*-[(Et$_3$P)$_2$Pt]$_2$ [(μ–SiXCy)(μ–SiYCy)] [3o]	2N (15)	yellow —	—	—		—	—	IR X-ray	78, 79
2-94 *trans*-[(Et$_3$P)$_2$Pt]$_2$-[(μ–SiXPh)(μ–SiYPh)] [3o]	2N (10-20) [3p]	yellow —	—	S		4.37 (m)	-92.8 [3q]	IR, MS X-ray [3r] MO calc.	15b, 79, 80
2-95* (dmpe)(H)Pt-(μ-SiHPh)$_2$[μ-η^1,η^1-PhHSiSiHPh]Pt(H)-dmpe) [3s]	2O (—) [3t]	—	—	—		—	—	X-ray	74 [3a]
2-96 [(dcpe)Pt]$_2$-(μ-SiH$_2$)$_2$	2L (51)	orange —	—	—		—	—	—	76 [3a]
2-97* [dcpe)Pt]$_2$-(μ-SiH$_2$SiH$_2$)$_2$ [3e]	2L (—)	white —	—	—		—	—	X-ray	76 [3a]
2-98 [Pt]Si(t-Bu) [3u]	2P (—)	—	—	—		—	—	TPRS RAIR	81

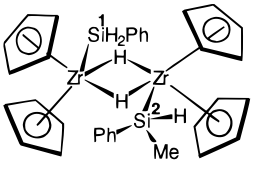
* Structural formulas for compound numbers marked with an asterisk may be found at the end of the table. † Abbreviations: Cp, C$_5$H$_5$; Cp′; C$_5$H$_4$Me; Cp*, C$_5$Me$_5$; Ph, C$_6$H$_5$; Me, CH$_3$; Et, C$_2$H$_5$; Hex, *n*-hexyl; Bu, C$_4$H$_9$; Pr, C$_3$H$_7$; Cy, c-C$_6$H$_{11}$; c-C$_5$H$_9$, cyclopentyl; *i*-Pr, isopropyl; *t*-Bu, *tert*-butyl; DMI, 1,3-dimethyl-2-imidazolidinone; Tx, CH$_2$C(CH$_3$)HCH(CMe$_3$)$_2$; *p*-Tol, *p*-CH$_3$C$_6$H$_4$; coe, cyclooctene; acac, acetylacetonate; Mes, 2,4,6-trimethylphenyl; dcpe, bis(dicyclohexylphosphino)ethane; dmpe, bis(dimethylphosphino)ethane; dppm, bis(diphenylphosphino)methane; dippe, bis(diisopropylphosphino)ethane; dppe, bis(diphenylphosphino)ethane; dmpp, bis(dimethylphosphino)propane; dpam, Ph$_2$AsCH$_2$CH$_2$AsPh$_2$; d, decomposes; dk, dark; lt., light; TPRS, temperature-programmed reaction spectroscopy; RAIR, reflection−absorption infrared spectroscopy.

Footnotes: [1a]General reactant key (L is a neutral ligand such as CO or phosphine; hydrosilanes are coreactants in all cases): A, Cp$_2$MR$_2$; B, CpCp*M[Si(SiMe$_3$)$_3$]Cl; C, CpCp′MCl$_2$ + BuLi + B(C$_6$F$_5$)$_3$; D, Cp$_2$MH$_3$; E, Cp$_2$MRL + heat; F, Cp′$_2$MH$_3$; G, Cr(CO)$_6$ + *hν*; H, Cp$_2$MH$_2$; I, Cp(OC)$_2$MSiH$_2$Me + Co$_2$(CO)$_8$; J, (Cp′)M(CO)$_3$; K, CpMn(LL)(CO); L, L$_2$H$_7$Re; M, M$_x$(CO)$_y$ (*hν* or Δ); N, Cp′(CO)$_2$FeSiMe$_3$; O, (Ph$_2$EtP)$_3$FeH$_3$SiMe$_3$; P, Cp*LRu(CH$_2$SiHPh$_2$); Q, Cp*RuClL; R, CpFe(CO)$_2$SiMe$_3$; S, Fe$_2$(CO)$_9$; T, Cp(OC)$_2$Co + *hν*; U, (OC)$_2$(Cy$_3$P)Ir(OCOCH$_3$); V, *trans*-(OC)(Et$_3$P)$_2$IrI; W, (OC)(Ph$_3$P)$_3$IrH; X, (OC)(dppe)IrH$_3$ + heat; Y, (Cy$_3$P)(acac)Ir(coe); Z, Co$_2$(CO)$_8$; 2A, HCCo$_3$(CO)$_9$ + heat; 2B, Co$_4$(CO)$_{12}$; 2C, (OC)$_3$(dppm)$_2$Rh$_2$; 2D, (OC)$_2$(dpam)$_2$Rh$_2$H$_2$; 2E, (OC)$_2$(dppm)$_2$Rh$_2$H$_2$; 2F, [(dippe)Rh]$_2$(*μ*-H)$_2$; 2G, (OC)$_3$(dppm)$_2$Ir$_2$; 2H, (dmpe)PdMe$_2$ + heat; 2I, [(dcpe)Pd]$_2$(*μ*-H)$_2$; 2J, (Et$_3$P)$_3$Pt; 2K, [(dmpe)Pt(SiH$_2$Ph)$_2$]$_2$(*μ*-dmpe); 2L, (dcpe)PtH$_2$; 2M, (Pr$_3$P)$_3$Pt; 2N, (Et$_3$P)$_2$PtCl$_2$ + Na; 2O, [(dmpe)Pt(SiH$_2$Ar)$_2$]$_2$(*μ*-dmpe) + heat (Ar = Ph, *p*-tolyl); 2P, Pt(111) surface (low temperature). [1b] Solvent key: R, not specified; Q, CCl$_4$; X, CDCl$_3$; S, C$_6$D$_6$; S′, C$_6$H$_6$; T, C$_7$D$_8$; T′, C$_7$H$_8$; U, THF-*d*$_8$; Y, CD$_2$Cl$_2$; Y′, CH$_2$Cl$_2$; V, C$_2$D$_2$Cl$_4$; W, (CD$_3$)$_2$CO; Z, CD$_3$CN. Data are for ambient temperature (in °C) unless specified otherwise. [1c] In ppm. Coupling constants in Hz. Assignments: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad. [1d] Analysis is outside ±0.5% of calculated percentage value for carbon. [1e] A series of complexes were prepared from Cp$_2$TiMe$_2$, RSiH$_3$ and phosphines including Cp$_2$TiSiH$_2$R(PMe$_2$Ph) (R = Ph, CH$_2$Ph) and Cp$_2$TiSiH$_2$R(PMePh$_2$) (R = Ph, CH$_2$Ph) all of which were unstable above −20 °C but were characterized by EPR.[33b] [1f] Mixed with [Cp$_2$HfHCl]$_n$ (1:1 ratio). [1g] Reacting silane was: HSiMe(OMe)$_2$. [1h] Additional derivatives: CpCp*Hf(SiH$_2$R)Cl (R = *p*-Tol, *p*-MeOC$_6$H$_4$, *p*-FC$_6$H$_4$, Mes, CH$_2$Ph, Cy); CpCp*Hf(SiD$_2$Ph)Cl; CpCp*Hf(SiH$_2$R)Br (R = *p*-Tol); CpCp*Zr(SiH$_2$Ph)Cl (solution); Cp$_2$M(SiH$_2$Ph)Cl (M = Zr, Hf). [1i] Doublet of unresolved multiplets. [1j] Additional derivative: [Cp$_2$Zr(*μ*-H){SiH(CH$_2$Ph)$^+$}]$_2$[Bu$_n$(C$_6$F$_5$)$_{4-n}$B]$_2$ ($n = 0, 2$). [1k] Additional derivative based on (MeCp)$_2$Zr. Yield indicated for crude product. [1l] Yield is for the mixture of isomers. [1m] Ratio of symmetrical isomer to unsymmetrical isomer is 6:1. [1n] From reaction of [Mo(H)$_4$(dppe)$_2$] and excess PhSiH$_3$. Analysis is for the bis-toluene solvate. [1o] In the presence of 1,3-dimethyl-2-imidazolidinone (DMI). [1p] Prepared from Na[Cp′(OC)$_2$Fe] + (*t*-Bu)SiH$_2$Cl. [1q] AB quartet. [1r] From co-deposition of Fe$_{(v)}$ with CH$_3$C$_6$H$_5$ and H$_2$SiCl$_2$. [1s] AA′A″XX′X″. [1t] Additional derivative: R = *p*-Tol. [1u] L$_2$(OC)(H)Os(*η*^{2}-H$_2$BH$_2$) + H$_3$SiPh in MeOH. [1v] CS$_2$ solvent. [1w] Additional derivative: Cp$_2$(OC)$_2$(*μ*-OC)Fe$_2$[*μ*-Si(H)CHPh$_2$];[54] Cp$_2$(OC)$_2$(*μ*-OC)Fe$_2$[*μ*-Si(H)Tx].[47] [1x] From FpSiMe$_3$ and Et$_2$CHSiH$_3$. [1y] From Cp(OC)$_2$FeMe + MesSiH$_3$. [1z] Photostationary state, cis/trans = 70/30; thermal equilibrium, cis/trans = 2/98 in c-C$_6$D$_{12}$. [2a] In c-C$_6$D$_{12}$. [2b] From reaction of [Os$_3$(CO)$_{11}$(NCCH$_3$)]. [2c] See also Cr, Mn, and Fe triads for similar derivatives. [2d] Characterized in solution only and would not crystallize. [2e] Similar reaction reported with S(SiH$_3$)$_2$ and

Table 2 (Continued)

$Se(SiH_3)_2$. Product also seen with a large excess of $O(SiH_3)_2$ or when reaction run in light petroleum instead of benzene. [2f] Similar reaction reported with $N(SiH_3)_3$. [2g] When silanes $FSiH_3$ and H_3SiSiH_3 were used only one isomer isolated (cis-phosphines and hydrides). Additional derivatives formed with $BrSiH_3$, $ClSiH_3$, $ISiH_3$, and $MeSiH_3$ and cis isomer was major product formed. Products could not be separated from Ph_3P. [2h] Additional derivatives: $OC(dppe)(H)_2IrSiH_2Et$ and $OC(dppe)(H)Ir(SiH_2Ph)_2$. [2i] See also Tables 3 and 4, entries **3−77a**, **3−77b**, and **4−297b** for related derivatives. [2j] From reaction of $Co_2(CO)_8$ with Cp(OC)(MeNC)$FeSiH_3$. Related derivative formed from Cp(OC)[(*t*-Bu)NC]$FeSiH_3$. [2k] Reaction done with approximately 3:1 Si/Co ratio using Si_2H_6. [2l] Also prepared by reaction of $Co_2(CO)_8$ + $(OC)_4FeSiH_2Me$ in 37% yield. [2m] Additional derivatives: $(OC)_2(\mu\text{-}CO)(dppm)_2Rh_2(\mu\text{-}SiHR)$, R = Et, *n*-hexyl. [2n] Also prepared by reaction of CO with $(OC)_2(dppm)_2(H)_2Rh_2(\mu\text{-}SiHPh)$. [2o] Additional derivatives: $(OC)_2(dpam)_2(H)_3Rh_2(\mu\text{-}SiHR)(SiH_2R)$, R = Ph, *n*-hexyl. Observed at low-temperature only. [2p] Additional derivatives: $(OC)_2(dppm)_2H_2Rh_2(\mu\text{-}SiRH)$, R = Et, *n*-hexyl. [2q] Also formed initially upon reaction of $RSiH_3$ + $Rh_2(CO)_3(dppm)_2$. [2r] Additional derivatives: $(OC)_2(dpem)_2Rh_2(\mu\text{-}SiHR)_2$; R = *n*-hexyl, e = P; and e = As and R = Ph, Et, and *n*-hexyl. [2s] Isolated as an inseparable mixture of trans/cis isomers in ~85/15 ratio (ratio 90/10 for *p*-Tol derivative). NMR data are given for both isomers. Additional derivative: $[(dippe)Rh]_2[\mu\text{-}SiH(p\text{-}Tol)]_2$. [2t] Involves di- or polynuclear complexes with no M−M′ interaction. [2u] Similar reaction reported with $S(SiH_3)_2$ and $Se(SiH_3)_2$. [2v] Reaction done with 4-fold molar excess of $P(SiH_3)_3$. [2w] Also prepared by reaction of $[\{1,2\text{-}C_6H_4(SiH_2)_2Pd(dmpe)\}_2(\mu\text{-}dmpe)]$ with 3 equiv of 1,2-$C_6H_4(SiH_3)_2$ at 50 °C. [2x] Derivatives isolated in 50−70% yields as colorless to light yellow solids. See also Tables 3 and 4, entries **3−91**, **3−92**, and **4−329a** for related derivatives. [2y] Additional derivatives: $(Et_3P)_2Pt(SiH_2Mes)_2$, $(Et_3P)_2Pt[SiH_2(p\text{-}Tol)]_2$, formed by reaction of $ArSiH_3/Pt(PEt_3)_3$ in a ratio of 3:1. Reaction of $(Et_3P)_2Pt(SiH_2Mes)_2$ with dmpe afforded $(dmpe)Pt(SiH_2Mes)_2$. [2z] Bis(silyl) complexes formed with 3:1 ratio of silane to Pt precursor. In solution they isomerize to give mixtures of *cis*- and *trans*-bis(silyl) complexes and eventually rearrange to give Pt_2Si_2 dimers (see **2−90**). [3a] Data are in supplementary material of these references. [3b] Moderately air and thermally stable as a solid but unstable in solution at room temperature. Converts to dinuclear complex **2−92** when heated to 60 °C. [3c] Exists as a 3:1 mixture of isomers and is converted to bis chelate complex **2−83** by heating to 80 °C. [3d] Also formed by reaction of $4PhSiH_3$ with $(dmpe)(H)Pt(\mu\text{-}SiHPh)_2[\mu\text{-}\eta^1,\eta^1\text{-}PhHSiSiHPh]Pt(H)(dmpe)$ (**2−95**) along with $(PhH_2Si)_2$. [3e] Yield of $(dcpe)Pt(SiH_2SiH_3)_2$ and $[(dcpe)Pt]_2(\mu\text{-}SiH_2SiH_2)_2$ vary depending on addition rate. The former is made in approximately 4:1 ratio with rapid addition, whereas slower addition gives a 1:1 ratio. The complex, $[(dcpe)Pt]_2(\mu\text{-}SiH_2SiH_2)_2$ was formed by the reaction of $(dcpe)Pt(SiH_2SiH_3)_2$ with $(dcpe)PtH_2$. [3f] X-ray study of $(dcpe)Pt(SiH_2SiH_3)_2$ has been performed but not published. [3g] Both cis (minor) and trans (major) isomers formed. When $(Et_3P)_3Pt$ is reacted with $(Hex)SiH_3$ in hexanes for short reaction times a mixture of **2−87** and **7−60** is formed in a 3:4 ratio. Longer reaction times (~36 h) afforded predominantly **7−60** and trace amounts of **2−87**. Reaction with $(Pr_3P)_3Pt$ afforded mainly **2−88** and only trace amounts of *trans*-$[(Pr_3P)Pt(\eta^2\text{-}HSi(Hex)\{PtH(PPr_3)_2\})]_2$ over any reaction time. [3h] ^{29}Si NMR assignment tentative. [3i] Compound isolated from reaction mixture containing approximately 20:1 ratio of *trans*-$[(Et_3P)_2Pt]_2[(\mu\text{-}SiXCy)(\mu\text{-}SiYCy)]$ to *cis*-$[(Et_3P)_2Pt]_2[(\mu\text{-}SiHCy)]_2$. [3j] Overall yield based on the two isomers (see **2−93** for trans isomer, ratio of trans/cis ~20/1). [3k] Additional derivatives: $[(Et_3P)_2Pt]_2[\mu\text{-}SiH(p\text{-}Tol)]_2$ and $[(Et_3P)_2Pt]_2[\mu\text{-}SiH(Mes)]_2$. [3l] Bridging silylene dimer products formed from 2:1 ratio of Pt precursor to silane. Also generated by reaction of $(Et_3P)_3Pt$ with $(Et_3P)_2Pt(SiH_2Ar)_2$ (Ar = Ph, Mes, *p*-Tol). [3m] Data not given. [3n] Can also be prepared by thermal reaction (60 °C) of $(Et_3P)_2Pt(SiH_2C_6H_4SiH_2)$. [3o] Product isolated as cocrystallized mixture of isomers containing: X = Y = H; X = Y = Cl; X = H, Y = Cl. [3p] Pt_2Si_2 dimer also prepared from $(H_2PhSi)_2$ or by reaction of $LiSiPh_2H$ + $(Et_3P)_2PtCl_2$. [3q] ^{29}Si NMR data for X = Y = H (unpublished). [3r] Compound with X = Y = Cl was also structurally characterized. [3s] Additional derivatives: $(dmpe)(H)Pt\{\mu\text{-}SiH(p\text{-}Tol)\}_2[\mu\text{-}\eta^1,\eta^1\text{-}(p\text{-}Tol)HSiSiH(p\text{-}Tol)]Pt(H)(dmpe)$. [3t] Product also generated by thermolysis (60 °C) of *fac*-dmpe(H)$Pt(SiH_2Ph)_3$ (**2−85**). [3u] Surface bound silylyne (RSi≡). Also reported reaction with (*t*-Bu)SiD_3, $MeSiH_3$, and $PhSiH_3$ at low temperature (≤ 250 K).

Compound structures for Table 2.



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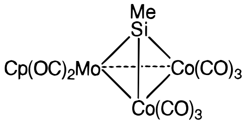

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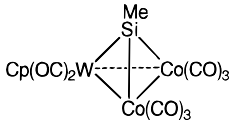

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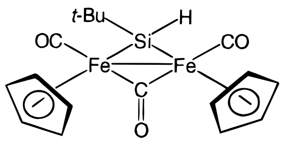

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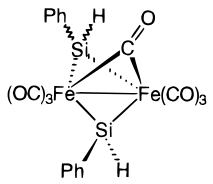

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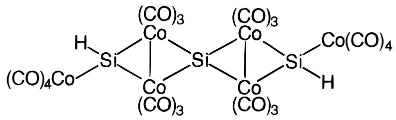

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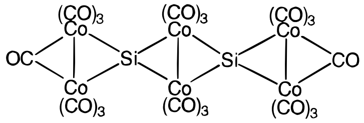

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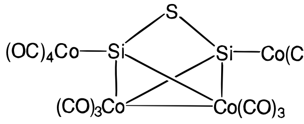
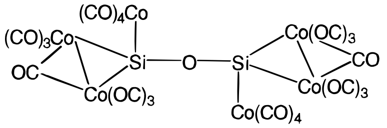
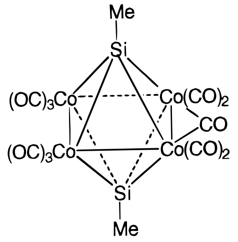


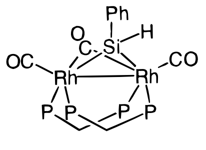
2-63



2-64a



2-68



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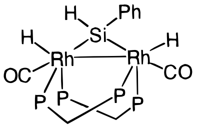
2-69



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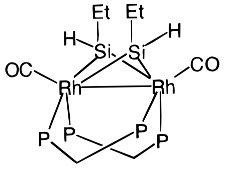
2-71



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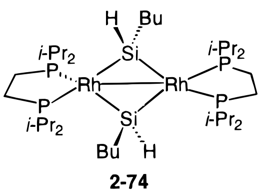
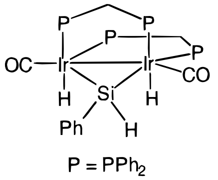
2-72

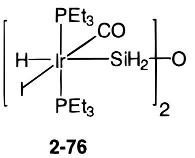


2-74

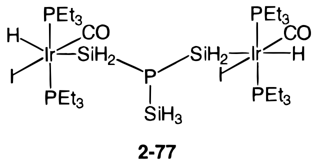


P = PPh2

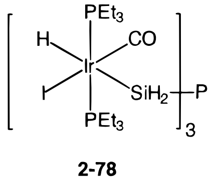
2-75



2-76

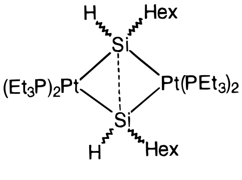


2-77

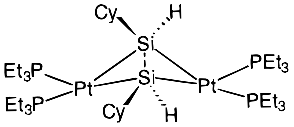


2-78

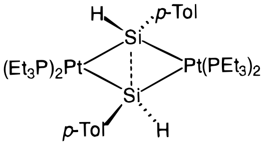
Table 2 (Continued)



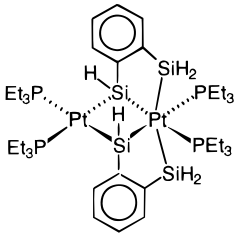
2-87



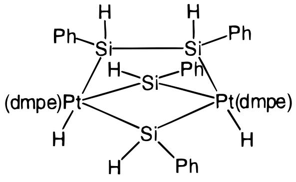
2-89



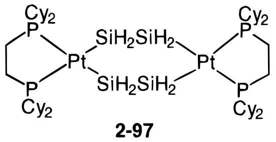
2-91



2-92



2-95

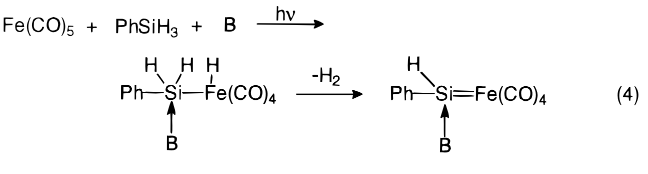


2-97

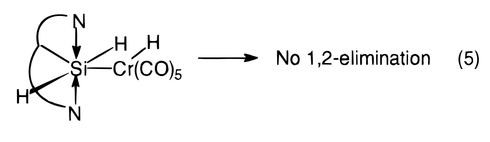
with Cp'_2NbH_3 ($Cp' = C_5H_4SiMe_3$), only the symmetrical (and thermodynamically preferred) isomer of $Cp'_2Nb(H)_2SiPhH_2$ (**2−15**; >90% yd) was isolated.[39] It was postulated that at the temperatures utilized for the reaction, the metallocene trihydride reductively eliminated H_2 before the oxidative addition of the silane occurred. When $Cp_2Ta(CH_2{=}CH_2)CH_3$ was reacted with $MeSiH_3$, the product consisted of two isomers of $Cp_2Ta(SiMeH_2)_2(H)$ (**2−13** and **2−14**).[13]

Chromocene does not react with $PhSiH_3$ at ambient temperatures.[84] Under photolytic conditions, Cp_2MoH_2 (but not Cp_2WH_2) reacts with $PhSiH_3$ (and other silanes), to give air-sensitive $Cp_2Mo(H)SiH_2Ph$ which slowly reverts back to Cp_2MoH_2 at room temperature.

Carbonyl derivatives are common sources of metal reactants. Under photolytic (or thermal) conditions CO is lost and oxidative addition of Si−H to the metal center can occur. In cases where additional hydrogens are present at the silicon center, a 1,2-elimination of dihydrogen to generate a silylene complex would be possible. Such eliminations would be determined by the acidity of the metal hydride bond and the basicity of the Si−H bond. In relatively simple systems, and in the presence of a strong base such as DMI, elimination of H_2 from HFeSiH (eq 4) but not HCrSiH (eq 5) was claimed.[40] It was suggested that the base-stabilized silylene complex of chromium did not form due to a combination of a less acidic Cr−H bond with a less basic Si−H bond.



$$Fe(CO)_5 + PhSiH_3 + B \xrightarrow{h\nu} PhSiH_2(\leftarrow B)\text{−}Fe(H)(CO)_4 \xrightarrow{-H_2} Ph(H)Si(\leftarrow B){=}Fe(CO)_4 \quad (4)$$



$$[C_6H_3(CH_2NMe_2)_2SiH_3] + Cr(CO)_6 \longrightarrow \longrightarrow \text{No 1,2-elimination} \quad (5)$$

The reaction of $CpFe(CO)_2SiMe_3$ with primary silanes (with bulky alkyl groups) gave the silylene-bridged dimer, $Cp_2Fe_2(CO)_3(\mu\text{-}SiHR)$ (such as **2−46a**, R = *tert*-butyl).[47] However, with $Cp^*Fe(CO)_2SiMe_3$, the product obtained from $RSiH_3$ (R = *tert*-alkyl) was the equivalent to an exchange of silicon groups, $Cp^*Fe(CO)_2SiH_2R$. Another variation was demonstrated in the reaction of (p-Tol)SiH_3 which provided an Fe(IV) complex, $Cp^*Fe(CO)SiMe_3(H)[SiH_2(p\text{-}Tol)]$ (**2−41a**) as the main photolysis product.[47]

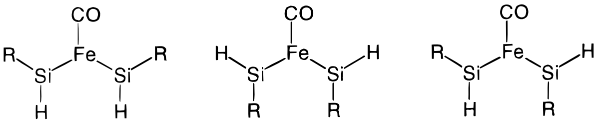


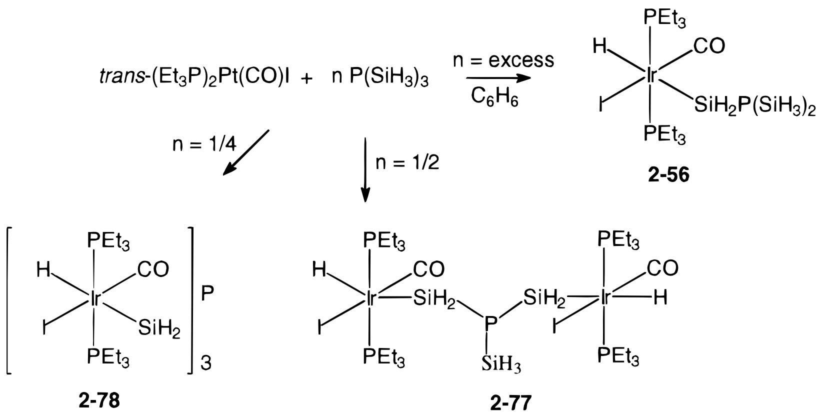
Figure 4. View down the Fe−Fe axis of **2−50**.

When $PhSiH_3$ was stirred with $Fe_2(CO)_9$, an iron dimer was produced in which two of the CO's in the starting material were replaced by bridging PhSiH groups to give $(OC)_3Fe(\mu\text{-}SiPhH)_2(\mu\text{-}CO)Fe(CO)_3$ (**2−50**). When viewed down the Fe−Fe axis, three possible arrangements as shown in Figure 4 are possible and either the isomer with nonequivalent Si−H groups is produced or there is a 1:1 ratio of each of the two isomers with equivalent Si−H groups.[56]

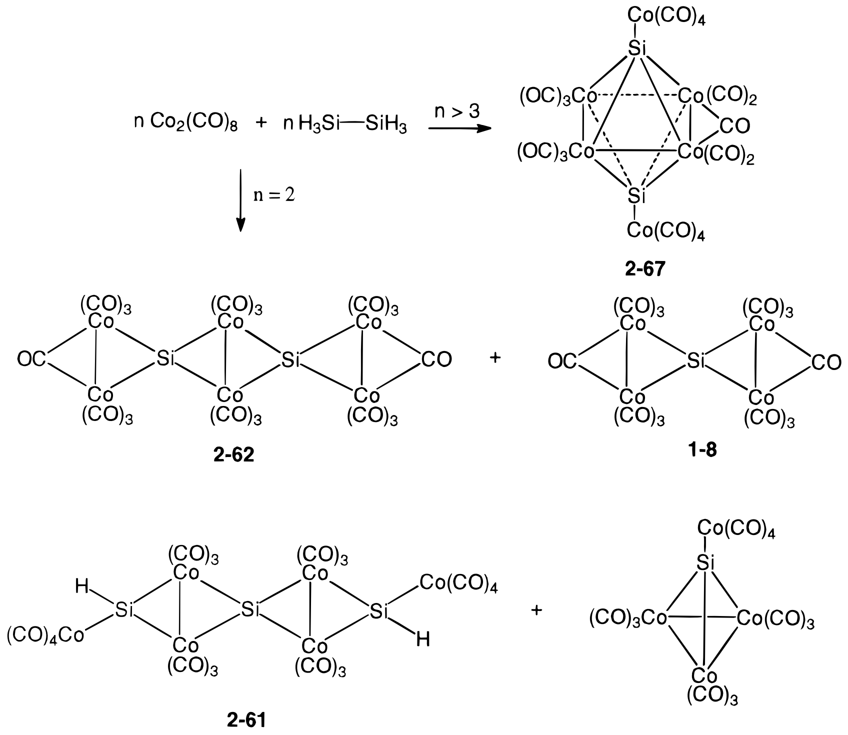
Only two cases are reported for mononuclear cobalt−silyl complexes prepared from reaction of a primary silane with a cobalt precursor and both are base-stabilized silylene complexes (**2−52** and **2−53**).[40] Interestingly, no mononuclear rhodium−silyl complexes were reported but several mononuclear iridium−silyl complexes have been prepared with a variety of primary silanes. All of the examples utilize both carbonyl and phosphine ligands at the iridium center (entries **2−54** through **2−60a,b**).[58−61] The preparation of most of these complexes involved a simple oxidative addition of a Si−H bond, whereas a few of the entries involved subsequent loss of H_2 (**2−59** and **2−60a**)[60] or phosphine (**2−57** and **2−58**).[28] Entries **2−54** and **2−60a** are examples of bis(silyl) iridium complexes.

Halosilanes, $XSiH_3$ (X = F, Cl, Br, and I), methylsilane, and disilane react rapidly with $(Ph_3P)_3(OC)IrH$ to give products with the general formula, $(Ph_3P)_2(OC)(H)_2Ir(SiH_2R)$ [examples are shown in entries **2−57** and **2−58**, the latter being formed from H_3SiSiH_3].[28]

Scheme 7



Scheme 8



The oxidative addition of a Si—H bond can also be extended to silanes containing heteroatom substituents, for example, the reaction of *trans*-$(Et_3P)_2IrI(CO)$ with $Y(SiH_3)_2$ (Y = O, S, and Se; entries given for Y = O: **2—55** and **2—76**) or $Z(SiH_3)_3$ (Z = P or N) (Z = P: **2—56**, **2—77**, and **2—78**).[59] The relative ratio of the reagents used had a pronounced effect on the nature of the product that was formed. For example, when an excess of $P(SiH_3)_3$ was reacted with *trans*-$(Et_3P)_2IrI(CO)$, complex **2—56** was generated.[59] When a 2:1 molar ratio of the iridium complex to phosphine was used, **2—77** was the main product and a 4-fold molar excess of the iridium complex to $P(SiH_3)_3$ afforded **2—78** (Scheme 7).[59]

The reaction of the primary silanes, $ArSiH_3$ (Ar = [2-$(Me_2NCH_2)C_6H_4$], [8-$(Me_2NCH_2)C_{10}H_6$]) with $CpCo(CO)_2$ under photochemical conditions afforded the intramolecular base-stabilized cobalt—silylene complexes, **2—52** and **2—53**, respectively.[40] The mechanism of formation is believed to be similar to that shown for $Fe(CO)_5$ in eq 4.

The following two paragraphs illustrate the extensive chemistry that can occur with simple hydrosilanes. Several novel cobalt clusters were obtained from reaction of dicobalt octacarbonyl with $H_3Si—SiH_3$, and the products formed were dependent upon the starting Co:Si ratio. For example, when >3 mol equiv of $Co_2(CO)_8$ were reacted with disilane, the *closo*-cluster, **2—67**[62a,65] was generated (the decarbonylation product of **2—62**, Scheme 8) in addition to complex **1—8** and the known cluster $(OC)_4CoSi[Co_3(CO)_9]$ (the decarbonylation product of **1—8**).[32] Complex **2—67** is the first example of a silicon derivative of the extensive *closo*-E_2M_4 family. Lower Co:Si ratios resulted in the formation of the unusual clusters **2—61** (X-ray) and **2—62**.[62a]

Some interesting cobalt clusters were obtained from the reaction of $Co_2(CO)_8$ with $Y(SiH_3)_2$ (Y = O, S).[62a] A number of products were obtained with $O(SiH_3)_2$ including μ_4-$Si[Co_2(CO)_7]_2$ (**1—8**; X-ray),[26,27] and IR data suggested the formation of $\{(OC)_7Co_2[(OC)_4Co]Si\}_2O$ (**2—64a**[62a]). The former must be

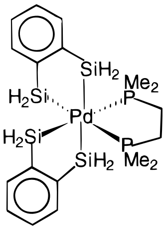


Figure 5. Structure of **2−79**.

generated by cleavage of the strong Si−O bond in the starting siloxane which could be catalyzed by the cobalt carbonyl. Reaction with silylthiane gave the novel cluster **2−63** (X-ray) when shorter reaction times, lower temperatures, and lower Co:Si ratios were used. Longer reaction times and higher temperatures afforded non-silicon containing clusters.

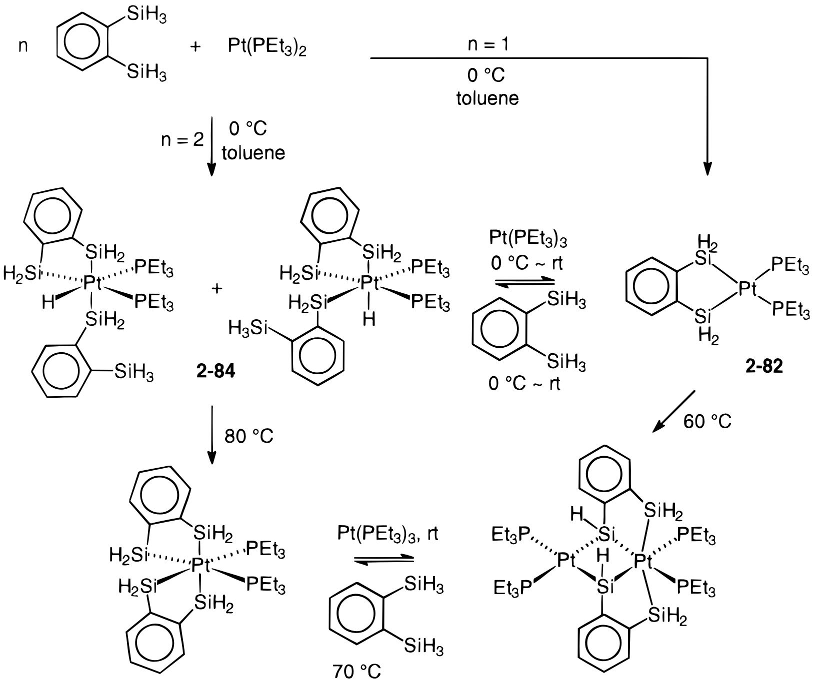
A number of dinuclear rhodium [entries **2−69**,[67,68] **2−70**,[68] **2−71**,[67,68] **2−72** and **2−73**,[67,68] **2−74**[70]] and iridium (**2−75**[71]) complexes containing bridging silylene ligands were prepared by reaction of a primary silane with the appropriate dinuclear metal complex. Stable bis(μ-SiHR) complexes of the formula $(OC)_2(dppm)_2Rh_2(\mu\text{-SiHR})_2$ were prepared by reaction of $RSiH_3$ (R = Ph, Et, hexyl) with $(OC)_2(dppm)_2Rh_2H_2$ [examples given in entries **2−72** (R = Et; X-ray) and **2−73** (R = Ph; X-ray)]. Fluxional mono(μ-SiHR) complexes such as $(OC)_2(dppm)_2(H)_2Rh_2(\mu\text{-SiHPh})$ (**2−71**) were isolated as intermediate products in the preparation of the stable bis(μ-SiHR) complexes but could not be obtained in analytical purity. Conversion of the mono(μ-SiHR) to the bis(μ-SiHR) complexes is favored with prolonged reaction times, heating the reaction mixture, or by adding an additional equivalent of $RSiH_3$. The mono(μ-SiHR) complexes could be trapped with CO (see **2−69**[67,68]). Replacement of the chelating phosphinomethane ligand with the arsine analogue gave similar results. Unlike the rhodium mono(μ-SiHR) complexes, the iridium complex **2−75** (X-ray) was not fluxional.[71]

Both butylsilane and *p*-tolylsilane react with $[(dippe)Rh]_2(\mu\text{-H})_2$ to afford bis(μ-SiHR) dirhodium complexes. An example is given for R = *n*-Bu (**2−74**; X-ray of trans isomer) where the product was isolated as a mixture of cis and trans isomers in a ratio of 15:85.[70]

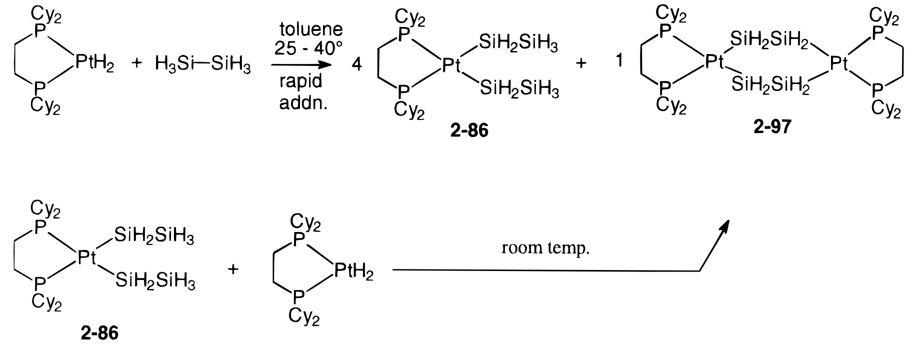
There are no entries for mononuclear nickel−silyl complexes obtained from primary silanes and only two palladium complexes were reported [**2−79**, Figure 5;[72] and **2−80**[73]]. The unusually stable bis(silyl)palladium complex **2−80** was the first isolated example of a *cis*-bis(silyl)palladium system having only organic groups and hydrogens on silicon (for additional examples see also **3−91**, **3−92**, and **4−329a**).[73] The cis orientation of the bis(silyl) complex was ensured by use of the chelating silane, 1,2-disilylbenzene, *o*-$(H_3Si)_2C_6H_4$ (disil). The first silylpalladium(IV) complex (**2−79**; X-ray) was prepared by reaction of $(dmpe)PdMe_2$ with 3 equiv of 1,2-disilylbenzene at 50 °C (Figure 5).[72]

A few bis(silyl)platinum complexes have also been prepared utilizing 1,2-disilylbenzene and these transformations are shown in Scheme 9.[75] The first Pt(IV) tetrakis(silyl) complex, **2−83** (X-ray), was prepared by reaction of 2.5 equiv of 1,2-disilylbenzene at 80 °C with the Pt(0) complex, $(Et_3P)_3Pt$.[75] When the reaction is carried out at 0 °C, **2−84** (X-ray), as a mixture of two isomers in a 3:1 ratio, was formed. Heating this mixture to 80 °C allowed for the quantitative conversion to **2−83**. When only 1 equiv of *o*-$(H_3Si)_2C_6H_4$ was reacted with $(Et_3P)_3Pt$ at 0 °C, another new complex, **2−82**, was generated. This complex was relatively stable in the solid state but reactive in solution. When the ratio of reactants was

Scheme 9



Scheme 10



changed to 1:1 at 60 °C quantitative formation of **2−92** (X-ray) was observed. This was the first example of a mixed-valence $Pt^{II}Pt^{IV}Si_4P_4$ complex. Interconversion of these various complexes was found to occur. For example, reaction of $(Et_3P)_3Pt$ with **2−84** at 0 °C to room temperature gave mainly complex **2−82** and reaction of *o*-$H_3SiC_6H_4SiH_3$ with complex **2−82** at 0 °C to room temperature gave complex **2−84**. Likewise, reaction of **2−92** with *o*-$H_3SiC_6H_4SiH_3$ at 70 °C gave complex **2−83**. Reaction of **2−83** with $(Et_3P)_3Pt$ at room temperature gave complex **2−92**. The conversions between these complexes are illustrated in Scheme 9.[75]

Bis(silyl) complexes of platinum (see, in addition, **3−94**) were prepared from the rapid addition of disilane, $H_3Si{-}SiH_3$, to (dcpe)PtH_2 to afford **2−86** (X-ray) and the dimeric complex **2−97** in about a 4:1 ratio (see Scheme 10).[76] The amount of the dimeric complex **2−97** was increased when a slower addition rate was used (giving an approx 1:1 ratio of **2−86**/**2−97**). Complex **2−86** was the first isolated example of a platinum derivative containing a terminal $-SiH_2SiH_3$ group. The air stable complex **2−97** arises from oxidative addition of the Si−H bonds in **2−86** to (dcpe)PtH_2. An X-ray crystal structure was reported for **2−97** and **2−86** but the latter was not published. When much slower addition rates of disilane were used, a new complex, $[(dcpe)Pt]_2(\mu\text{-}SiH_2)_2$, **2−96**, was observed in approximately 50% yield in addition to **2−97**.

Several Pt_2Si_2 dinuclear complexes were reported by Tessier, Youngs, and co-workers including complexes **2−87**,[77] **2−88**,[77] **2−89**,[78,79] **2−91**,[79] **2−93**,[78,79] and **2−94**.[15b,79,80] They are generally prepared by reaction of a primary silane $ArSiH_3$ or $RSiH_3$ with $(Et_3P)_2PtCl_2$ in the presence of Na metal or by reaction of the silane with $(R'_3P)_3Pt$ (R′ = Et, Pr). When R = Ph or Cy, a cocrystallized mixture of three platinum−silyl dimers, $[(Et_3P)_2Pt(SiRX)(SiRY)Pt(PEt_3)_2]$, **2−93** and **2−94** (X = Y = H; X = Y = Cl; and X = H, Y = Cl), could be isolated.[15b,78−80] An X-ray crystal structure was obtained for the complex **2−94** with X = Y = Cl. Structures were also determined for the complexes with R = Cy (**2−93**), R = *p*-Tol, X = Y = H (**2−91**), R = Cy (X = Y = H; cis isomer, **2−89**), and R = Hex, X = Y = H (**2−88**).

Similar dinuclear Pt_2Si_2 complexes were prepared by Tilley and co-workers from reaction of the primary silanes, $ArSiH_3$ (Ar = Ph, mesityl, and *p*-Tol) with $(Et_3P)_3Pt$.[74] Complex **2−90** was formed in quantitative yield when a 1:2 ratio of silane to Pt was used. When the silane-to-Pt ratio was increased to 3:1, monomeric complexes such as **2−81** were formed. The initially formed cis isomer was found to isomerize in solution to a mixture of *cis*- and *trans*-**2−81**. Complex **2−81** decomposed in solution over several days to give the dimer **2−90**. Direct reaction of **2−81** (a secondary silane) with $(Et_3P)_3Pt$ also afforded complex **2−90**. Scheme 11[74] summarizes the interrelationship between complexes **2−81**, **2−85**, **2−90**, and **2−95**. The unusual complex **2−95** was formed upon thermolysis of $[(dmpe)Pt(SiH_2Ph)_2]_2(\mu\text{-dmpe})$ at 60 °C. The mechanism of formation of **2−95** was not established but may involve successive addition/elimination or α-migrations and again can be viewed as a reaction involving a secondary silane. This complex possesses an η^1,η^1-disilene ligand and two bridging silylene groups and was characterized by X-ray crystallography. Reaction of $[(dmpe)Pt(SiH_2Ph)_2]_2(\mu\text{-dmpe})$ or complex **2−95** with $PhSiH_3$ gave the *fac*-tris(silyl)platinum complex, **2−85** (X-ray). In addition, thermolysis of complex **2−85** regenerates complex **2−95**.

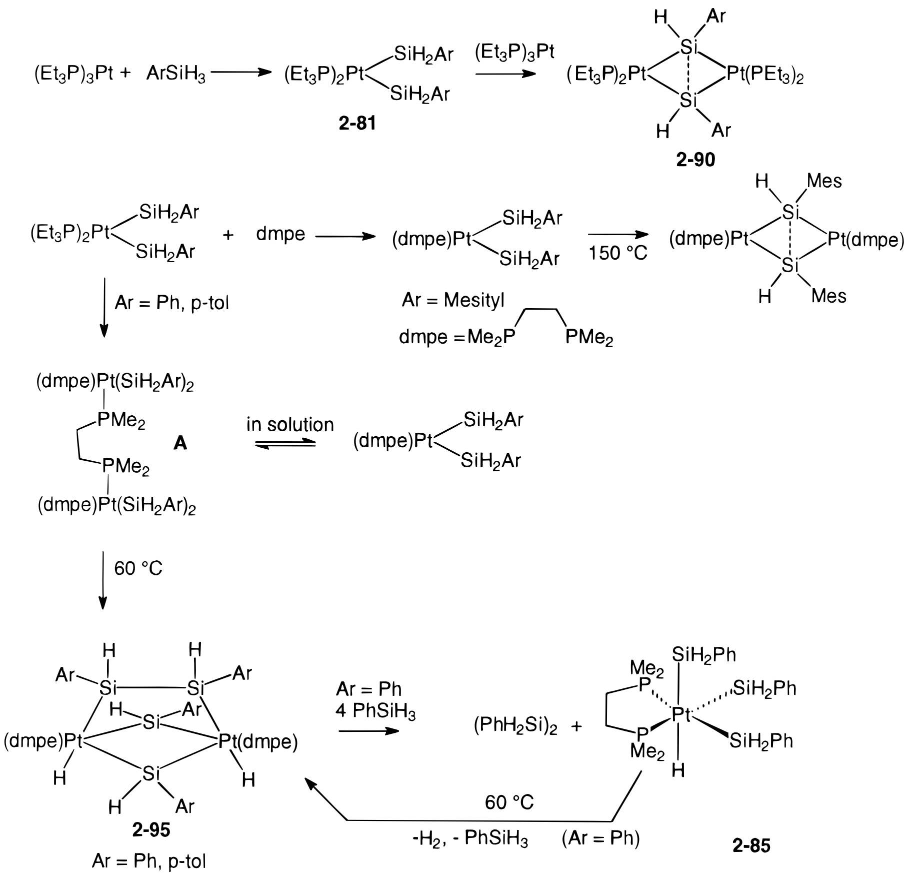
Primary silanes such as (*t*-Bu)SiH_3, (*t*-Bu)SiD_3, $MeSiH_3$, and $PhSiH_3$ were found to react with Pt (111) surfaces to give surface-bound silylynes, (RSi≡) (see entry **2−98**).[81] The number of Si−H bonds cleaved is dependent upon the temperature and coverage and when the temperature reached 250 K all three bonds were cleaved to afford the surface attached organosilylyne units.

C. Secondary Silanes

The products from the reactions of metal complexes with secondary silanes are shown in Table 3.[85−130]

The removal of an organic group from an appropriate metal complex by a hydrosilane is a common tactic for the formation of an TM−Si bond when TM is an early transition metal. Although not well explored, the size of the metal-bound organic group and the size of the substituents on the silane both appear to play a role in successful formation of TM−Si bonds. As an example, $Cp^*_2YCH_3$ transfers a Me group to a hydrosilane, but $Cp^*_2YCH(SiMe_3)_2$ reacts with $H_2Si(SiMe_3)_2$ to provide the new silyl complex, $Cp^*_2Y[SiH(SiMe_3)_2]$ (**3−1**).[85] However, the secondary silane, (*i*-Pr)$_2SiH_2$, which contains a shorter Si to substituent bond, does not react with $Cp^*_2YCH(SiMe_3)_2$. The limits that define the TM−R/H−Si exchange either from the standpoint of the metal or substituents on silicon have yet to be established.

Scheme 11



The reaction of Cp_2TiMe_2 with silanes gives high yields of Ti(III) derivatives. The actual product that is isolated depends on the presence or absence of a trapping reagent. When only the silane and the TM complex are present, dimer products such as $Cp_2Ti(\mu\text{-}H)(\mu\text{-}SiHMeBu)TiCp_2$ (**3−12**) were obtained in moderate yield.[87] However, if PMe_3 was present, $Cp_2Ti(SiHRR')(PMe_3)$ [**3−2** (R = Me, R′ = Ph; **3−3** (R = R′ = Ph, X-ray) and **3−4** (R = H, R′ = Ph)] were isolated in about 90% yield.[33,34] In contrast, the reactions of silanes with Cp_2ZrMe_2 lead to Zr(IV) products.[82] Hydride-bridged dimers were observed by NMR spectroscopy when secondary silanes of the type $PhRSiH_2$ were reacted with Cp_2ZrMe_2 (ratio of Si/Zr = 3:1). At least three unsymmetrical dimers were observed with Ph_2SiH_2: $Cp_2Zr(Me)(\mu\text{-}H)_2(Ph_2MeSi)ZrCp_2$, $Cp_2Zr(SiHPh_2)(\mu\text{-}H)_2(Ph_2MeSi)ZrCp_2$ (10% of the observable ZrH species), and $Cp_2Zr(Me)(\mu\text{-}H)_2(Ph_2HSi)ZrCp_2$ (**3−15**) but only **3−15** was actually isolated (21% yield).[36] The reaction was somewhat cleaner with $PhMeSiH_2$ but the dimer $Cp_2Zr(SiHPhMe)(\mu\text{-}H)_2(PhMe_2Si)ZrCp_2$ (**3−13**, the only product assigned, representing 55% of the Zr species; disordered X-ray structure) was isolated in 44% yield. However, when Cp_2ZrBu_2 (formed from Cp_2ZrCl_2 and *n*-BuLi) and Ph_2SiH_2 were reacted, the symmetrical dimer, $[Cp_2Zr(H)(SiHPh_2)]_2$ (**3−14**, X-ray), was obtained in 85% yield.[83] It is possible that in this case Cp_2ZrBu_2 was converted under the reaction conditions to $[Cp_2Zr(CH_2{=}CHEt)]$ which may be considered a Zr(II) species and thus provides a more direct route to $Cp_2Zr(H)(SiHPh_2)$. A feature observed in the spectra of solutions that contain Cp_2ZrMe_2 and secondary silanes was a Zr−H resonance at high field (−12 ppm) which was tentatively assigned to a Zr(III) species but no Zr(III) product was isolated. An EPR study of toluene solutions of Cp_2ZrCl_2/*n*-BuLi, supports the presence of a Cp_2Zr(III) allyl species in yields up to 60% (chemical derivatization).[131] Secondary silanes without aryl substituents are less reactive toward Cp_2ZrMe_2 and heat is required. It appears that symmetrical dimers of both Zr(IV) and Zr(III) are formed (the latter characterized by the ZrH resonance at −12 ppm). Curiously, Cp_2HfMe_2 does not appear to react with silanes even at temperatures up to 90 °C.[84] The product obtained from $Cp_2TaMe(PMe_3)$ and $(t\text{-}Bu)_2SiH_2$ was $Cp_2Ta[SiH(t\text{-}Bu)_2](PMe_3)$ (**3−17**, X-ray).[13,88]

Complexes that contain a TM(H)R unit can eliminate RH to provide a lower valent, coordinatively unsaturated intermediate. As an example, $RuH(Ph)(CO)L_2$ [L = $PMe(t\text{-}Bu)_2$] eliminates C_6H_6 in the presence of H_2SiPh_2 to give $(OC)[(t\text{-}Bu)_2MeP](H)RuSiHPh_2$ (**3−48**, NMR study) which has also been prepared and isolated from reaction of $RuHCl(CO)L_2$ with *t*-BuLi followed by H_2SiPh_2.[97] In the presence of excess silane, $RuH_3(SiHPh_2)(CO)L$ was formed whose origin may involve addition of H_2 produced from a side reaction involving metal-catalyzed dehydrocoupling of the silane.

Although Cp_2HfMe_2 does not appear to react with hydrosilanes, the olefin complex, $Cp_2Hf(H_2C{=}CMe_2)PMe_3$, can be a good starting point for formation of silyl−hafnium derivatives (see section III.D). An ethylene complex of Ta, $Cp_2Ta(CH_2{=}CH_2)Me$, reacts with Me_2SiH_2 displacing the olefin to give Cp_2Ta-

Table 3. Reaction of R_2SiH_2 with Metal Complexes*,†

Complex	Prep.[1a] (%Yd)	Color m.p., °C	Anal.	NMR solvent (temp.)[1b]	^{1}H[1c] M-H	^{1}H[1c] Si-H	^{29}Si[1c]	Other Data	Ref.
Scandium Triad									
3-1 $Cp^*_2Y[SiH(SiMe_3)_2]$	A (23)	yellow 117-120	HRMS	S (22)		—	-120.0 (d) $^1J_{YSi} = 92$ -7.3 (d) $^2J_{YSi} = 3.6$	^{13}C IR	85
Titanium Triad									
3-2 $Cp_2(Me_3P)TiSiHMePh$[1d]	B (88)	—	Y[1c]	—		—	—	EPR	33
3-3 $Cp_2(Me_3P)TiSiHPh_2$	B (93)	violet —	Y[1c]	—		—	—	X-ray EPR MM Calc	33, 34
3-4 $Cp_2(Me_3P)TiSiHPh$-SiH_2Ph	B (—)	—	—	—		—	—	EPR	33
3-5 $Cp_2(Me_3P)(H)ZrSiHPh_2$ Isomer ratio: 3.2:1.0	C (40)	dull yellow —	Y	S (major)	0.06 (dd) J = 3	6.22 (d)	50.5	^{13}C, ^{31}P	82
				S (minor)	-1.11 (dd) J = 10	5.51 (dd) J = 10 J = 13			
3-6 $Cp_2(Me_3P)(H)ZrSiHPh_2$ Isomer ratio: 5:1	D (90)[1f]	yellow —	—	U (major)	-0.01 (dd) J = 68, 3	5.59 (d)	—	^{13}C IR X-ray	83
3-7 $CpCp^*(H)Hf$-$[SiH(SiMe_3)_2]$	E (72)	orange	Y	S (24)	15.85 (s)	2.71 (s)	-4.85 -4.89 -29.7	^{13}C IR X-ray	86
3-8 $CpCp^*(Cl)Hf$-$[SiH(SiMe_3)_2]$	E (32)	yellow oil	Y	S (22)		2.81 (s)	-48.6 -4.7	^{13}C IR	86
3-9 $CpCp^*(Cl)HfSiHMePh$ 7:5 mix of diastereomers[1g]	E (64)	yellow 128-130	Y	S (22)		5.31 (q) J = 4.5 (major) 5.23 (q) J = 4.5 (minor)	21.8 (d) $^1J_{SiH} = 153$ 25.1 (d) $^1J_{SiH} = 153$	^{13}C IR	21a
3-10 $Cp_2(Cl)HfSiHPh_2$	E (—)[1h]	yellow —	—	S (22)		5.80 (s)	31.9 (d) $J_{SiH} = 148$	^{13}C IR	21a
3-11a $CpCp^*(Cl)Hf(SiHPh$-$SiH_2Ph)$[1i] 1:1 mix of diastereomers	E (65)	yellow oil	Y	S (22)		4.65-4.92 (m)	-9.0, -9.9 (d) (Hf-*Si*) $J_{SiH} = 152$ -43.9, -50.4 (t), (HfSi*Si*) $J_{SiH} = 183$	^{13}C IR	21a
3-11b $CpCp^*(Cl)Hf(SiHPh$-$SiHPhSiH_2Ph)$[1j]	E (60)	yellow —	N	S(22)		4.6-5.1 (m)	-8.0 (m) -50 (m) -60 (m)	^{13}C IR	21b
Titanium Triad Dimers									
3-12* $Cp_2Ti(\mu\text{-}H)(\mu\text{-}SiHMeBu)TiCp_2$	B (63)	black —	Y[1c]	T (-80)	-19.9 (br s) -13.3 (br s)	—	—	MS	87
3-13* $Cp_2Zr(SiHPhMe)(\mu\text{-}H)_2(PhMe_2Si)ZrCp_2$[1k]	B (44)	orange —	—	S	~ -5.1[1l]	4.88 (m)	—	X-ray (disord)	36
3-14 $[Cp_2(H)Zr(SiHPh_2)]_2$[1m]	F (85)	yellow —	—	S	-4.88 (s)	5.40 (s)	—	^{13}C IR X-ray	83

Table 3 (Continued)

Complex	Prep.[1a] (%Yd)	Color m.p., °C	Anal.	NMR				Other Data	Ref.
				solvent (temp.)[1b]	^{1}H[1c] M-H	^{1}H[1c] Si-H	^{29}Si[1c]		
3-15 $Cp_2Zr(Me)(\mu\text{-}H)_2\text{-}(Ph_2HSi)ZrCp_2$[1n]	B (21)	orange —	—	S	~ -3.3[1l]	—	—	—	36
Vanadium Triad									
3-16 $(C_5H_4SiMe_3)_2(H)_2Nb\text{-}SiHPh_2$	G (93)	white —	Y	S	-4.64 (br s)	5.86	-0.3 $(SiMe_3)$ 23.8 (d) $^1J_{SiH} = 177$	^{13}C IR X-ray	39
3-17 $Cp_2(Me_3P)TaSiH(t\text{-}Bu)_2$	H (92)[1o]	red —	Y	S		4.06 (s)	46.4	VT-NMR ^{31}P IR X-ray	13, 88
3-18 $Cp_2(H)Ta(SiHMe_2)_2$	H (77)	—	Y[1e] HRMS	S	-3.90 (s)	5.12 (sept) $^3J = 4.0$	11.5	IR X-ray	13
Chromium Triad									
3-19 $(OC)_5Cr{=}SiC_6H_5\text{-}[C_6H_4CH_2NMe_2\text{-}2]$	I (68)	yellow 171-72	Y	X			122	^{13}C IR, MS	89
3-20 $(OC)_5Mo{=}SiC_6H_5\text{-}[C_6H_4CH_2NMe_2\text{-}2]$	I (48)	yellow —	Y	X	unresolved		111	^{13}C IR	89
3-21 $Cp_2(H)MoSiHMe_2$[1p]	H (79)	yellow —	N	S	-7.93 (br s)	4.80 (sept) $^3J_{HH} = 3.8$	19.9	^{13}C X-ray	90
3-22 $Cp_2(H)MoSiHMePh$	H (—)	yellow 115-118	—	T	-7.99	5.08	—	IR, MS	41
3-23 $Cp_2(H)MoSiHPh_2$	H (—)	yellow 109-111	—	T	-7.90	5.65	—	IR, MS	41
3-24 $Cp'_2(H)MoSiH(t\text{-}Bu)_2$	H (74)	yellow —	Y	S	-7.68 (s)	4.03 (s)	68.2	VT-NMR ^{13}C X-ray	90
3-25 $Cp_2W(SiMe_3)\text{-}[SiH(t\text{-}Bu)_2]$[1q]	[1q] (88)	yellow —	Y	S (25°C)		3.85 (s)	38.8 $[Si(t\text{-}Bu)_2H]$ $^1J_{WSi} = 118$ -3.3 $(SiMe_3)$ $^1J_{WSi} = 111$	VT-NMR X-ray	90
Manganese Triad									
3-26 $Cp(OC)_2Mn{=}Si\text{-}[C_6H_4CH_2NMe_2\text{-}2]_2$	J (68)	brown 139-141	Y	X			147	^{13}C IR, MS	89, 91
3-27 $Cp(OC)_2Mn{=}SiPh[C_{10}H_6CH_2NMe_2\text{-}8]$	J (62)	— 226-227	Y	X			125	^{13}C IR, MS	89, 91
3-28 $Cp'(OC)_2Mn{=}SiPh\text{-}[C_6H_4CH_2NMe_2\text{-}2]$	J (63)	— 133-134	Y	X			145	^{13}C IR, MS	89, 91
3-29 $Cp'(OC)_2Mn{=}SiPh\text{-}[C_{10}H_6CH_2NMe_2\text{-}8]$	J (45)	— 230-231	Y	X			124	^{13}C IR, MS	89, 91, 92
3-30 $Cp'(OC)_2Mn{=}SiAr\text{-}[C_{10}H_6CH_2NMe_2\text{-}8]$ $Ar = 1\text{-}C_{10}H_7$	J (40)	— 249-250	Y	X			127	^{13}C IR, MS	91
3-31 $Cp(dmpm)(H)Mn\text{-}SiHPh_2$	K (20)	lt. yellow-green —	—	Y	-9.59 (ddd) $J_{HH} = 6.2$	6.15 (m)	—	^{13}C, ^{31}P IR	45

Table 3 (Continued)

Complex	Prep. [1a] (%Yd)	Color m.p., °C	Anal.	NMR				Other Data	Ref.
				solvent (temp.) [1b]	^{1}H [1c] M-H	^{1}H [1c] Si-H	^{29}Si [1c]		
3-32 Cp(dmpe)(H)Mn-SiHPh$_2$	K [1o] (80)	lt. yellow green —	Y	Y	-14.42 (ddd) J_{HH} = 10.4	6.24 (ddd) J_{HH} = 10.4	—	^{13}C, ^{31}P IR X-ray	45
3-33 Cp(dmpp)(H)Mn-SiHPh$_2$	K (80)	yellow-orange	Y [1e]	Y	-14.47 (ddd) J_{HH} = 10.2	6.37 (ddd) J_{HH} = 10.4	—	VT-NMR ^{13}C, ^{31}P IR	45
3-34 Cp(Me$_3$P)$_2$(H)Mn-SiHPh$_2$	K (48)	orange-red —	Y	Y	-14.23 (ddd) $J_{HH'}$ = 8.6	6.35 (br s)	—	^{13}C, ^{31}P IR	45
3-35 Cp(OC)$_2$(H)ReSiHPh$_2$ [1r]	L [1o] (10)	white 103-105	Y	X	-9.70 (d)	5.97 (d) J_{HH} = 2.7	—	IR	93
3-36 (Ph$_3$P)$_2$(H)$_6$ReSiHEt$_2$	M (62)	off-white —	Y [1e]	Y (25)	-5.62 (t)	5.04 (s)	—	^{13}C, ^{31}P IR	94
				Y (-100)	-3.47 (br, 2) -6.99 (br, 4)	5.01 (s)			
3-37 [Ph$_2$(*i*-Pr)P]$_2$(H)$_5$Re-(SiHPh$_2$)$_2$	M	trans-parent	Y	—			—	N. D.	46
Manganese Triad: M$_2$									
3-38 [(OC)$_6$Mn$_2$(η-H$_2$SiPh$_2$)-(μ-dppm)]	N (—)	—	—	S	-13.09 (pt)	—	—	^{31}P IR	95
Iron Triad									
3-39 (OC)$_4$Fe=SiPh$_2$(DMI)	O [1o] (93) [1s] (90)	black-red —	Y	X: (^{1}H) T'/S: (^{29}Si)			91.3	^{13}C IR, MS	89, 91
3-40 (OC)$_4$Fe=SiPh$_2$(HMPA)	O (43)	— 121-122	Y	X			79.5 (d)	^{13}C, ^{31}P IR, MS	89, 91
3-41 (OC)$_4$Fe=SiPhAr Ar = C$_6$H$_4$CH$_2$NMe$_2$-2	O (80) (82)	red 130 (d) 140 (d)	Y	X			118 (101.1)	^{13}C IR, MS X-ray	89, 91
3-42 (OC)$_4$Fe=SiMeAr Ar = C$_6$H$_4$CH$_2$NMe$_2$-2	O (72)	red-brown —	Y	X			123.6	^{13}C IR	91
3-43 (OC)$_4$Fe=SiAr$_2$ Ar = C$_6$H$_4$CH$_2$NMe$_2$-2	O (65)	red-brown —	Y	X			115	^{13}C IR, MS	91
3-44 (OC)$_4$Fe=SiPh(1-Ar) Ar = C$_{10}$H$_6$CH$_2$NMe$_2$-8	O (61) O [1t] (75)	brown-red 140-141	Y	X			101	^{13}C IR, MS	91a
3-45a (OC)$_4$Fe=SiPh(1-Ar) Ar = C$_{10}$H$_6$NMe$_2$-8	O (56)	—	Y	X			126	^{13}C IR, MS	91a
3-45b (η^6-Tol)Fe(H)$_2$-(SiHCl$_2$)$_2$	[1u] (1-2%)	yellow —	Y [1e]	S	-18.66 (t)	6.07 (t) $^3J_{HH}$ = 5.2	—	X-ray	48
				Z	-18.66 (t) $^3J_{HH}$ = 4.8 $^2J_{SiH}$ = 17.6	5.86 (t)			
3-46 (Ph$_2$BuP)$_3$(H)$_3$FeSiHPh$_2$	P (98)	— 99 (d)	Y	S	-14.12 [1v]	5.07 (s) $^1J_{SiH}$ = 198.4	—	^{31}P IR	49
3-47 Cp*[Ph(*i*-Pr)$_2$P](H)$_2$Ru-SiHPh$_2$ [1w]	Q (—)	brown. oil	N	T (25)	-11.52	5.90 (s)	25.9 J_{SiH} = 182	^{31}P	96
				T (-60)	-11.78 (d) -11.12 (d)				
3-48 (OC)[(*t*-Bu)$_2$MeP](H)-RuSiHPh$_2$ [1x]	[1x] (95)	—	N	T	-0.84 (t)	5.43 (t)	—	^{31}P IR X-ray [1x]	97, 98

Table 3 (Continued)

Complex	Prep.[1a] (%Yd)	Color m.p., °C	Anal.	NMR				Other Data	Ref.
				solvent (temp.)[1b]	^{1}H[1c] M-H	^{1}H[1c] Si-H	^{29}Si[1c]		
3-49 $(Ph_3P)_3(H)_3RuSiHPh_2$	R (—)	white —	Y[1f]	Y'	-9.84	5.22	—	IR	99
3-50 $(OC)_2(Ph_3P)_2(H)Os$-$SiHPh_2$ (two isomers)[1y]	S[1o] (54)	colorless 192-194	Y	X	-9.12 (dd) (A)[1y] -6.89 (t) (B)	5.05 (d) (A)[1y] 4.88 (dd) (B)	—	^{13}C, ^{31}P IR	100
3-51 $(OC)[(i\text{-}Pr)_3P]_2(H)_3Os$-$SiHPh_2$	[1z] (75)	white —	Y	S	-9.65 (br)	6.52 (t)	—	VT-NMR ^{31}P IR X-ray	52
Iron Triad Dimers and Trimers									
3-52* $Cp_2(OC)_2Fe_2Si(Ar)_2$ $Ar = 2,4,6\text{-}C_6H_2(i\text{-}Pr)_3$[2a]	T[1o] (51)	violet —	Y	S	[2b]		—	IR FAB-MS X-ray	101
3-53* $Cp^*(OC)Fe(\mu\text{-}SiHPh)$-$(\mu\text{-}PPh_2)Fe(CO)_3$	[2c] (13)	brown —	—	S		7.01[2d]	209.1 (dd) $J_{SiH} = 185$	^{13}C, ^{31}P IR, MS	102
3-54 $Cp^*(OC)Fe(\mu\text{-}SiHR)(\mu$-$PPh_2)Fe(CO)_3$ (R = *p*-Tol)[2e]	[2c] (12) [2c,2f] (16)	brown —	—	S		7.04[2f]	209.1 (dd) $J_{SiH} = 185$	^{13}C, ^{31}P IR, MS	102
3-55a* $(OC)_4Fe_2Si(Ar)_2$ $Ar = 2,4,6\text{-}C_6H_2(Me)_3$	O (42)	orange —	HRMS	S			145.1 (s)	^{13}C IR, MS X-ray	103
3-55b* $(OC)_4Fe_2Si(Ar)_2$ $Ar = 2,6\text{-}C_6H_2(O\text{-}i\text{-}Pr)_3$	O (42)	orange —	HRMS	Y			88.4 (s)	^{13}C IR, MS	103
3-55c* $[(OC)_4FeSiPh_2]_2$	O (54)	yellow-orange 151-154	Y	—			—	IR, MS	104
3-56* $(OC)_7Fe_2(SiMePh)_2$	O (22)	yellow-orange 198-200	Y	Y			—	IR,MS	104
3-57 $(OC)_7Fe_2(SiC_{12}H_8)_2$	O (—)	—	—	—			—	X-ray	105, 106
3-58a $Cp(OC)Ru(\mu\text{-}CH_2)_2$-$Ru(H)(SiHEt_2)Cp$ $CH_2)(\mu\text{-}SiEt_2)(H)$-$(SiHEt_2)$	[2g] (34)	yellow —	Y	S	-15.1 (s)	3.25 (m)	—	^{13}C IR	107
3-58b $Cp_2Ru_2(\mu\text{-})(CO)$	[2h] (41)	yellow —	Y	S	-15.4 (s)	4.04 (m)	—	^{13}C IR	107
3-58c*$Cp^*{}_2Ru_2$-$(\mu\text{-}SiPhOMe)$-$(\mu\text{-}OMe)(\mu\text{-}H)$ (isomer 1)	U (42)	dk. maroon 284-287	Y[1e]	S	-18.72 (s)		211.1	^{13}C IR X-Ray	108
3-59 $Cp^*{}_2Ru_2(\mu\text{-}SiPhOMe)$-$(\mu\text{-}OMe)(\mu\text{-}H)$ (isomer 2)	[2i] (60)	—	—	S	-18.81 (s)	—	193.5	^{13}C	108
3-60 $[(OC)_{11}(\mu\text{-}H)Os_3\{2$-$BrC_6H_4CH_2SiMeH]$	[2j] (95)	—	Y	—	-18.76	—	—	—	57
3-61* $(OC)_{10}(\mu\text{-}H)_2HOs_3$-$(SiHPh_2)_2$	V (—)	yellow 101-102	Y[1e]	S	-17.5 (s) -17.35 (d) $J_{HH} = 12.7$ -9.4 (d) $J_{HH} = 12.7$	6.62 (s)	—	IR, MS X-ray	109

Table 3 (Continued)

Complex	Prep. [1a] (%Yd)	Color m.p., °C	Anal.	NMR				Other Data	Ref.
				solvent (temp.) [1b]	^{1}H [1c] M-H	^{1}H [1c] Si-H	^{29}Si [1c]		
Co Triad									
3-62a *mer*-$(Me_3P)_3Cl(H)$-$RhSiHPh_2$ [2k]	W (96)	yellow —	Y	S	-8.85 (ddt) $J_{RhH} = 15$	5.30 (dt) J = 10, 10, 12 [21]	14.9 (ddt) $J_{SiRh} = 43$	^{13}C, ^{31}P IR X-ray	110
3-62b *mer*-$(Me_3P)_3Cl(H)$-$Rh[SiH(p\text{-}MeOC_6H_4)_2]$	W (81)	—	Y	S	-8.80 (ddt) $J_{RhH} = 15$	5.35 (dt) J = 10, 10, 12 [21]	[2m]	^{13}C, ^{31}P IR X-ray	110
3-62c *mer*-$(Me_3P)_3Cl(H)$-$Rh[SiH(p\text{-}FC_6H_4)_2]$	W (94)	—	Y	S	-8.99 (ddt) $J_{RhH} = 15$	5.16 (dt) J = 10, 10, 12 [21]	[2m]	^{13}C, ^{31}P IR X-ray	110
3-62d *mer*-$(Me_3P)_3Cl(H)$-$Rh[SiH(p\text{-}F_3CC_6H_4)_2]$	W (88)	—	Y	S	-9.00 (ddt) $J_{RhH} = 13$	5.10 (dt) J = 10, 10, 12 [21]	[2m]	^{13}C, ^{31}P IR X-ray	110
3-62e *mer*-$(Me_3P)_3Cl(H)$-$RhSiClPh_2$	W [2n] (70)	lt. yellow —	Y [1e]	S	-8.78 (ddt) $J_{RhH} = 15$		41.7 (ddt) $J_{SiRh} = 48$	^{13}C, ^{31}P IR	110
3-62f *mer*-$(Me_3P)_3(PhS)(H)$-$RhSiHPh_2$ [2o]	X (79)	colorless —	Y	S	-8.97 (ddt) $J_{RhH} = 16$	5.47 (dt)	—	^{31}P IR	111, 112
3-63 $Cp^*(Me_3P)(H)Ir$-$SiPh_2(OTf)$	Y (89)	—	—	—	—		—	[2p]	113
3-64 $(OC)_3(Cy_3P)IrSiHPh_2$ [2q]	Z (—)	—	N	S		6.3 (d)	—	^{31}P	58
3-65 $(OC)_2Cy_3P(H)Ir$-$(SiHPh_2)_2$	Z (70) [2r]	white —	Y	S	-9.8 (d)	5.8 (d) 5.7 (d)	—	^{31}P IR	58
3-66 $(OC)_2Cy_3P(H)_2Ir$-$SiHPh_2$	Z (—) [2s]	—	N	S	-10.6 (dd) $^3J_{HH} = 1.9$	6.3 (dt)	—	^{31}P	58
3-67 $(OC)_2Cy_3P(H)_2Ir$-$[SiPh_2(OCOCH_3)]$	Z (26) [2t]	white —	Y	S	-10.4 (d)		—	^{31}P IR	58
3-68 $OC(Ph_3P)(Cl)(H)Ir$-$(SiMeHCH_2CH_2PPh_2)$ [2u]	2A (50)	colorless (80-85)	N	X	-7.09 (t) [2v]	4.60 (m) [2w] 4.15 (m)	—	^{31}P IR	114
3-69 $OC(dppe)(Mes)(H)Ir$-$SiHPh_2$	2B (65)	off-white —	Y	S	- 8.42 (t)	5.76 (m)	—	^{13}C, ^{31}P IR	115, 116
3-70 $OC(dppe)(H)_2IrSiHPh_2$ [2x]	2C (—)	colorless —	N	S or T	-9.28 (ddd) $^2J_{HH\,cis} = 2.4$	6.04 (m)	—	IR	60
3-71 $OC(dppe)(H)Ir$-$(SiHMe_2)(SiMe_2Cl)$	2C [2y] (—)	colorless —	N	S or T	-9.87 (t)	4.99 (m) 4.67 (m)	—	^{31}P IR X-ray	60
3-72 $OC(dppe)(H)Ir$-$(SiHPh_2)_2$ [2z]	2C (—)	colorless —	N	S or T	-9.59 (t)	6.14 (dd)	—	^{31}P IR	60
3-73 *mer*-$(Me_3P)_2Cl(H)Ir$-$[SiH(Mes)CH_2CH_2PPh_2]$ [3a]	2D (80)	—	Y	S	-9.41 (dt)	4.77 (dd) $^3J_{HH} = 6.4$, 20.1	-19.8 (ddd)	^{31}P IR, MS	117
3-74 $(Me_3P)_3(H)_2Ir$-$SiH(t\text{-}Bu)_2$ [3b]	2E (71)	colorless —	N	S	-13.06 (dd)	4.50 (q)	23.7 (dt)	^{13}C IR	118
3-75 $(Me_3P)_3(H)_2IrSiHPh_2$ [3b]	2E (87)	colorless —	Y	S	-12.12 (dd)	5.51 (q)	-0.32 (dt)	^{13}C, ^{31}P IR X-ray	118
3-76 $[(i\text{-}Pr)_3P](TFB)(H)_2$-$Ir{=}SiPh_2(\leftarrow OTf)$ [3c]	2F (39)	white —	Y	S	-15.16 (d)		—	^{31}P IR X-ray	119
3-77a $(Cy_3P)_2(acac)(H)Ir$-$SiHPh_2$ [3d]	2G (55)	white —	Y	S	-25.44 (t)	5.30 (t)	—	^{31}P IR	61

Table 3 (Continued)

Complex	Prep. [1a] (%Yd)	Color m.p., °C	Anal.	NMR				Other Data	Ref.
				solvent (temp.) [1b]	^1H [1c] M-H	^1H [1c] Si-H	^{29}Si [1c]		
3-77b $Cy_3P(acac)(H)Ir-SiHPh_2$ [3e]	2G [3f] —	—	N	S	-22.70 (d)	7.75 (d)	—	^{31}P	61
3-77c $Cy_3P(acac)Ir-\{C[CH(OCH_3)OSiPh_2]=CHCO_2CH_3\}$ [3g]	2H (53)	yellow —	Y	S			—	^1H, ^{13}C ^{31}P IR X-ray	120
3-78 $Ph_3P(TFB)(H)_2Ir-[Si(Ph)_2OCOCH_3]$ [3h]	2I (40)	white —	Y	S	-14.30 (d) [3i]		—	^{31}P IR	121
Co Triad Clusters									
3-79* $(OC)_6Co_2[\eta^2-PhC{\equiv}C-SiHPhCo(CO)_4]$	2J (87) [3j]	— (77)	Y	X		6.0 (s)	—	IR, MS	122
3-80* $(\mu-OC)[(OC)_3Co]_2-[\mu-SiMeMoCp(CO)_3]$ [3k]	2J (44)	yellow 110-112 (d)	Y	S			—	^1H IR	123
3-81 $(\mu-OC)[(OC)_3Co]_2-(\mu-SiMeR)$ R = $WCp(CO)_2(PMe_3)$	2J (49)	ocher 113 (d)	Y [1e]	S			—	^1H, ^{31}P IR, MS	64
3-82 $(\mu-OC)[(OC)_3Co]_2-(\mu-SiMeR)$ [3k] R = $WCp(CO)_3$	2J (31)	yellow 116 (d)	Y	S			—	^1H IR	123
3-83 $(\mu-OC)[(OC)_3Co]_2-(\mu-SiMeR)$ [3l] R = $FeCp(CO)_2$	2J (58) 2J (32)	dk. red 62 yellow 59-61 (d)	Y	S			83.2	^1H IR, MS	64, 123
3-84* $(OC)_3(\mu-CO)(dppm)_2-Rh_2(\mu-SiEt_2)$	2K (—) [3m]	—	N	S			—	^1H, ^{31}P IR	68
3-85* $(OC)_2(\mu-CO)(dppm)_2-Rh_2(\mu-SiEt_2)$ [3m]	2K (—)	—	N	Y			—	^1H, ^{31}P IR	68
3-86* $(OC)_2(dppm)_2(H)_2-Rh_2(\mu-SiEt_2)$ [3n]	2L (—)	—	N	S Y	S: -8.27 (m) Y: -9.15 (tquin)		—	VT-NMR ^{31}P IR	68, 69
3-87* $(OC)_2(dppm)(\mu-H)Rh_2-(Ph_2PCH_2PPhSiEt_2)$ [3o]	2L (—)	yellow —	Y	S	-9.60 (m)		—	^{31}P IR X-ray	68
3-88* $(dippe)_2Rh_2(\mu-SiPh_2)_2$	2M [3p] (—)	brt. orange —	Y	S			—	^1H, ^{31}P	124, 125
3-89* $(OC)_2(dppm)_2(H)_2Ir_2-(\mu-SiPh_2)$ [3q]	2N (82)	lt. yellow —	Y	Y	-11.99 (m)		—	VT-NMR ^{31}P IR X-ray	71
Ni Triad									
3-90 $(Ph_2MeP)_2Pd-(SiHMePh)_2$ [3r]	2O (—)	—	N	S		2.97 (m)	—	^{31}P	126
3-91 $(dcpe)Pd(SiH_2Me)_2$ [3s]	2P [3t] (—) [3u]	— 126	Y	S		4.65 (m)	—	^{13}C, ^{31}P IR, MS	73
3-92 $(dcpe)Pd(SiHPhMe)_2$	2P (—) [3u]	— 128 [3u]	Y	S		5.22 (m)	—	^{13}C, ^{31}P IR, MS	73
3-93 *cis*-$(Ph_3P)_2(H)Pt-[SiH(R_F)_2]$	2Q (88)	gold-orange —	N	S	-3.43 (dd) $^1J_{PtH}$ = 866	5.42 (m) $^1J_{SiH}$ = 189	-23.8 (br d) $^1J_{PtSi}$ = 1617	^{19}F, ^{31}P IR X-ray	127

Table 3 (Continued)

Complex	Prep. [1a] (%Yd)	Color m.p., °C	Anal.	NMR solvent (temp.) [1b]	NMR ^{1}H [1c] M-H	NMR ^{1}H [1c] Si-H	NMR ^{29}Si [1c]	Other Data	Ref.
3-94 (dcpe)Pt$(SiH_2Me)_2$	2R [3v] (100)							[2p]	76
3-95 $[Ph_2PCH_2CH_2$-$SiH(Me)]_2Pt$ [3w]	2S [3x] (—)	—	N	X		—	—	^{1}H, ^{31}P	128, 129
Ni Triad dimers									
3-96* $(OC)_2(dppm)_2Pt_2$-$(\mu\text{-}SiPh_2)$ [3y]	2T (95)	yellow —	Y [1e]	Y			—	^{1}H, ^{13}C, ^{31}P, ^{195}Pt IR	130
3-97* $(dcpe)_2Pt_2(\mu\text{-}SiHMe)_2$	2R [3z] (100)	—	—	—		—	—	[2p]	76

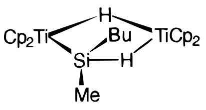
* Structural formulas for compound numbers marked with an asterisk may be found at the end of the table. † Abbreviations: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Cy, cyclohexyl; Cp, C_5H_5; Cp*, C_5Me_5; Cp′, $C_5H_4CH_3$; Ph, phenyl; *p*-Tol, *p*-tolyl; Mes, 2,4,6-trimethylphenyl; TFB, tetrafluorobenzobarralene; R_F, 2,4,6-tris(trifluoromethyl)phenyl; acac, acetyl acetonate; coe, cyclooctene; cod, cyclooctadiene; OTf, OSO_2CF_3; dippe, 1,2-bis(diisopropylphosphino)ethane; dcpe, 1,2-bis(dicyclohexylphosphino)ethane; dppm, 1,2-bis(diphenylphosphino)methane; DMI, 1,2-dimethyl-2-imidazolidinone; HMPA, hexamethylphosphoramide; dmpm, 1,2-bis(dimethylphosphino)methane; dmpe, 1,2-bis(dimethylphosphino)ethane; dmpp, 1,2-bis(dimethylphosphino)propane; N. D., neutron diffraction; lt., light; brt., bright; dk., dark; d, decomposes.

Footnotes: [1a] General reactant key (L is a neutral ligand such as CO or phosphine; hydrosilanes are coreactants in all cases); A, $Cp^*_2YCH(SiMe_3)_2$; B, Cp_2MR_2; C, $Cp_2M(CH_2{=}CHEt)PMe_3$; D, $Cp_2MBu_2 + PMe_3$; E, $CpCp'M[Si(SiMe_3)_3]X$ ($Cp' = C_5H_5$ or C_5Me_5; X = Cl, H)); F, Cp'_2M(olefin) (generated in situ) + heat; G, $Cp_2MH_{2\text{ or }3}$; H, Cp_2MRL; I, $M(CO)_6 + h\nu$; J, $(\eta^5\text{-}Cp')M(CO)_3$; K, CpMn(LL)CO; L, $CpRe(CO)_3$; M, ReH_7L_2; N, $Mn_2(\mu\text{-}H)_2(CO)_6(Ph_2PCH_2PPh_2)$; O, $M_x(CO)_y$ ($h\nu$ or Δ); P, $H_3L_3FeSiR_3$ (R = Me or Bu); Q, $Cp^*RuL(OCH_2CF_3)$; R, Cl_2RuL_3 ($ClHRuL_3$ or H_2RuL_3); S, $Os(CO)_2L_3$; T, $CpFe(CO)_2Me$; U, $[Cp^*Ru(\mu\text{-}OMe)]_2$; V, $Os_3(\mu\text{-}H)_2(CO)_{10}$; W, $[(Me_3P)_4Rh]Cl$; X, $Rh(SAr)(PMe_3)_3$; Y, $Cp^*(PMe_3)Ir(CH_3)(OTf)$; Z, $(OC)_2(Cy_3P)Ir(OCOCH_3)$; 2A, $IrCl(CO)(PPh_3)_2$; 2B, (dppe)-OCIr(Mes); 2C, $(OC)dppeIrH_3$; 2D, $[Ir(CO)(PMe_3)_4]Cl$ + heat (sealed tube); 2E, $(Me_3P)_4IrH$; 2F, $(i\text{-}Pr_3P)(TFB)Ir(OTf)$; 2G, $(Cy_3P)(acac)Ir(coe) + PCy_3$; 2H, $Ir(acac)(\eta^2\text{-}CH_3O_2C{-}C{\equiv}C{-}CO_2CH_3)(PR_3)$, R = *i*-Pr, Cy; 2I, $(Ph_3P)(TFB)Ir(OCOCH_3)$; 2J, $Co_2(CO)_8$; 2K, $Rh_2(CO)_3(dppm)_2$; 2L, $Rh_2H_2(CO)_2(dppm)_2$; 2M, $[(dippe)Rh]_2(\mu\text{-}H)_2$; 2N, $Ir_2(CO)_3(dppm)_2$; 2O, $(Ph_2MeP)_2PdMe_2$; 2P, $[(dcpe)Pd]_2(\mu\text{-}H)_2$; 2Q, $(Ph_3P)_2Pt(C_2H_4)$; 2R, $(dcpe)PtH_2$; 2S, $(cod)_2Pt$; 2T, $[Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$. [1b] Solvent key: X, $CDCl_3$; S, C_6D_6; T, C_7D_8; U, THF-d_8; Y, CD_2Cl_2; Y′, CH_2Cl_2; V, $C_2D_2Cl_4$; W, $(CD_3)_2CO$; Z, CD_3CN. Data for ambient temperature in °C unless specified otherwise. [1c] In ppm. Coupling constants in Hz. Assignments: s, singlet; d, doublet; t, triplet; pt, pseudotriplet; q, quartet; quin, quintet; sept, septet; m, multiplet. [1d] The reactions of Cp_2TiMe_2 with $RR'SiH_2$ and PMe_xPh_{3-x} gave complexes of the type $Cp_2TiSiHRR'(L)$ (R, R′ = Ph, **3−3**; R = Ph, R′ = SiH_2Ph) which were identified in solution from EPR studies.[33b] [1e] Analysis is outside ±0.5 of calculated percent value for carbon. [1f] Determined by ^{1}H NMR. [1g] Additional derivatives: $CpCp^*ClHfSiHPh_2$, $CpCp^*ClHfSiHPhSiH_2Ph$. [1h] Mixed with $[Cp_2HfHCl]_n$ (10%). [1i] The reaction of $CpCp^*Hf[Si(SiMe_3)_3]Me$ with $H_2SiPhSiPhHSiPhHSiPhH_2$ has also been described as has the reaction of $H_2SiPhSiPhH_2$ with $CpCp^*HfH_2$ to give complexes $CpCp^*Hf[SiHPh(SiPhH)_xSiPhH_2]X$.[21b] [1j] Four diastereomers in 1:1:1:1 ratio. [1k] Additional derivative: $Cp_2Zr(SiHPh_2)(\mu\text{-}H)_2(Ph_2MeSi)ZrCp_2$. [1l] Center of multiplet. [1m] Additional derivative: $[Cp_2(H)Zr(SiHBuMe)]_2$. [1n] Identified in solution in a mixture of $Cp_2Zr(R)(\mu\text{-}H)_2R'ZrCp_2$, R = Ph_2SiH, R′ = Ph_2MeSi; R = Me, R′ = Ph_2MeSi; R = Me, R′ = Ph_2SiH (isolated). [1o] Photolysis. [1p] Additional derivatives prepared from $H_2Si(t\text{-}Bu)_2$. [1q] From reaction of $Cp_2W(CH_2{=}SiMe_2)$ with $H_2Si(t\text{-}Bu)_2$. Additional derivatives prepared from $HSiMe_3$, $HSiMe_2Cl$, and $HSi(i\text{-}Pr)_2Cl$ (X-ray). [1r] A related complex was prepared from $CpRe(CO)_3$ and Et_2SiH_2 but decomposed on workup.[93b] [1s] $[Ph_2SiFe(CO)_4]_2 + h\nu$ + DMI. [1t] In THF without photolysis. [1u] From reaction of $Fe_{(v)}$ with toluene and H_2SiCl_2. [1v] AA′A″XX′X″ system. [1w] Byproduct: $Cp^*[Ph(i\text{-}Pr)_2P](H)_2Ru[Si(OCH_2CF_3)Ph_2]$. [1x] Reaction of $(CO)[PMe(t\text{-}Bu)_2]_2(H)RuPh$ with Ph_2SiH_2. Yield determined by NMR. Isolated previously as an adduct with $Li_2(RuL_4)(\mu_6\text{-}O)(\mu_3\text{-}Cl)_8$ (X-ray).[97] [1y] Isomer A, H is trans to PPh_3; isomer B, H trans to CO. [1z] From $L_2(OC)H_2Os(CH_2{=}CHEt)$ and H_2SiPh_2. [2a] Additional derivatives: Ar = 2,6-$C_6H_3Et_2$ (41%); mesityl (22%). [2b] Signals are broad and unassigned due to triplet state of derivative. Additional derivatives: $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-}SiAr_2)$, Ar = 2,6-$Et_2C_6H_3$, 2,4,6-$Me_3C_6H_2$. [2c] $Cp^*(OC)Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3 + R_2SiH_2$. [2d] Confirmed by COSY experiment. [2e] Additional derivative: $Cp^*_2Fe_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}SiMeH)$. [2f] $Cp^*(OC)Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3 + HPh_2SiSiPh_2H$. [2g] From $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ and H_2SiEt_2. Additional derivative: $Cp(OC)Ru(\mu\text{-}CH_2)_2Ru(H)(SiHPh_2)Cp$. [2h] From $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ and H_2SiEt_2. Additional derivative: $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiPh_2)(H)(SiHPh_2)(CO)$. [2i] Isomerization of isomer 1. [2j] Reaction of $[Os_3(CO)_{11}(NCCH_3)]$. [2k] Additional derivatives: $(Me_3P)_4Cl(H)Rh[SiH(p\text{-}MeC_6H_4)_2]$, $(Me_3P)_4Cl(D)RhSiDPh_2$ (see also **3−62b** through **3−62e**). [2l] Identity of *J* values not specified. Values reported as *J* = 10, 10, and 12 Hz for coupling to Rh and P. [2m] Information not given in reference. [2n] Also prepared by heating $(Me_3P)_3Cl(H)RhSiHPh_2$ (**3−62a**) or by reaction of $HSiClPh_2$ with $(Me_3P)_3(H)_2RhSiClPh_2$. [2o] Additional derivatives: *mer*-$(Me_3P)_3(ArS)(H)RhSiR_2H$, Ar = *p*-tolyl, *p*-$MeOC_6H_4$, R = Ph; Ar = Ph, R = *m*-tolyl, *p*-tolyl; Ar = *p*-$MeOC_6H_4$, R = *m*-tolyl; Ar = *p*-tolyl, R = *p*-FC_6H_4. Upon standing at >30 °C complexes convert to *fac*-$(Me_3P)_3(H)_2RhSiPh_2SAr$ (X-ray structure obtained for R = Ph derivative). See also **4−239b** to **4-239d** for related derivatives. [2p] Data are in supplementary material for these references. [2q] Observed in solution only by ^{1}H and $^{31}P\{^{1}H\}$ NMR during the formation of $(OC)_2Cy_3P(H)_2Ir[SiPh_2(OCOCH_3)]$ (**3−67**). [2r] Reaction performed with a 2:1 ratio of Ph_2SiH_2 to $(OC)_2(Cy_3P)Ir(OCOCH_3)$. [2s] Observed in solution only by ^{1}H and $^{31}P\{^{1}H\}$ NMR during the formation of $(OC)_2Cy_3P(H)_2Ir(SiPh_2H)_2$ (**3−65**). Complexes are fluxional at room temperature. [2t] Reaction performed with a 1:1 ratio of Ph_2SiH_2 to $(OC)_2(Cy_3P)Ir(OCOCH_3)$. Also prepared by reaction of $(OC)_2Cy_3P(H)Ir(SiHPh_2)_2 + CH_3COOH$ in 45% yield. [2u] Additional derivatives: $OC(Ph_3P)Cl(X)Ir(SiRHCH_2CH_2PPh_2)$, R = CD_3, X = D; R = Ph, X = H. [2v] Apparent triplet by coupling to ^{31}P. [2w] Mixture of diastereomers. Si−H resonances are given for both diastereomers. Only one hydride resonance observed. [2x] Additional derivative: $(OC)(dppe)(H)_2Ir(SiHMe_2)$. [2y] Complex prepared by using 1 equiv each of Me_2SiH_2 and Me_2SiHCl. [2z] Additional derivative: $(OC)(dppe)(H)Ir(SiHMe_2)_2$. [3a] Hydride is trans to a PMe_3 ligand. Complex undergoes isomerization when irradiated to give *mer*-$(Me_3P)_3Cl(H)Ir[SiH(Mes)CH_2CH_2PPh_2]$ where H is opposite to the PPh_2 moiety. An X-ray structure was reported for the latter complex and thermolysis (80 °C) regenerates **3−73**. [3b] Additional derivatives: $(Me_3P)_3H(D)IrSiDR_2$, R = Ph and *t*-Bu. [3c] Additional derivatives: $(Cy_3P)TFB(H)_2Ir\{Si(OTf)Ph_2\}$. [3d] See also **2−60b** (Table 2) and **4−297b** (Table 4) for related derivatives. [3e] Characterized in solution by ^{1}H and ^{31}P NMR spectroscopy. [3f] Reaction does not require presence of excess PCy_3. [3g] Additional derivatives: $[(i\text{-}Pr)_3P](acac)Ir\{C[CH(OCH_3)OSiPh_2]{=}CHCO_2CH_3\}$. [3h] Additional derivatives: $(R_3P)(TFB)(H)_2Ir(Ph_2SiOCOCH_3)$, R = *i*-Pr; R = Cy. [3i] Hydride resonance appears at the same position in the ^{1}H NMR spectrum at 20 °C and −55 °C (toluene-d_8). [3j] Can also be prepared by reaction of 0.5 $Co_2(CO)_8 + [\eta^2\text{-}PhC{\equiv}CSiH_2Ph]Co_2(CO)_6$. [3k] Additional derivatives: $\{(OC)_3Co\}_2(\mu\text{-}CO)(\mu$-

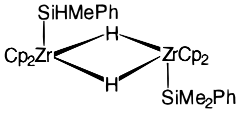
Table 3 (Continued)

SiPhML$_n$), ML$_n$ Mo(CO)$_3$Cp, W(CO)$_3$Cp, Fe(CO)$_2$Cp. [3l] Additional derivative: {(OC)$_3$Co}$_2$(μ-CO)[μ-Si(Ph)FeCp(CO)$_2$]. [3m] Complex (OC)$_2$(μ-OC)(dppm)$_2$Rh$_2$(μ-SiEt$_2$) appears to form after initial generation of (OC)$_2$(dppm)$_2$(H)$_2$Rh$_2$(μ-SiEt$_2$). When the reaction is carried out under CO then (OC)$_3$(μ-OC)(dppm)$_2$Rh$_2$(μ-SiEt$_2$) (**3−84**) is formed (process is reversible). Addition of CO to (OC)$_2$(μ-OC)(dppm)$_2$Rh$_2$(μ-SiEt$_2$) gives (OC)$_3$(μ-OC)(dppm)$_2$Rh$_2$(μ-SiEt$_2$) (**3−84**) (removal of CO gives the reverse reaction). The latter complex is believed to contain a dangling dppm ligand. [3n] Additional derivatives: (OC)$_2$(dppm)$_2$(H)$_2$Rh$_2$(μ-SiRR′), R = R′ = Me; R = Me, R′ = Ph. Compounds are fluxional on NMR time scale and are thermally unstable. See also **2−69**, **2−70**, and **2−71** for related derivatives. [3o] Additional derivatives: (OC)$_2$(dppm)(μ-H)Rh$_2$(Ph$_2$PCH$_2$PPhSiRR′), R = R′ = Me; R = Me, R′ = Ph. These are final products from reaction of RR′SiH$_2$ + Rh$_2$H$_2$(CO)$_2$(dppm)$_2$ (after 24 h, room temperature). Product formed by formal cleavage of P−C (aryl) bond and formation of Si−P bond. [3p] Also prepared by reaction of Ph$_2$SiH$_2$ with [(dippe)Rh]$_2$(μ-H)(μ-η^2-HSiPh$_2$) (**7−53**). [3q] Additional derivatives: (OC)$_2$(dppm)$_2$(H)$_2$Ir$_2$(μ-SiR$_2$), R = Me, Et. Complexes are fluxional on NMR time scale at room temperature. [3r] Additional derivative with H$_2$SiPh$_2$. Complexes detected by spectroscopy only and decomposed readily to give H$_2$Si$_2$R$_4$. [3s] Additional derivative: (dcpe)Pd(SiHPh$_2$)$_2$ (prepared from H$_2$SiPh$_2$). [3t] Prepared by reaction of [(dcpe)Pd]$_2$(μ-H)$_2$ with (H$_2$MeSi)$_2$. [3u] Products are isolated as colorless to pale yellow solids in 50−70% yield. [3v] Rapid addition of H$_2$MeSi−SiMeH$_2$ in toluene at room temperature provided **3−94**. [3w] Additional derivative: Pt(SiHPhCH$_2$CH$_2$PPh$_2$)$_2$. Observed in solution as a mixture of isomers but not isolated in solid state (see also **4−342**). [3x] Also prepared with (cod)PtCl$_2$ + Et$_3$N. [3y] Additional derivatives: (OC)$_2$(μ-dppm)$_2$Pt$_2$(μ-SiRR′), R = R′ = Me, Et; R = Me, R′ = Ph. [3z] Slow addition of H$_2$MeSi−SiMeH$_2$ in toluene at 40 °C, or reaction of (dcpe)Pt(SiH$_2$Me)$_2$ + (dcpe)PtH$_2$ at 40 °C provided **3−97** (two geometric isomers).

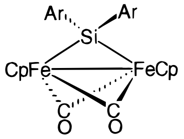
Compound structures for Table 3:



3-12

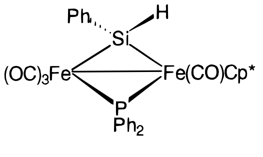


3-13

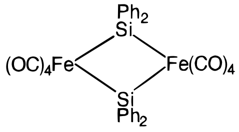


Ar = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$

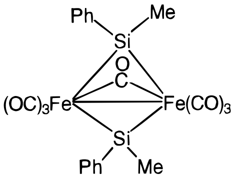
3-52



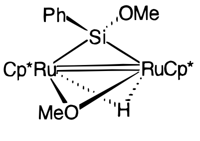
3-53



3-55c

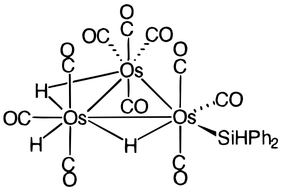


3-56

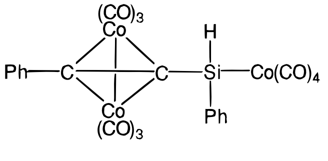


(isomer 1)

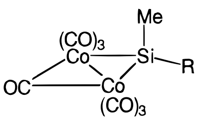
3-58c



3-61

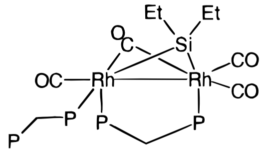


3-79



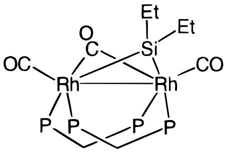
R = MoCp(CO)$_3$

3-80



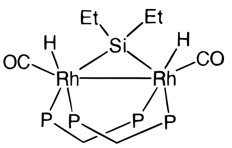
P = PPh$_2$

3-84



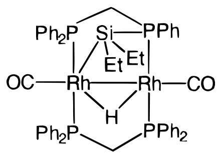
P = PPh$_2$

3-85

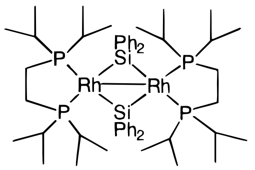


P = PPh$_2$

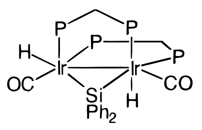
3-86



3-87

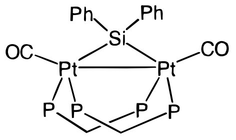


3-88



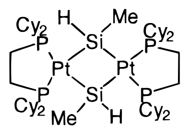
P = PPh$_2$

3-89



P = PPh$_2$

3-96



3-97

(Me)H(SiHMe$_2$) (speculative) followed by elimination of CH$_4$ and addition of a second mole of Me$_2$SiH$_2$ to give the final product, Cp$_2$Ta(H)(SiHMe$_2$)$_2$ (**3−18**).[13] With bulkier substituents on silicon a second mole of silane does not react (see **3−17**). Reaction of OsHCl(CO)L$_2$ [L = P(*i*-Pr)$_3$] with *n*-BuLi provides the dihydrido complex, OsH$_2$(η^2-CH$_2$=CHEt)(CO)L$_2$,[132] which in turn reacts with H$_2$SiPh$_2$ to give OsH$_3$(SiHPh$_2$)(CO)L$_2$ (**3−51**; X-ray).[52]

Probably the best route to silyl−hafnium systems involves the displacement of the large Si(SiMe$_3$)$_3$ group. Reaction of Cp$_2$Hf[Si(SiMe$_3$)$_3$]Cl with Ph$_2$SiH$_2$ provided Cp$_2$Hf(SiHPh$_2$)Cl although the product was contaminated with [Cp$_2$HfHCl]$_n$ which would result from the formal extrusion of a silylene from the silylhafnium product. Replacement of one of the Cp substituents with Cp* results in the formation of several stable CpCp*Hf(SiHRR′)Cl complexes (**3−7** to **3−9**).[21,86] This tactic has also been utilized in replacement of a SiPh$_3$ group at Zr. When Cp$_2$ZrH(SiPh$_3$)PMe$_3$ was reacted with H$_2$SiPh$_2$, 2 of the 3 isomers of Cp$_2$ZrH(SiHPh$_2$)PMe$_3$ **3−5** formed.[82] In the titanium triad the exchange of silyl groups appears to occur if the group added is smaller than the silyl group originally bound to the metal. However, this may not always be the driving force with other metals. For example, exchange of silyl groups in L$_3$FeH$_3$(SiMe$_3$) (L = PPh$_2$R, R = Et, Bu) occurs with primary, secondary (**3−46**), and tertiary silanes.[49]

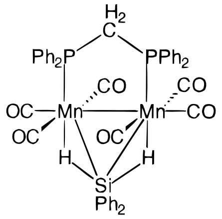


Figure 6. Structure of **3−38**.

Although not extensively employed in early-transition-metal chemistry, metal hydrides also interact with hydrosilanes. For example, $Cp_2TaH(CO)$ and H_2SiMe_2 gave $Cp_2Ta(H)_2SiMe_2H$, although the product was only studied in solution (for isolated examples, see section III.D). Earlier work suggested that Cp_2MH_3 (M = Nb, Ta) did not react with silanes under photolysis conditions or in refluxing silane.[84] However, $Cp'_2Nb(H)_2SiPh_2H$ [**3−16**, symmetrical isomer (X-ray); $Cp' = C_5H_4SiMe_3$] was recently isolated from addition of Ph_2SiH_2 to Cp'_2NbH_3.[39] Since the reaction was conducted at 65 °C, it is likely that thermal loss of H_2 from the starting complex occurred prior to the oxidative addition of the silane. Although Cp_2MoH_2 does not react with Me_2SiH_2 at room temperature under ambient lighting, photolysis with 350-nm radiation provided $Cp_2Mo(H)SiMe_2H$ (**3-21**, X-ray).[90] Labeling experiments demonstrated that a photolytically induced reductive elimination of H_2 occurred to give the $16e^-$ molybdocene which then oxidatively adds the silane. Several hydrosilanes were successfully reacted with Cp_2MoH_2 to give isolated silylmolybdenum products but comparable reactions of Cp_2WH_2 were too slow to be of practical use[90] although examples of silyltungsten complexes from tertiary silanes have been reported by this method (see section III.D). Silylmolybdenum complexes formed from secondary silanes that contain phenyl substituents, i.e., $Cp_2Mo(H)(SiRPhH)$ (R = Me, Ph), decompose to the starting Cp_2MoH_2 at room temperature.[84]

Metal hydrides that do not contain Cp ligands are also precursors to silylmetal complexes. The polyhydride, ReH_7L_2, has been reacted with Et_2SiH_2 and Ph_2SiH_2 to give the two different products, $ReH_6(SiHEt_2)L_2$ ($L = PPh_3$), **3−36**,[94] and $ReH_5(SiHPh_2)_2L_2$ [$L = PPh(i\text{-}Pr)_2$, **3−37**;[46] neutron diffraction study], respectively. Spectroscopic data for **3−36** are consistent with a classical nine-coordinate tricapped trigonal-prismatic structure (non-hydrogen ligands occupying the three equatorial sites) and the neutron diffraction study of **3−37** provided a structure described as a monocapped twisted rhombic prism. It is not clear why two different complexes are formed although **3−36** was prepared at room temperature in THF and **3−37** at 55 °C in hexane.

The manganese dimer, $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$), reacted with Ph_2SiH_2 to provide a complex formulated as $[Mn_2(\mu\text{-}H_2SiPh_2)(CO)_6(\mu\text{-dppm})]$, **3−38** (Figure 6, discussed further in section VI) based on spectroscopic data.[95] It is not clear whether the starting complex loses dihydrogen and then reacts with Ph_2SiH_2 or whether the hydrogens in the product are derived from the reacting silane.

The majority of the silylmetal complexes of manganese and iron are formed from a suitable carbonyl derivative where thermolysis or photolysis generates an electron-deficient metal fragment. Some metal carbonyls have been utilized with secondary silanes to provide isolated examples of base-stabilized metal−silylene complexes. Reaction of $M(CO)_6$ (M = Cr, Mo) provided $(OC)_5Cr{=}Si(C_6H_5)[C_6H_4CH_2NMe_2\text{-}2]$ (**3−19**)[89] and that of $Cp'Mn(CO)_3$ the corresponding manganese analogues, **3−26** through **3−30**.[91,92] Since reaction of $Cp'Mn(CO)_3$ and $Cp'Mn(PPh_3)(CO)_2$ with Ph_2SiH_2 both gave $Cp'(OC)LMnH(SiHPh_2)$ (section VI; L = CO, PPh_3), the isolation of the silylene complex from the secondary silane must require a substituent at silicon that contains a pendant base capable of coordinating to the silicon center and thus stabilizing the metal−silylene formed. A series of phosphine-chelating systems, $CpMn(LL)CO$ [LL = $Me_2P(CH_2)_xPMe_2$ (x = 1, 2, 3)] also gave oxidative addition products with hydrosilanes after loss of CO (**3−33** and **3−34**).[45] The normal oxidative addition product, $CpRe(CO)_2(H)SiHPh_2$ (**3−35**)[93] was produced from $CpRe(CO)_3$ and Ph_2SiH_2.

The reaction of $Fe(CO)_5$ with $RR'SiH_2$ where R or R′ has a pendant amine in the ortho position of an aromatic ring has provided a series of silanediyliron(0) complexes, **3−39** through **3−45a**.[91a] If the photolysis of $Fe(CO)_5$ and Ph_2SiH_2 was conducted in the presence of a coordinating base such as DMI or HMPA, the base-stabilized metal−silylenes, $(OC)_4Fe{=}SiPh_2(DMI)$ (**3−39**) and $(OC)_4Fe{=}SiPh_2(HMPA)$ (**3−40**) were produced.

Transition-metal chlorides may be converted to metal hydrides by hydrosilanes and if the reaction is conducted with excess silane, subsequent reaction can lead to silylmetal complexes. When $RuCl_2(PPh_3)_3$ was heated with a 10-fold excess of Ph_2SiH_2, the product isolated was $RuH_3(SiHPh_2)L_3$ (**3−49**, L = PPh_3[99]). In a related process, $Cp^*Ru[P(i\text{-}Pr)_3](OCH_2CF_3)$ reacted with H_2SiPh_2 to give *cis*-$Cp^*RuL(H)_2(SiXPh_2)$ where X = H or OCH_2CF_3.[96] The formation of $Cp^*RuL(OCH_2CF_3)(H)(SiHPh_2)$ occurred on addition of H_2SiPh_2 but was followed by elimination of $HSi(OCH_2CF_3)Ph_2$ to give $Cp^*RuL(H)$. The latter then reacted with excess H_2SiPh_2 or $HSi(OCH_2CF_3)Ph_2$ to give the observed product mixture. A novel entry into silyltungsten complexes was provided from the “silaolefin” precursor, $Cp_2W(CH_2{=}SiMe_2)$, which, upon reaction with $H_2Si(t\text{-}Bu)_2$, provided the disilyl-substituted derivative, $Cp_2W(SiMe_3)[SiH(t\text{-}Bu)_2]$ (**3−25**,[90] X-ray).

In the absence of a coordinating base, silicon-bridged dimers $(OC)_4Fe(\mu\text{-}SiPh_2)_2Fe(CO)_4$ (**3−55c**) and $(OC)_3Fe(\mu\text{-}SiPhMe)(\mu\text{-}CO)Fe(CO)_4$ (**3−56**) are formed from $Fe(CO)_5$ and possibly $Fe_2(CO)_9$ with secondary silanes under photolysis conditions.[102−104] However, without photolysis, the combination of $Fe_2(CO)_9$ and Ph_2SiH_2 formed $[(OC)_4Fe{-}Fe(CO)_3(SiHPh_2)](\mu\text{-}\eta^2\text{-}HSiPh_2)$ which will be described in section VI. The silylene-bridged dimer $Cp_2(OC)_2Fe_2SiAr_2$ [Ar = 2,4,6-$C_6H_2(i\text{-}Pr)_3$ **3−52**], which exhibited a triplet ground state, was formed from $Cp(OC)_2FeMe$ and secondary silanes that contain bulky aryl groups.[101] In this case it is probable that loss of CO

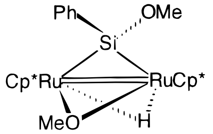


Figure 7. Structure of **3−58c**.

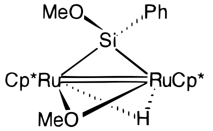


Figure 8. Structure of **3−59**.

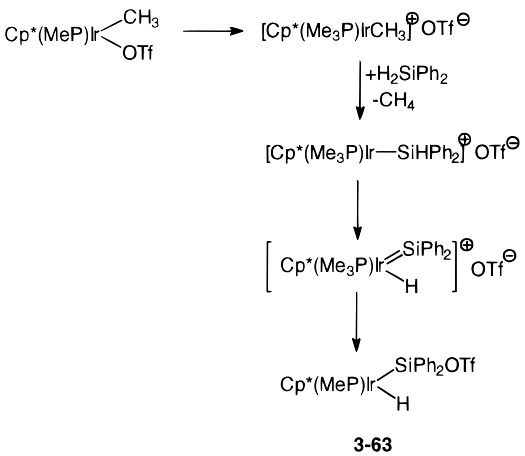
occurs from $Cp(OC)_2FeMe$, followed by addition of the secondary silane. Elimination of methane, reattachment of CO, and then reaction with the Cp(OC)FeMe fragment accounts for the silylene-bridged dimer product (yields are ≤50%).

The dimer, $Cp^*(OC)Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$, also reacted with secondary silanes to give silylene bridged dimers (CO is replaced by RR′Si, see **3−53**); however, a redistribution of R_2SiH_2 (R = Ph) occurred to give $RSiH_3$ and R_3SiH and it is the RSiH unit (from $RSiH_3$) that was incorporated into the bridging position.[102] Treatment of the unsaturated complex $[Cp^*Ru(\mu\text{-}OMe)]_2$ with Ph_2SiH_2 resulted in substitution of one of the phenyl groups on silicon and a Cp*Ru=RuCp* unit which is bridged by a OMe group, a PhSiOMe group, and a hydride (two isomers, **3−58c**, Figure 7, and **3−59**, Figure 8).[108] However, when a dialkylsilane was utilized, an entirely different product containing nonclassical RuHSi interactions (see section VI) was obtained.

As the number of metal atoms increases in the cluster, the pathway from starting complex to the silicon-containing product becomes less clear. The cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$ has been used as the starting material in a reaction with Ph_2SiH_2 to give what appears to be the oxidative addition product, $H(OC)_{10}(\mu\text{-}H)_2Os_3(SiHPh_2)$ (**3−61**).[109] However, addition of $ArMeSiH_2$ to $Os_3(CO)_{11}(NCCH_3)$ provided $(OC)_{11}(\mu\text{-}H)Os_3(SiHArMe)$ (Ar = $2\text{-}BrC_6H_4CH_2$−, **3−60**).[57]

The reaction of secondary silanes with metals of the cobalt triad clearly shows a gap in entries involving monomeric cobalt and rhodium complexes (the only examples are **3−62a−f**). However, there are several monomeric iridium complexes [**3−63**,[113] **3−64** to **3−67**,[58] **3−68**,[114] **3−69**,[115,116] **3−70** to **3−72**,[60] **3−73**,[117] **3−74**, **3−75**,[118] **3−76**,[119] **3−77a,b**,[61] **3−77c**,[120] and **3−78**[121]] most of which contain carbonyl and/or phosphine ligands at the metal center and there are a few that also contain an Ir−H bond. The majority of the entries for Co, Rh, and Ir involve the oxidative addition of a secondary silane to a 16-electron unsaturated metal complex. In some cases the silyl(hydride)metal complex was generated and in others subsequent loss of a ligand from the coordination sphere occurred. There are other examples in Table 3 that involve 18-electron complexes but these require initial loss of a ligand before addition of the silane occurs. An interesting trend observed with a number of monomeric cobalt triad complexes was a formal migration of a ligand from the metal (primarily iridium) to silicon and examples are described in the following paragraphs.

Scheme 12



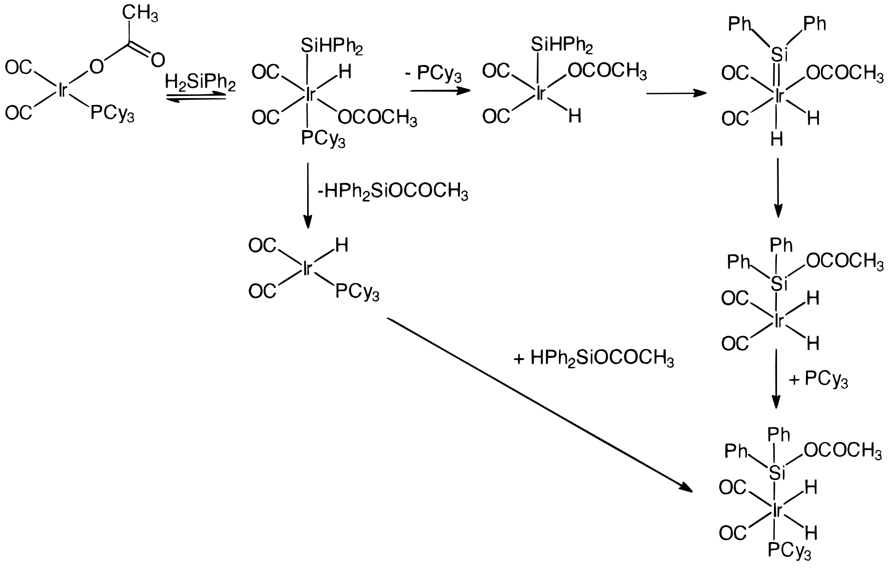
3-63

The rhodium−silyl complex, *mer*-$(Me_3P)_3(PhS)(H)RhSiHPh_2$ (**3−62f**), was prepared by reaction of diphenylsilane with the phosphine rhodium(thiolate) complex, $(Me_3P)_3Rh(SPh)$. Upon standing at temperatures >30 °C, an unusual rearrangement occurred to give the (thiolate)silyl complex, *fac*-$(Me_3P)_3H_2Rh[SiPh_2(SPh)]$.[111]

A number of rearrangements have been reported for iridium. For example, $Cp^*(Me_3P)(H)IrSiPh_2OTf$ (**3−63**) was generated by a formal migration of a triflate group from Ir to Si.[113] The reaction is believed to involve initial oxidative addition of a Si−H bond in Ph_2SiH_2 to $Cp^*(Me_3P)Ir(Me)(OTf)$ followed by facile rearrangement to afford **3−63** (Scheme 12[113]).

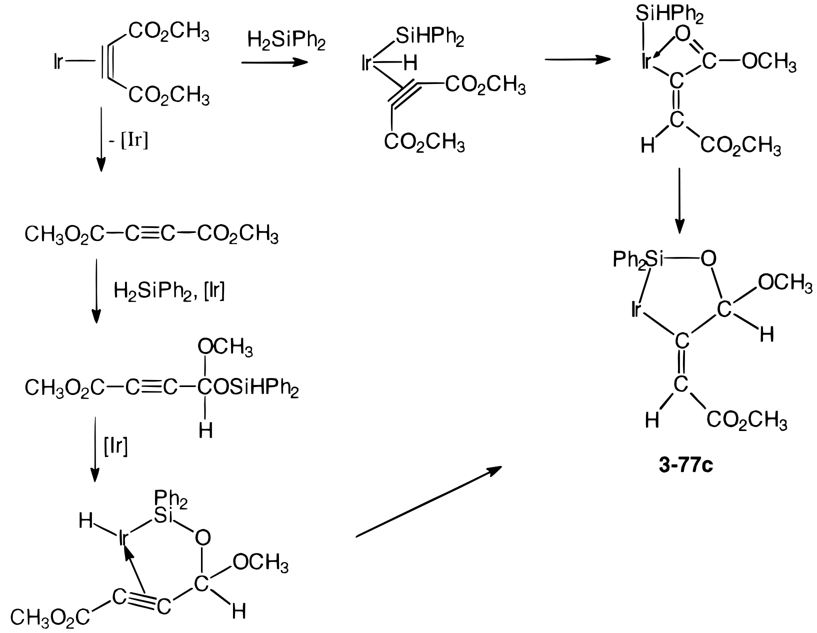
Several iridium−silyl complexes (**3−64** through **3−67**) were generated by reaction of $(OC)_2(Cy_3P)IrOCOCH_3$ with Ph_2SiH_2.[58] When a 1:1 molar ratio of reagents was used complex **3−67** was isolated but when a 2:1 ratio was used, $(OC)_2(Cy_3P)(H)Ir(SiHPh_2)_2$ (**3−65**) was obtained. The formation of complex **3−67** has been rationalized through initial oxidative addition of a Si−H bond in Ph_2SiH_2 to afford a silyl(hydrido)iridium intermediate. Two pathways were proposed to generate the acetoxysilyl ligand: (a) loss of phosphine from the silyl(hydrido)iridium intermediate and formation of a silylene complex by an α-hydride migration then attack of the acetoxy ligand at the unsaturated silicon center or (b) reductive elimination of an acetoxysilane followed by oxidative addition to the iridium center.[58] The possible pathways are summarized in Scheme 13. The reaction was monitored by ^1H and ^{31}P NMR spectroscopy and products **3−67** and $(OC)_3LIrSiHPh_2$ (**3−64**) or $(OC)_2L(H)_2IrSiHPh_2$ (**3−66**) (L = PCy_3) were observed depending upon the stoichometry used. Migration of an acetoxy group to silicon was also observed in the reaction of $(Ph_3P)(TFB)Ir(OCOCH_3)$ with Ph_2SiH_2 to afford $(Ph_3P)(TFB)(H)_2Ir(SiPh_2OCOCH_3)$ (**3−78**).[121] The proposed mechanism is similar to that shown in Scheme 12, and the silylene route was believed to be the favored pathway. Indeed, base-stabilized silylene−iridium complexes were isolated from the reaction of $(PR_3)(TFB)Ir(OTf)$ with diphenylsilane. A representative example is $[(i\text{-}Pr)_3P](TFB)(H)_2Ir{=}SiPh_2(\leftarrow OTf)$ (**3−76**).[119] A mechanism similiar to that proposed for the formation of complexes $(OC)_2(Cy_3P)(H)_2IrSiPh_2OAc$ (**3−67**; Scheme 13) and (Ph_3P)-

Scheme 13



3-67

Scheme 14



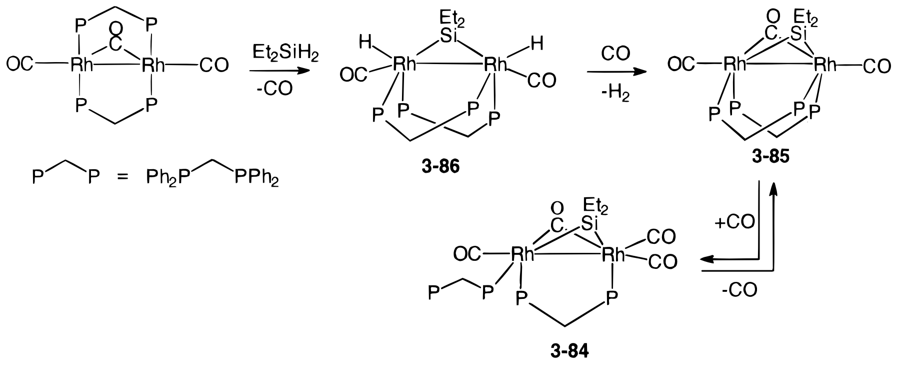
3-77c

$(TFB)(H)_2IrSiPh_2OAc$ (**3−78**), was postulated. The molecular structure was confirmed by X-ray crystallography and the data suggested partial unsaturated character at the silicon center. Complexes **3−76** and **3−78** also showed fluxional behavior at room temperature by NMR spectroscopy (section V).[119,121]

A chelated silylvinyl ligand (**3−77c**) was formed by a net transformation involving addition of a Si−H bond of Ph_2SiH_2 across a C=O bond and the second Si−H bond across the triple bond in the initially coordinated acetylenedicarboxylic methyl ester ligand in $(acac)Ir(\eta^2\text{-}CH_3O_2C{-}C{\equiv}C{-}CO_2CH_3)(PCy_3)$ (Scheme 14).[120] Infrared data supported the formation of **3−77c** which could occur by initial dissociation of the alkyne and selective hydrosilylation of one of the carbonyl groups. The resulting silane can oxidatively add to the iridium center followed by insertion of the alkyne into the Ir−H bond to give complex **3−77c**. An X-ray crystal structure was reported for **3−77c** and the authors proposed that the bonding could be described as intermediate between a donor-stabilized metal−silylene complex and a tetrahedral silicon center.

Several mono- and bis(silyl)iridium complexes were reported in a reaction of the metal trihydride, $(OC)(dppe)IrH_3$, with secondary silanes such as Ph_2SiH_2 and Me_2SiH_2 (representative examples are given in entries **3−70** through **3−72**) to give complexes with the general formula, $(OC)(dppe)H_2Ir(SiR_2H)$ or $(OC)(dppe)HIr(SiR_2H)_2$ (R = Me, Ph), respectively.[60] When excess silane was used, the bis(silyl) complexes were generated. The mixed bis(silyl) complex, $(OC)(dppe)(H)Ir(SiHMe_2)(SiMe_2Cl)$ (**3−71**, X-ray), was surprising since no chlorine was present in the starting reagents but it may have originated from the solvent, CH_2Cl_2, or as a contaminant in Me_2SiH_2.

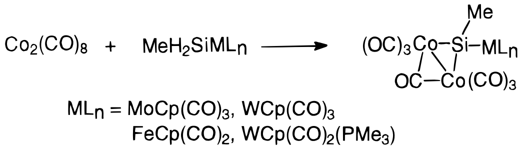
Scheme 15



Mono(silyl)iridium complexes containing only Me_3P and hydride ligands have been generated by reaction of $(Me_3P)_4IrH$ with the secondary silanes, Ph_2SiH_2, Ph_2SiD_2, $(t\text{-}Bu)_2SiH_2$, and $(t\text{-}Bu)_2SiD_2$ to give complexes with the general formula, $(Me_3P)_3(H)_2Ir(SiXR_2)$ ($X = H, D$). Representative examples are shown in entries **3−74** ($R = t$-Bu) and **3−75** ($R = Ph$).[118] The latter complex was structurally characterized by X-ray crystallography and all complexes are believed to have a facial arrangement of the phosphine ligands.

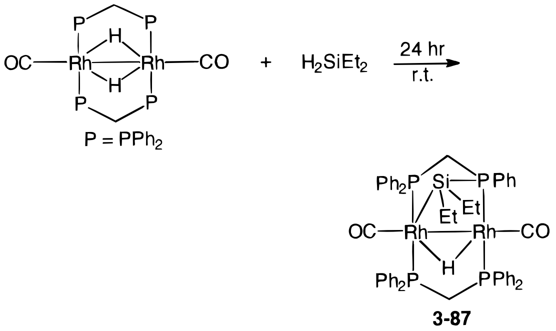
Chelating silanes containing a phosphine moiety have been used to prepare stable complexes such as $OC(Ph_3P)(Cl)(H)Ir(SiHMeCH_2CH_2PPh_2)$ (**3−68**), by reaction of Vaska's complex, $(OC)(Ph_3P)_2IrCl$, with $H_2MeSiCH_2CH_2PPh_2$.[114] The product was isolated as a single stereoisomer containing an Ir(III) center. A sterically demanding mesityl ligand (at silicon) was incorporated into a chelating silane in *mer*-$(Me_3P)_2$-$Cl(H)Ir[SiH(Mes)CH_2CH_2PPh_2]$ (**3−73**).[117] In both examples, the strong trans-influencing silyl ligand occupied a position opposite to the chloro ligand.

Di- and trinuclear metal complexes of the cobalt triad have representative examples for all three elements in the triad (entries **3−79**,[122] **3−80**,[123] **3−81**,[64] **3−82**,[123] **3−83**,[64,123] **3−84** to **3−87**,[68] **3−88**,[124,125] and **3−89**[71]). Several mixed-metal−cobalt clusters were obtained by reaction of a secondary silane of the general formula, RH_2SiML_n, with $Co_2(CO)_8$ (eq 6). The metal used in the ML_n fragment varied from Mo (**3−80**[123]) to W (**3−81**,[64] **3−82**[123]) to Fe (**3−83**[64,123]). The silicon moiety in these complexes bridges the two cobalt centers. Complex **3−79** was also generated by reaction of $Co_2(CO)_8$ with a silane where the Si−H moiety was bound to a terminal position of an η^2-coordinated alkyne ligand.[122]

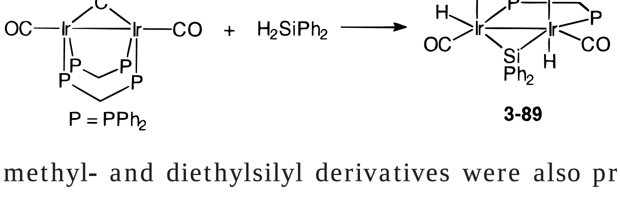


(6)

A number of dinuclear rhodium and iridium complexes (**3−84** through **3−89**) have been reported that contain bridging silylene units.[68,69,71,124,125] They were generally prepared by reaction of a secondary silane with a dinuclear bridged phosphine−metal complex. Mono(μ-SiR_2) rhodium complexes **3−84** and **3−85** were both prepared from $Rh_2(CO)_3(dppm)_2$ and Et_2SiH_2, but the former required the presence of added CO (Scheme 15). The two complexes can be interconverted by removal or addition of CO, respectively. Complex **3−84** was believed to have a dangling dppm ligand. Similar chemistry was observed with Me_2SiH_2 and $MePhSiH_2$. Although complexes such as **3−86** could be isolated, they were relatively reactive.[68,69] Indeed, when the reaction to prepare **3−86** was allowed to run for 24 h at room temperature an unusual rearrangement product (**3−87**) was observed (eq 7). Interestingly, the product shows that one phenyl group of the dppm ligand had been cleaved and a new bond was formed between P and Si. The silylene moiety no longer bridged the two metal centers but was now bound to P and one Rh center. The complex was structurally characterized by X-ray crystallography. Unlike complexes **3−86** and **3−89** which showed fluxional behavior on the NMR time scale, complex **3−87** exhibited a static structure. The relative stabilities of the (μ-SiR_2) bridging unit in complexes such as **3−86** have been determined by a number of exchange reactions with free alkylsilane (R_2SiH_2 and $RSiH_3$). From the study it was determined that steric and electronic factors influence the order of stability which was found to be μ-SiPhH > μ-SiCyH > μ-$SiPh_2$ > μ-SiPhMe > μ-$SiEt_2$. The facile oxidative addition reaction between $Ir_2(CO)_3(dppm)_2$ and H_2SiPh_2 occurred with concomitant loss of CO to afford complex **3−89** (eq 8) in high yield.[71] Dimethyl- and diethylsilyl derivatives were also pre-

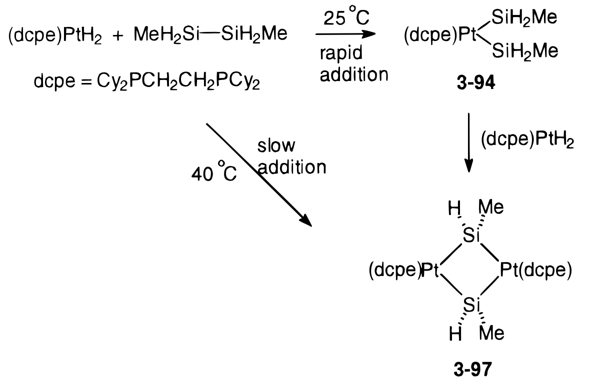


(7)



(8)

Scheme 16



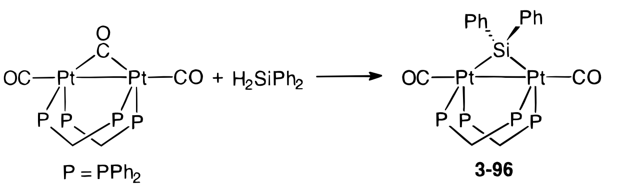
pared by this route and all show fluxional behavior on the NMR time scale. In addition, an X-ray crystal structure of **3−89** was reported and confirmed the cis arrangement of the chelating phosphine ligands.

Bis(silyl) complexes of palladium have been prepared by reaction of $(MePh_2P)_2PdMe_2$ [**3−90**[126]] or $[(dcpe)Pd]_2(\mu\text{-}H)_2$ (**3−91** and **3−92**)[73] with a silane. Complex $(Ph_2MeP)_2Pd(SiHMe_2)_2$ (**3−90**) was somewhat unstable and was detected spectroscopically. Elimination of $HR_2Si{-}SiR_2H$ occurred readily from $(Ph_2MeP)_2Pd(SiHMePh)_2$ (**3−90**). Use of a chelating phosphine such as dcpe increased the stability of complexes of this type with respect to reductive elimination of disilane. *cis*-Bis(silyl) palladium complexes with a chelating dcpe ligand were prepared from 1,2-dihydrodisilanes or hydrosilanes to give $(dcpe)Pd(SiHMe_2)_2$ (**3−91**) and $(dcpe)Pd(SiHMePh)_2$ (**3−92**), respectively. These were the first isolated examples of *cis*-bis(silyl)palladium complexes that contained only hydrogens and simple organic groups on silicon. Complexes **3−91** and **3−92** were air stable in the solid state and thermally stable on brief heating to 120 °C. The dcpe ligand was also utilized in the preparation of the platinum−bis(silyl) complex **3−94**.[76] Rapid addition of 1 equiv of $H_2MeSi{-}SiMeH_2$ to $(dcpe)PtH_2$ at 25 °C gave a quantitative yield of complex **3−94** (Scheme 16). Slower addition at 40 °C gave two geometrical isomers of complex **3−97**. It was also observed that independent reaction of complex **3−94** with $(dcpe)PtH_2$ afforded **3−97**. The formation of complex **3−94** was monitored by low-temperature NMR spectroscopy and the data suggested that at −80 °C the initial product was a Pt(IV) intermediate, *fac*-$(dcpe)Pt(SiMeHSiMeH_2)H_3$. Upon warming to −25 °C, H_2 was eliminated to give a silylhydride−platinum complex, $(dcpe)Pt(H)(SiMeHSiMeH_2)$. Further warming led to cleavage of the Si−Si bond in the latter complex to give the final product, complex **3−94**.

Bifunctional chelates such as $Ph_2PCH_2CH_2SiMeH_2$ reacted with $Pt(cod)_2$ to afford the bis(chelate) complex, $[Ph_2PCH_2CH_2SiH(Me)]_2Pt$ (**3−95**).[128,129] These complexes were characterized in solution only and attempted crystallization gave intractable materials, probably due to further reaction of the Si−H bonds.

Complex *cis*-$(Ph_3P)_2(H)Pt[SiH(R_F)_2]$ (**3−93**) prepared from $(R_F)_2SiH_2$ and $(Ph_3P)_2Pt(C_2H_4)$, utilizes the sterically hindered silyl group, $(R_F)_2HSi$ [R_F = 2,4,6-tris(trifluoromethyl)phenyl], bound to platinum.[127] The complex appears to be the only example of a hydridosilylplatinum complex obtained from a secondary silane to be characterized in the solid state.

A number of dinuclear platinum complexes with bridging silylene groups have been prepared by reaction of $Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ with dialkyl-, diaryl-, and alkylarylsilanes. A representative example is given in entry **3−96** (eq 9).[130] The reaction



(9)

with Ph_2SiH_2 was monitored by low-temperature NMR spectroscopy and an intermediate formulated as $Pt_2(H)(SiHPh_2)(CO)$ (μ-dppm)$_2$ was detected. This complex is formed by oxidative addition of a Si−H bond to one Pt center with concomitant loss of CO. Upon warming, H_2 is lost and CO is added to give the final product, **3−96**.

D. Tertiary Silanes

The majority of the reported studies of reactions of silanes with metal complexes involve tertiary silanes and examples are illustrated in Table 4.[133−304] Although Table 4 contains more examples than are found in Tables 1−3 combined, the variations on starting metal complexes are not significantly more extensive than has been previously discussed. Approximately half of the entries in Table 4 involve silanes that fall into the following groupings: $HSiX_3$ (X = Cl, F), $HSiR_3$, (R = Me, Et), $HSiPh_3$ or $HSi(OR)_3$ (R = Me, Et) all of which are commercially available.

With tertiary silanes there are no residual Si−H bonds on the metal-coordinated silyl group and thus, fewer side reactions. However, since all but one Si−H bond has been replaced with a larger substituent, steric problems may arise in the addition of $HSiR_3$ to the metal complex. Steric issues are infrequently explored and the few examples that have been addressed, are outlined in the following paragraphs.

A possible steric effect can be seen in a comparison of the ^1H NMR data for $Cp^*_2Zr(Cl)SiPh_3$, where all Ph resonances are broad at room temperature, to the data reported for $CpCp^*Zr(Cl)SiPh_3$ where these same resonances are sharp.[305] The line broadening was attributed to restricted rotation about Si−C bonds in $Cp^*_2Zr(Cl)SiPh_3$. Nonetheless, the ZrCl bond in $Cp^*_2Zr(Cl)SiPh_3$ can be substituted by MeMgX. Since exchange of silyl groups at metal centers can lead to isolable new silylmetal derivatives, the size of both the metal-bound groups and the reacting silane may be important in successful conversions to new complexes. The reaction of $CpCp^*(Cl)HfSiPh_3$ with $PhSiH_3$ occurs with 80% conversion in 5.5 h to give $CpCp^*(Cl)HfSiH_2Ph$ (**2−5**),[21] whereas the corresponding reaction of $Cp^*_2(Cl)HfSiPh_3$ requires 2 days and the products include $Cp^*_2Hf(H)Cl$ and $HSiPh_3$ as well as $H(PhSiH)_xH$. The zirconium derivative, $Cp^*_2(Cl)ZrSiPh_3$ reacts more rapidly than the hafnium analogue but in a similar fashion.

Table 4. Reaction of R_3SiH with Metal Complexes*,†

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR			Other Data	Ref.
				solvent (temp.)[1b]	^{1}H[1c] M-H	^{29}Si[1c]		
Titanium Triad								
4-1 $Cp_2L(H)TiSiCl_3$ L = -, CO (mixture)	A (—)	brown —	—	—	—	—	—	133
4-2 $Cp_2(Me_3P)(H)ZrSiPh_3$	B (48)	orange-red —	Y	S	0.35 (d)	39.5	^{13}C, ^{31}P IR	82
4-3 $Cp_2(Me_3P)(H)HfSiPh_3$ [1d]	B (65)	—	Y [1e] HRMS	S	1.90 (d)	—	^{13}C, ^{31}P IR	82
Vanadium Triad								
4-4 $Cp_2V(SiCl_3)_2$	C (<50)	yellow-green 160 (d)	Y	—		—	—	133
4-5 $Cp_2(H)_2NbSiMe_3$	D (50)	yellow-green —	Y [1e]	S	-4.9 (br s) [1f]	—	—	134
4-6 $Cp_2(H)_2NbSiMe_2Ph$	D (83)	yellow 106	Y [1e]	T	-4.79 (s)	—	IR, MS	135
4-7 $Cp_2(H)_2NbSiMe_2OSiMe_3$ [1g]	D (—)	lt. brown. —	—	—		—	—	135
4-8 $(C_5H_4SiMe_3)_2(H)_2Nb$-$SiMe_2Ph$ [1h]	D (88)	white or lt. yellow —	Y [1e]	S	-4.96 (br s)	—	^{13}C IR	39
4-9 $Cp_2(H)Nb(SiMe_2Cl)_2$ [1i]	E (61)	pale —	Y	T	-5.15 (br s)	90.0	^{13}C X-ray	136 [1j]
4-10 $Cp_2(H)Nb(SiMe_3)_2$	E (39)	lt. green —	Y	S	-3.6 (br s) [1k]	—	—	134
4-11 $Cp_2(Me_3P)TaSiMe_3$	F (85)	—	HRMS	S	—	9.7 (d)	^{31}P X-ray	13
4-12 $Cp_2(H)_2TaSiMe_2Cl$ (symm. isomer) [1l]	D (66)	white —	Y HRMS	S	-4.03 (s)	76.2	IR	13
4-13 $Cp_2(H)(H)TaSiMe_2Cl$ (unsymm. isomer) [1m]	D (—)	—	—	S	-4.08 (d) -4.18 (d)	83	IR	13
4-14 $Cp_2(H)_2TaSiMe_3$ (symm. isomer)	D (86)[1n]	white —	HRMS	S	-4.52 (s)	10.4	IR	13
4-15 $Cp_2(H)(H)TaSiMe_3$ (unsymm. isomer)	D (—)	—	—	S	-3.30 (d)	27.3	—	13
4-16 $Cp_2(H)_2TaSiMe_2Ph$	D (85)	lt. yellow 116	Y	T	-4.32 (s) -4.88 (d)	—	MS X-ray	135
4-17 $Cp_2(H)_2Ta[Si(OMe)_3]$ (symm. isomer)	G (86)[1n]	white —	Y [1e] HRMS	S	-4.78 (s)	40.9	—	13
4-18 $Cp_2(H)(H)Ta[Si(OMe)_3]$ (unsymm. isomer)	G (—)	—	—	S	-4.02 (d) -4.66 (d)	40.7	—	13
4-19 $Cp_2(H)Ta(SiMe_3)_2$	D (90)	—	Y HRMS	S	-3.75 (s)	24.7	IR	13
4-20 $Cp_2(H)Ta(SiMe_2Cl)_2$	F (77)	—	Y [1e] HRMS	S	-5.01 (s)	81.0	IR	13
4-21 $Cp_2(H)Ta[Si(OMe)_3]_2$	F (76)	—	—	S	-4.79 (s)	36.6	IR	13
Chromium Triad								
4-22 $(C_6H_6)(OC)_2Cr(SiCl_3)_2$	H [1o](43)	gold —	Y	S		—	^{1}H, IR, MS UV	137

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H [1c] M-H	NMR ^{29}Si [1c]	Other Data	Ref.
4-23 $CH_3C_6H_5(OC)_2Cr(SiCl_3)_2$	H [1o](52)	yellow —	Y	S		—	^{1}H IR, MS	137
4-24 $(C_6H_5F)(OC)_2Cr(SiCl_3)_2$ [1p]	H [1o](55)	golden —	Y [1e]	S		—	X-ray	138, 139
4-25 $[(CH_3)_3C_6H_3](OC)_2Cr(SiCl_3)_2$	H [1o] (45)	yellow —	Y	Y		—	IR X-ray	137
4-26 $C_6Me_6(OC)_2Cr(SiCl_3)_2$	H [1o] (44-80) [1q]	yellow —	Y	S		—	IR, MS	137
4-27 $CH_3C_6H_5(OC)_2(H)CrSiCl_3$	H [1o] (—)	yellow —	N	S	-10.45 (s)	—	IR	137
4-28 $(C_6H_5F)(OC)_2(H)CrSiCl_3$ [1r]	H [1o] (66)	yellow-green —	Y [1e]	S	-10.2 (s)	—	IR	139
4-29 $[(CH_3)_3C_6H_3](OC)_2(H)CrSiCl_3$	H [1o] (70)	—	N	S	-9.98 (s)	—	IR, UV	137
4-30 $(C_6H_5F)(OC)(H)_2Cr(SiCl_3)_2$ [1s]	H (9)	brown-orange —	Y	S	-10.97 (s) -11.22 (s)	—	IR X-ray [1s]	138
4-31 $[C_6H_3(CH_3)_3](OC)(H)_2Cr(SiCl_3)_2$ [1t]	H (63)	orange —	Y	S	-10.84 (s)	—	VT-NMR IR X-ray	138
4-32 $(OC)_3(dppe)(H)CrSiCl_3$	I [1o](15)	—	Y	Y'	-2.34 (dd)	—	^{31}P IR	140
4-33 $Cp_2(H)MoSiMe_2Cl$ [1u]	J (78)	yellow —	Y [1e]	S	-8.18 (s)	86.4	^{13}C	90
4-34 $Cp_2(H)MoSiPh_3$	J (—)	yellow 118-121	—	T	-7.43	—	IR, MS	41
4-35 $Cp'_2(H)MoSiMe_3$	J (98)	yellow —	Y	S	-7.52 (s)	27.8	^{13}C	90
4-36 $(\eta\text{-}C_7H_7)(OC)_2MoSiCl_3$	[1v] (35)	red-brown 160 (d)	Y [1e]	X	—	—	IR	141
4-37 $(OC)_3(dppe)(H)MoSiCl_3$	I [1o](73)	ocher 74 (d)	Y	Y'	-3.17 (dd)	—	^{31}P IR	140
4-38 $(OC)_3(dppe)(H)MoSi(p\text{-}Tol)Cl_2$	I [1o](64)	ocher 52 (d)	Y	Y'	-2.89 (dd)	—	IR	140
4-39 $(OC)_2(tdppme)(H)MoSiMeCl_2$	I [1o](—)	dark yellow —	N	S	-3.67 (dt)	—	^{31}P IR	140
4-40 $(OC)_2(tdppme)(H)MoSiCl_3$	I [1o](—)	dark yellow —	N	S	-3.43 (dt)	—	^{31}P IR	140
4-41 $Cp_2(H)WSiMe_2Cl$ [1w]	J (50)	orange-yellow —	N	S	-11.48 (s)	55.8	^{13}C	90
4-42 $Cp_2(H)WSiCl_3$	J (<50)	yellow 170 (d)	Y	[1x]		—	—	133
4-43 $Cp_2W(SiMe_3)_2$ [1y]	[1y] (88)	yellow —	Y	S		3.3	^{13}C	90
4-44a $Cp(OC)_2W\{SiMe_2\cdots OMe\cdots SiMe_2\}$	[1z] (50)	lt. yellow —	Y	S		99.3 $^{1}J_{WSi} = 99.3$	^{13}C Ir, MS X-ray	142

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-44b Cp(OC)$_2$W {SiMe$_2$$\cdots$NEt$_2$$\cdots$SiMe$_2$}	[1z] (54)	yellow —	Y	S		62.1 $^1J_{WSi}$ = 91.5	^{13}C Ir X-ray	142
4-45a (OC)$_3$(dppe)(H)W-SiMeCl$_2$ [2a]	I [1o] (83)	ocher 98 (d)	Y	Y	-4.02 (dd) ^1J = 46.0	52.4 (dd)	^{13}C, ^{31}P MS	140
4-45b (OC)$_3$(dppe)(H)W-SiPh$_2$Cl [2b]	I [1o] (80)	—	N	S	-3.61 (dd)	—	^{31}P IR	140
4-46 (OC)$_3$(dppe)(H)WSiCl$_3$	I [1o] (73)	yellow 101 (d)	Y	Y	-3.83 (dd) ^1J = 38	22.2 (br t) $^2J_{SiWH}$ = 19.9	^{13}C, ^{31}P IR, MS	140
4-47 (OC)$_3$(tdppme)(H)W-SiMeCl$_2$ [2c]	I [1o] (60)	ocher —	N	S	-2.40 (dt)	—	^{31}P IR	140
Manganese Triad								
4-48 [CpMn(CO)$_2$]$_2$SiMe$_2$	[2d] (—)	—	—					143
4-49 (Cp)(Me$_2$PCH$_2$CH$_2$-PMe$_2$)(H)MnSiPh$_3$	K [1o] (62)	yellow —	Y	Y	-14.13 (dd)	—	VT-NMR ^{13}C, ^{31}P IR	45
4-50 (Cp)(Me$_2$PCH$_2$CH$_2$-PMe$_2$)(H)MnSiPh$_2$Cl [2e]	K [1o] (76)	yellow —	Y	S	-14.54 (dd)	—	^{13}C, ^{31}P IR	45
4-51 Cp(OC)$_2$(H)MnSiCl$_3$ [2f]	L (21)	lt. yellow 82-83	Y	Z'	-9.70	—	IR	144
4-52 (OC)$_5$MnSiMe$_2$SiMe$_3$	M (12)	colorless liquid	Y	Y'		—	IR	145
4-53 (OC)$_5$MnSiMe(SiMe$_3$)$_2$	M (19)	white —	N	Y'		—	IR	145
4-54 (OC)$_5$MnSi(SiMe$_3$)$_3$	M (20)	white —	Y	Y'		—	IR	145
4-55 (OC)$_4$Mn[*o*-Ph$_2$PC$_6$H$_4$-CH$_2$SiMe$_2$]	M (6)	lt. yellow 158-159	Y	—		—	IR	146
4-56a Cp(OC)$_2$(H)Re-Si(CH$_2$Ph)$_3$ (mixture of *cis* and *trans*)	L [1o] (36)	lt. yellow 130 (d)	Y	X	-10.63 -10.59	—	IR	93
4-56b (Cp)(OC)$_2$(H)Re-SiPh$_2$SiHPh$_2$ [2g]	L (22)	— 79	Y	S	-9.06 (s) [2h]	-25.6 (SiHPh$_2$) -19.1	^{13}C IR	147
4-57 Cp(OC)$_2$(H)ReSiPh$_3$ (*cis*) [2i]	L (15)	white 151-153	Y	X	-9.10	—	IR	93
4-58 (OC)$_5$ReSiCl$_3$	M (95)	white —	N	Y		16.1	IR, MS	148a
4-59 (OC)$_4$Re[2-SiMe$_2$ C$_5$H$_4$N]	M (26)	yellow 145-148	Y	—		—	IR	149
4-60 (OC)$_4$Re[*o*-Ph$_2$P-C$_6$H$_4$CH$_2$SiMe$_2$]	M (40)	off-white 169-171 (d)	Y	—		—	IR	146
4-61 (OC)(PhMe$_2$P)$_2$(H)$_2$Re-SiPh$_3$ [2j]	[2k] (76)	off-white —	Y	Y	-6.06 (c)	—	^{13}C, ^{31}P IR X-ray	150

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	^{29}Si[1c]	Other Data	Ref.
4-62 $(Ph_3P)_2(H)_6ReSiEt_3$ [2l]	N (65)	beige —	Y [1e]	Y (25) Y (-80)	-5.91 (t) -3.69 (t) -7.31 (t)	—	^{13}C, ^{31}P IR	94
4-63 $(Ph_3P)_2(H)_6ReSiPh_3$	N (75)	beige —	Y	Y (25) Y (-80)	-4.82 (t) -2.83 (t) -6.31 (t)	—	VT-NMR ^{13}C, ^{31}P IR X-ray	94
4-64 (dppf)$(H)_6ReSiPh_3$	N (76)	yellow —	Y	Y(25) Y(-60)	-5.11 (t) -6.25 (d) -3.33 (d)	—	VT-NMR ^{13}C, ^{31}P IR	151
4-65 (dppb)$(H)_6ReSiPh_3$ [2m]	—	—	—	[2n] (25) [2n] (-80) [2n] (-110)	-5.57 (br t) -4.21 (t) -6.52 (d) -4.20, -4.49 (br t)	—	—	151
4-66 $(Ph_3P)_2(H)_5Re$-$[SiMe_2CH_2CH_2SiMe_2]$	N (31)	off-white —	Y [1e]	Y	-6.98 (t)	—	^{13}C, ^{31}P IR	152
4-67 $(Ph_3P)_2(H)_5Re$(disil)	N (62)	tan —	Y [1e]	Y	-6.65 (t)	—	VT-NMR ^{13}C, ^{31}P IR X-ray	152
Mn Triad Dimers								
4-68* $(OC)_8Re_2[\mu$-η^2-$Si(OMe)_3](\mu$-$H)$	[2o] (51)	—	Y	X	-15.26 (s)	—	IR X-ray	153
Iron Triad								
4-69 $(OC)_4Fe{=}Si(NMe_2)_2(NHMe_2)$ [2p]	M (70)	white —	Y	S: (^{1}H) X: (^{29}Si)		68.2 (s)	^{13}C IR, MS	154
4-70 $(OC)_3[EtO(Me_2N)_2P]$-$Fe{=}Si(OEt)_2(\leftarrow NHMe_2)$	[2q] (70)	lt. brown	Y	S: (^{1}H) X: (^{29}Si)		57.4 (d)	^{13}C, ^{31}P IR, MS X-ray	154
4-71 $(OC)_3\{P(OMe)(NMe_2)_2\}$ $Fe{=}Si(OMe)_2(\leftarrow NHMe_2)$	[2r] (84)	White —	N	S/S'		64.4	^{13}C, ^{31}P IR, MS	155
4-72 $Cp(OC)_2FeSiMe_3$	—	—	—	Y'		41.0	—	148a,b
4-73 $Cp(OC)_2FeSiMe_2Cl$	O (2s)	—	—	Y'		69.4	—	148a
4-74 $Cp(OC)_2FeSiMeCl_2$	O (2s)	—	—	Y'		61.4	—	148a
4-75 $Cp(OC)_2FeSiCl_3$	P (11)	yellow 128-130	Y	Y'		39.4	^{1}H IR X-ray PES	148a, 156, 157
4-76 $(Cp)(OC)(Ph_3Sn)(H)Fe$-$SiPh_3$ [2t]	Q (67)	lt. yellow —	Y	S	-11.69 (s)	26.2 $^{2}J_{SiFeH} = 23$	^{119}Sn IR	158
4-77 $Cp(OC)(H)Fe(SiMe_3)_2$	P (—)	lt. yellow oil	Y	S	-13.97 (s)	—	^{13}C	159
4-78 $Cp(OC)(H)Fe(SiCl_3)_2$	O (35) [2u]	lt. yellow 130-131	Y	Z'	-11.64 $J_{HFeSi} = 20$	—	IR	156
4-79 $(\eta^6$-$C_6H_5CH_3)(H)_2Fe$-$(SiF_3)_2$	R (1)	yellow —	N	S	-19.00 (sept)	—	IR X-ray	160

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H [1c] M-H	NMR ^{29}Si [1c]	Other Data	Ref.
4-80 $(\eta^6\text{-}C_6H_5CH_3)(H)_2Fe(SiCl_3)_2$ [2v]	R (5)	yellow —	Y [1e]	S	-17.07 (s)	—	^{13}C, IR X-ray Mossb.	161, 162
4-81 *cis*-$(OC)_4(H)FeSiMe_3$	M (—)	white r. t.	N	Y'	—	27.4	IR	148a
4-82 *cis*-$(OC)_4(H)FeSiMe_2Cl$	M (—)	—	—	[2w]	—	63.2	IR	148a
4-83 $(OC)_4(H)FeSiMeCl_2$	M (—)	—	—	[2w]	—	70.7	IR	148a
4-84 $(OC)_4(H)FeSiCl_3$	M (50)	colorless liquid	—	[2w]	—	46.5 $^2J_{SiH} = 21.7$	IR	148a
4-85 $(OC)_4Fe(SiMe_3)_2$ (*cis*)	M (—)	(green) impure —	N	Y'		26.6 [2x]	—	148a
4-86 $(OC)_4Fe(SiMe_2Cl)_2$ (*cis*)	M (—)	—	N	Y'		61.3 $^2J_{SiH} = 5.1$	IR	148a
4-87 $(OC)_4Fe(SiMeCl_2)_2$ (*cis*)	M (50)	lt. yellow liquid	N	Y'		68.5 $^2J_{SiH} = 6.2$	IR	148a
4-88 *trans*-$(OC)_4Fe(SiCl_3)_2$	M (~100)	— 91-93	Y	[2y]		41.8 (*cis*) 46 (*trans*)	IR, MS X-ray [2z] (*trans*)	148a, 163
cis-$(OC)_4Fe(SiCl_3)_2$	M (20)	pale green 93-96	Y	X		21.5 (*cis*)	^{13}C IR UPS	164
4-89* $[Me_2SiAr\text{-}ArSiMe_2]\text{-}Fe(CO)_4$	M (9)	white 110	HRMS	S		8.8	^{13}C IR, MS	165
4-90 *cis-mer*-$(OC)_3Ph_3P(H)\text{-}FeSiEt_3$	S [1o](—)	brown- yellow oil	—	S	-9.13 (d) [3a]	—	^{13}C IR, UV	166
4-91 *trans-mer*-$(OC)_3Ph_3P\text{-}(H)FeSiPh_3$	S [1o] (—)	—	Y	R	-8.44 (m) [3a]	—	^{13}C IR X-ray	167
4-92a *cis-mer*-$(OC)_3Ph_3P(H)\text{-}FeSiPh_3$ [3b]	S [1o] (—)	green-yellow —	—	S	-8.44 (d) [3a]	—	^{13}C IR, UV	166, 168
	S (41)	yellow 185-187	Y	Y	-9.00 (d) $^2J_{SiH} = 10$			
4-92b *mer*-$(OC)_3Ph_3P(H)\text{-}FeSiPh_2SiHPh_2$ [3c]	[3d] (78)	beige 87	Y	S	-8.42 (d) [3e]	-26.3 (s) $(SiPh_2H)$ 9.60	^{13}C, ^{31}P IR	147
4-93a *cis-mer*-$(OC)_3Ph_3P(H)\text{-}FeSi(OMe)_3$ [3b]	S [1o](—)	—	—	—	—	—	IR, UV	166
4-93b $(OC)_3(Ph_3P)(H)FeSiCl_3$ [3f]	S [1o](35)	lt. yellow 69 (d)	Y	S	-8.46	—	^{31}P IR	169
4-94 *mer*-$(OC)_3[(EtO)_3P](H)\text{-}FeSiPh_3$	S [1o](80)	colorless 110 (d)	Y	S'	-9.2 (d) $J_{PFeH} = 36$	26.8	VT-NMR ^{31}P IR	170
4-95 *mer*-$(OC)_3[(PhO)_3P]\text{-}(H)FeSiMePh_2$	S [1o](50)	— 63-66	Y	S'	-9.4 (d) $J_{PFeH} = 37$	—	VT-NMR ^{31}P IR	170
4-96a *cis-mer*-$(OC)_3\text{-}[(PhO)_3P](H)FeSi(OEt)_3$	S [1o](60)	— 72 (d)	Y [1e]	S'	-9.7 (d) $J_{PFeH} = 34$	—	^{31}P IR	170

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR			Other Data	Ref.
				solvent (temp.)[1b]	^{1}H[1c] M-H	^{29}Si[1c]		
4-96b (OC)$_3$[(PhO)$_3$P] (H)Fe-SiCl$_3$	S [1o](33)	— 75	Y	R	-8.9 (d)	54.6	^{13}C, ^{31}P IR	171
4-96c (OC)$_3$Ph$_3$PFe(SiMeCl$_2$)$_2$ [3g]	S [1o](58)	— 208 (d)	Y	S		73.8 79.3	^{31}P IR	169
4-97 *mer*-[(OC)$_3$(H)Fe-SiMeCl$_2$]$_2$(μ-dppe)	S' [1o](60)	—	Y[e]	S'	-9.3 (d)	—	^{31}P IR	172
4-98 *mer*-[(OC)$_3$(H)FeSiCl$_3$]$_2$-(μ-dppe) [3h]	S' [1o](45)	—	Y	Y'	-9.4 (d)	—	^{13}C, ^{31}P IR	172
4-99 (OC)$_2$[(EtO)$_3$P]$_2$(H)Fe-[SiMeCl$_2$] [3i]	S [1o](—)	pale yellow 41-43	Y[1e]	S'	10.1 (t)	—	IR	170
4-100 (OC)$_2$[(PhO)$_3$P]$_2$(H)Fe-SiMe$_2$Ph [3j]	T[1o] (45)	red 58-60 (d)	Y	S'	-10.5 (t)	—	^{31}P IR	170
4-101 (OC)$_2$[(PhO)$_3$P]$_2$HFe-SiMePh$_2$ [3j]	T[1o] (75)	red 87-88	Y	W	-10.2 (t)	19.6	^{31}P IR	170
4-102 *cis*-(OC)$_2$[(PhO)$_3$P]$_2$-(H)FeSiMeCl$_2$ [3k]	T(65)	— 102-103	Y	W	-9.9 (t)	—	^{31}P IR	170
4-103 (OC)$_2$[(PhO)$_3$P]$_2$(H)Fe-Si(OEt)$_3$ [3j,3k]	T[1o] (70)	red 68-70 (d)	Y	S'	-10.2 (t)	-86.1 (t)	^{31}P IR	170
4-104 (OC)$_2$(dppe)(H)Fe-SiMe$_3$	S[1o] (80)	— 94-96 (d)	Y [1e]	S'	-10.1 (t)	—	^{13}C, ^{31}P IR X-ray	172
4-105 (OC)$_2$(dppe)(H)Fe-SiMe$_2$Cl	T[1o] (45)	— 146-148	Y	Y'	-9.9 (t)	—	^{13}C, ^{31}P IR	172
4-106 (OC)$_2$(dppe)(H)Fe-Si(OEt)$_3$ [3l]	T[1o] (80)	— 116-118	Y	S'	-9.7 (t)	—	^{13}C, ^{31}P IR	172
4-107 (OC)$_2$(dppe)Fe-(SiMeCl$_2$)$_2$ [3m]	S (34)	— 143	Y [1e]	S/Y'		—	^{31}P IR	172
4-108 (OC)(dppe)(H)$_3$Fe Si(OEt)$_3$ [3n]	[3o] (55)	— 114 (d)	Y	S (25)	-10.5 (t)	—	VT-NMR ^{13}C, ^{31}P IR X-ray	49, 173
4-109 (Ph$_2$EtP)$_3$(H)$_3$Fe SiPh$_3$ [3p]	[3q] (28)	— 90 (d)	N	S (25)	-14.39 [3r]	—	VT-NMR ^{31}P IR	49
4-110 [*p*-MeC$_6$H$_4$(*i*-Pr)](H)$_2$-Ru(SiMe$_3$)$_2$ [3s]	[3s] (—)	colorless —	—	—	—	—	—	174 [1j]
4-111 Cp(OC)(H)Ru(SiMe$_3$)$_2$	[3t] (9)	colorless oil	Y	S	-10.87	—	^{13}C IR	175
4-112a Cp(Me$_3$P)$_2$RuSiCl$_3$ [3u]	U (81)	yellow —	Y	S		42.1	^{13}C	176
4-112b Cp(Me$_3$P)$_2$RuSiCp*Cl$_2$ [3v]	U (71)	white —	Y	S		82.7	^{13}C	177
4-113 Cp(Ph$_3$P)$_2$RuSiEt$_3$	U (93)	yellow —	Y	S		16.2	^{13}C	176
4-114* Cp(Ph$_3$P)Ru[SiMe$_2$⋯OMe⋯SiMe$_2$]	U (56)	yellow —	Y	S		108.7 (d)	^{13}C, ^{31}P MS X-ray	178

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	^{1}H[1c] M-H	^{29}Si[1c]	Other Data	Ref.
4-115 Cp($Ph_3P)_2RuSiMe_2$(*p*-Tol)	U (64)	yellow-orange —	Y	S		4.1 (t)	^{13}C, ^{31}P IR, MS	178
4-116 Cp*($Me_3P)_2RuSiMePh_2$	U (92)	yellow —	Y	Y		—	^{13}C	180
4-117 Cp*($Me_3P)_2RuSiPh_3$	U (78)	yellow —	Y	S		—	—	180
4-118 Cp*($Me_3P)_2RuSiPh_2Cl$ [3w]	U (~100) [3x] (92)	yellow —	Y	Y		74.1 (t)	^{13}C, ^{31}P IR	180, 181
4-119 Cp*($Me_3P)_2RuSi(OEt)_3$	[3y] (41)	—	N	U		—	^{31}P	182
4-120 Cp*($Me_3P)_2$Ru-Si[S(*p*-Tol)]$_3$	[3z] (85)	— 219-228 (d)	Y	S: (^{1}H) Y: (^{29}Si)		49.0 (t)	^{13}C, ^{31}P IR X-ray E.C.	183
4-121 Cp(Ph_3P)(H)Ru($SiCl_3)_2$	U (69) [4a]	yellow	N	Y	-8.39	56.9	—	176
4-122 Cp*(Me_3P)(H)Ru-($SiPh_2Cl)_2$ [4b]	U (—)	lt. yellow —	Y[1e]	Y	-11.60 (d)	37.8	^{13}C IR	180, 181
4-123 Cp*[(*i*-Pr)$_3$P](H)$_2$Ru-$SiMe_3$	U [4c] (60)	—	Y	S	-12.33 (d)	—	^{31}P	50
4-124 Cp*[Ph(*i*-Pr)$_2$P](H)$_2$ $RuSiMe_3$	V (—)	brown oil	N	T (25)	-12.33	—	^{31}P	96
				T (-80)	-11.90 (d) -12.53			
4-125 Cp*[Ph(*i*-Pr)$_2$P](H)$_2$ $RuSiPh_3$	V (—)	brown oil	N	T (25)	-11.41 (d)	—	^{31}P	96
				T (-60)	-11.52 (d) -11.11 (d)			
4-126 Cp*[Ph(*i*-Pr)$_2$P](H)$_2$ $RuSi(OMe)_3$ [4d]	V (—)	brown oil	N	T (25)	-12.21 (d)	—	^{31}P	96
				T (-80)	-12.55 (dd) -11.76 (dd)			
4-127 $(OC)_4(H)RuSiCl_3$ [4e]	M (35)	— 2-3	N	S'	-7.35	30.4	IR, MS	148a, 184
4-128 *cis*-$(OC)_4Ru(SiMe_3)_2$	—	—	N	Y'		2.1	—	148a
4-129 $(OC)_4Ru(SiMeCl_2)_2$	M (57)	white 96-97	Y	Y'		56.2 (*cis*) $^2J_{SiH} = 6.2$ 57.4 (*trans*) $^2J_{SiH} = 6.2$	MS	148a, 185
4-130 *cis*-$(OC)_4Ru(SiMe_2Cl)_2$	—	—	N	X: (^{1}H) Y': (^{29}Si)		47.9 $^2J_{SiH} = 5.7$	—	148a
4-131 *cis*-$(OC)_4Ru(SiCl_3)_2$	M (95) (47)	white 120-21	Y	Y'		28.3	^{31}P IR, MS	148a, 163, 184, 185
4-132 *trans*-$(OC)_4Ru(SiCl_3)_2$	M (44)	—	N	Y'		30.7	IR	148a
4-133 *cis-mer*-$(OC)_3Ph_3P$(H)-$RuSiEt_3$	S (—)	orange —	—	S	-6.89 (d)	—	^{13}C IR, UV	166
4-134 *cis-mer*-$(OC)_3Ph_3P$(H)-$RuSiPh_3$	S (—)	orange —	Y	S	-6.24 (d)	—	^{13}C IR, UV X-ray	166, 167

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-135 $(OC)_3Ph_3PRu(SiCl_3)_2$ [4f]	[4g] (≥ 85)	— 204-206	Y[1c]	X		—	^{31}P IR	163
4-136 $(OC)_2(H)Ru[SiMe(CH_2CH_2CH_2PPh_2)_2]$ [4h]	M (8)	yellow —	Y	R	-6.29 (t)	—	X-ray	186
4-137 $(OC)_2Ru(SiMe_2CH_2CH_2PPh_2)_2$	M (37)	white 224-225	Y	X		—	^{31}P IR	187
4-138 $(OC)_2Ru(SiMePhCH_2\text{-}CH_2PPh_2)_2$	M (35)	white ~280 (d)	Y	X		—	^{31}P IR	187
4-139 $(OC)_2Ru(SiPh_2CH_2\text{-}CH_2PPh_2)_2$	M (46)	fawn 224-225	Y	X		—	^{31}P IR	187
4-140a $(OC)(Ph_3P)_2(Cl)Ru\text{-}SiMe_3$	W (71)	yellow 160-161	Y	X		55.7 (t)	^{13}C IR	188
4-140b $(OC)(Ph_3P)_2(Cl)Ru\text{-}SiEt_3$	W (63)	yellow 146-148	Y	X		71.7 (t)	^{13}C IR	188
4-141 $(OC)(Ph_3P)_2(Cl)Ru\text{-}SiPh_3$ [4i]	W (84)	— 149-152	Y	X		40. 3 (t)	^{13}C IR	188
4-142 $(OC)[(t\text{-}Bu)_2MeP]_2(H)\text{-}RuSiMe_3$	[4j] (—)	deep red —	N	S	-1.08	—	^{31}P IR	189
4-143 $(Me_3P)_3(H)_3RuSiPh_3$	X (67)	white —	Y[1c]	S	-9.5 (m)	—	^{13}C, ^{31}P IR, MS	190
4-144 $(Ph_3P)_3(H)_3RuSiPh_2Me$	X (—)	white —	Y	—	—	—	IR	99
4-145 $(Ph_3P)_3(H)_3RuSiMe_2Cl$	X (—)	white —	Y	Y'	-10.0	—	IR	99
4-146 $(Ph_3P)_3(H)_3RuSiMeCl_2$ [4k]	X (—)	white —	Y	Y' S'	-9.80 -9.52	—	IR	99
4-147 $(Ph_3P)_3(H)_3RuSiMeF_2$	X (—)	white —	Y	Y'	-10.51	—	IR	99
4-148 $(Ph_3P)_3(H)_3RuSiPh_3$	X (—)	white —	Y	Y'	-9.82	—	IR	99
4-149 $(Ph_3P)_3(H)_3RuSiF_3$	X (—)	white —	Y[1c]	—	—	—	IR	99
4-150 $(Ph_3P)_3(H)_3RuSi(OEt)_3$ [4l]	X (—)	white —	Y[1c]	Y' S'	-10.41 -10.05	—	IR	99
4-151 $(Cy)_3P[(\eta^3\text{-}C_6H_8)P(Cy)_2]_2RuSiEt_3$	[4m] (91)	gray —	Y	S	-12.63 (ddd) -9.54 (br t)	—	^{31}P	191
4-152a $Cp^*(Me_3P)_2Os\text{-}SiMe_2Cl$ [4n]	[4o] (88)	white >360 (d)	Y	S		46.76 (t)	^{13}C, ^{31}P IR	192
4-152b $Cp^*(Me_3P)(H)Os\text{-}(SiMe_2Cl)_2$ [4p]	[4o] (66)	colorless 265 (d)	Y	S	-15.27 (d)	28.44	^{13}C, ^{31}P IR	192
4-152c$Cp^*(Me_3P)(H)Os\text{-}\{C_6H_3(3\text{-}Me)(6\text{-}S)\text{-}Si[S(p\text{-}Tol)]_2\}$ [4q]	[4o] (77)	white 149-50 (d)	Y	S	-15.10 (d) $^2J_{SiOsH} = 15$	30.55 (d)	^{13}C, ^{31}P IR X-ray	192
4-153 *cis*-$(OC)_4(H)Os\text{-}SiCl_3$ [4r]	M (33)	— 32	N	Y: (^{1}H) [2w]: (^{29}Si)	-7.94	-7.1 $^2J_{SiH}= 7$	IR, MS	148a 193a

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR			Other Data	Ref.
				solvent (temp.)[1b]	^{1}H [1c] M-H	^{29}Si [1c]		
4-154a $(OC)_4Os(SiMe_3)_2$ [4s]	M (43)	lt. yellow 25	Y	Y'		-22.9 (*cis*) -19.3 (*trans*)	IR	148a 193b
4-154b $(OC)_4Os(SiMe_2Cl)_2$	—	—	—	Y'		19.2 (*cis*) $^2J_{SiH} = 5.5$ 21.6 (*trans*) $^2J_{SiH} = 4.8$	—	148a 193a
4-155 *cis*-$(OC)_4Os(SiMeCl_2)_2$	—	—	—	X: (^{1}H) Y': (^{29}Si)		24.4 (*cis*) $^2J_{SiH} = 6.1$	^{1}H IR	148a 184
4-156 *trans*-$(OC)_4Os(SiMeCl_2)_2$	M (23)	white 125	Y	Y'		25.3 $J_{SiH} = 5.2$	^{13}C IR	148a 185
4-157 *cis*-$(OC)_4Os(SiCl_3)_2$	M (~100)	— 135-136	Y	Y'		-7.0	^{13}C IR, MS	148a 163
4-158 *trans*-$(OC)_4Os(SiCl_3)_2$	M (19)	white 182	Y	X		-6.6	^{13}C IR, MS	148a, 185, 194
4-159 $(OC)_4Os[Si(Ph)CH_2(CH_2)_4]_2$	M (37)	yellow 112-115	Y	X		—	^{1}H, ^{13}C IR	195
4-160 $(OC)_2(Ph_3P)_2(H)OsSiEt_3$	S (83)	colorless 139-140	Y	X	-9.17 (dd)	—	^{13}C, ^{31}P IR X-ray	100
4-161 $(OC)_2(Ph_3P)_2(H)OsSiPh_3$ [4t]	S (77)	colorless 175-176	Y	X	-8.91	—	^{13}C, ^{31}P IR	100
4-162 $(OC)_2Os(SiMe_2CH_2CH_2PPh_2)_2$	M (35)	white 230-231	Y	X		—	^{31}P IR X-ray	187
4-163 $(OC)_2Os(SiMePhCH_2CH_2PPh_2)_2$	M (43)	lt. yellow 316-318 [4u]	Y	X		—	^{31}P IR	187
4-164 $(OC)_2Os(SiPh_2CH_2CH_2PPh_2)_2$	M (40)	white > 325	Y	—		—	^{31}P IR	187
4-165 $(OC)[(i\text{-}Pr)_3P]_2(H)_3OsSiPh_3$	[4v] (75)	white —	Y	S	-9.76 (br) [4w]	—	^{31}P IR	52
4-166a $(OC)[(i\text{-}Pr)_3P]_2(Cl)(\eta^2\text{-}H_2)OsSiEt_3$	[4x] (—)	orange —	N	S	-1.70 (br)	—	^{31}P	196
4-166b $(OC)(Ph_3P)_2(Cl)OsSiCl_3$	[4x] (94) [4y] (88)	yellow 200-203	Y	X		—	^{13}C, ^{31}P IR X-ray	197
Iron Triad, M_2, M_3 and M_4 (noninteracting metals)								
4-167* $(OC)_4Ru(1,1'\text{-}Me_2SiFc)$	M (58)	orange 98-99	Y	S		—	^{13}C IR, MS UV-vis	198
4-168* $(OC)_4Ru(SiMe_2Fc)_2$	M (20)	yellow 146-147 (d)	Y	S		—	^{13}C IR UV-vis	198
4-169 $(OC)_4Fe(SiMe_2Fc)_2$	M (27)	yellow 156-157 (d)	Y	S		—	^{13}C IR UV-vis	198
4-170* D_4^{Fp}	O (30)	lt. beige 191 (d)	Y	S		—	IR	199

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
Iron Triad, M_2 and M_3								
4-171* $Cp^*(OC)_4(\mu\text{-}Ph_2P)Fe_2(\mu\text{-}SiHMe)$	[4z] (—)	—	HRMS	S		202.8 (d)	^{13}C, ^{31}P MS	102
4-172* $(OC)_8Fe_2SiMe_2$	[5a] (8)	dark-red —	N	S'		173	^{13}C IR	200
4-173* $(OC)_8Fe_2[Me_2SiCH_2GeMe_2]$	M (62)	oil 74°C/0.02 mm	N	S'		—	^{13}C IR, MS	201
4-174* $[(OC)_4Fe]_2(\eta{:}\eta\text{-}Ph_2SiOSiPh_2)$	M (11)	red —	Y	S		31.1	^{13}C IR X-ray	56
4-175a* $Cp_2(OC)_2(\mu\text{-}CH_2)Ru_2(SiMe_2Ph)_2$ [5b]	[5c] (33)	orange-yellow —	Y	X		—	^{13}C IR X-ray	175, 202
4-175b $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiMe_2)(H)(SiMe_2Ph)(CO)$ [5d]	[5e] (73)	yellow —	Y	S	-14.97 (s)	—	^{13}C IR X-ray [5f]	107
4-176* $Cp_2Ru_2(\mu\text{-}CH{=}CH_2)(SiMe_2Ph)(CO)_2$ [5g]	[5g] (45)	yellow —	Y	X		—	^{1}H, ^{13}C IR	203
4-177* $[(OC)_4RuSiMe_3]_2$ [5h]	M (90)	brt. yellow 129-131	Y	Y': (^{29}Si)		9.8	IR	148a, 204
4-178 $(OC)_8Ru_2(SiMeCl_2)_2$ [5i]	M (72)	lt. yellow 136-141	Y	Y': (^{29}Si)		59.3 $^2J_{SiH} = 9.8$	IR	148a, 204
4-179 $(OC)_8Ru_2(SiCl_3)_2$	M (36) M (61)	yellow 140-141 145-150	Y Y	Y': (^{29}Si)		31.5	IR	185, 204
4-180 $(OC)_8Ru_2[SiMe(CH_2)_4CH_2]_2$	M (32)	yellow 126-128	Y	X		—	^{13}C IR	195
4-181 $(OC)_8Ru_2[SiPh(CH_2)_4CH_2]_2$	M (29)	yellow 135-136	Y	X		—	^{13}C IR	195
4-182* $(OC)_6Ru_2[Me_2SiCH_2PPh_2]_2$	M (—)	lt. yellow —	Y	—		—	^{1}H, ^{31}P IR X-ray	205
4-183* $(OC)_{10}(\mu\text{-}H)_2Ru_3(SiMe_2C_5H_4FeC_5H_4SiMe_2)$	M (7)	red 149-151	Y	S	-17.04 (s) -14.78 (s)	—	^{13}C IR X-ray	206
4-184* $(OC)_9(\mu\text{-}H)_3Ru_3(SiMeCl_2)_3$	M (35)	yellow 121-122	Y	X	-14.88, 1.38	—	^{13}C IR	185
4-185 $(OC)_9(\mu\text{-}H)_3Ru_3(SiCl_3)_3$	M (48)	white 155-156	Y	X Y: (^{29}Si)	-15.52	24.3	^{13}C IR	148a, 185
4-186* $[(OC)_8(\mu\text{-}H)_2(\mu\text{-}C_4H_4N_2)Ru_3(SiEt_3)_2]$	[5j] (49)	green —	Y	W	-11.83 (s) -11.04 (s)	—	IR X-ray	207
4-187* $(OC)_8(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}ampy)Ru_3SiEt_3$	[5k] (93)	lt. yellow —	Y	Y	-8.64 (s) -11.84 (s)	—	^{13}C, ^{31}P IR X-ray	208
4-188 $[(OC)_8(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}ampy)Ru_3\{Si(OMe)_3\}]$	[5l] (93)	lt. yellow —	Y	S	-12.16 (s) -9.76 (s)	—	^{13}C IR	209
4-189 $[(OC)_8(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}ampy)Ru_3\{Si(OMe)_3\}_2]$	[5m] (—)	orange-red oil	N	S	-11.41 (s)	—	^{13}C IR	209

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^1H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-190* $(OC)_7(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}ampy)(Ph_3P)Ru_3SiEt_3$	[5n] (81)	yellow —	Y	Y	-8.50 (d) -11.20 (d)	—	^{13}C, ^{31}P IR	208
4-191* $[(OC)_7(\mu_3\text{-}ampy)\{\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Ph\}Ru_3\{Si(OMe)_3\}]$	[5m] (8)	red —	Y	S	-11.30 (s)	—	^{13}C IR	209
4-192* $[(OC)_6(Ph_3P)(\mu_3\text{-}ampy)\{\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Ph\}Ru_3\{Si(OMe)_3\}]$	[5o] (32)	red —	Y	S	-11.39 (d)	—	^{13}C IR X-ray	209
4-193* $(OC)_6(\mu\text{-}H)(\mu_3,\eta^2\text{-}ampy)(Ph_3P)_2Ru_3SiEt_3$	[5p] (70)	yellow-orange —	Y [1e]	Y	-7.62 (t) -10.28 (dd)	—	^{13}C, ^{31}P IR	208
4-194* $(OC)_8Os_2[SiMe(CH_2)_4CH_2]_2$	M (28)	yellow 147-151	Y	X		—	^{13}C IR	195
4-195 $(OC)_8Os_2(SiMeCl_2)_2$	M (—)	lt. yellow 142-144	Y	X		22.0 $^2J_{SiH} = 6.2$	^1H IR	148a, 210
4-196* $(OC)_6Os_2[Me_2SiCH_2PPh_2]_2$	M (—)	yellow —	N	—		—	X-ray [5q]	205
4-197* $(OC)_{12}Os_3(SiMeCl_2)_2$	M (61)	lt. yellow > 177 (d)	N	X Y': (^{29}Si)		21.8	^{13}C IR	148a, 194
4-198 $(OC)_{12}Os_3(SiCl_3)_2$	M (46)	lt. yellow >185 (d)	Y	X Y': (^{29}Si)		-10.9	^{13}C IR, MS X-ray	148a, 194
4-199 $(OC)_{11}(\mu\text{-}H)[SiMe_2(CH_2C_6H_4Br\text{-}2)]$	[5r] (95)	—	Y	—	-18.57	—	IR	57
4-200* $[(OC)_{11}(\mu\text{-}H)Os_3\{Si(OEt)_3\}]$	[5s] (93)	yellow —	Y	X	-18.61 (s)	—	—	211
4-201* $[\{(OC)_{10}HOs_3[Si(OMe)_3]\}_2(\mu\text{-}dppe)]$	[5t] (44)	yellow —	N	Y	-18.68 (d) (minor) -19.22 (d) (major)	—	^{31}P IR, MS X-ray	212
4-202 $(OC)_{10}(\mu\text{-}H)Os_3(o\text{-}Ph_2PC_6H_4CH_2SiMe_2)$ [5u]	Y (—)	yellow —	Y	X	-19.20 (d)	—	^{31}P IR X-ray	213
4-203 $[(OC)_{10}(\mu\text{-}H)Os_3(o\text{-}Me_2SiC_6H_4CH_2PPh_2)]$ [5v]	Y (—)	yellow —	Y	X	-19.49	—	^{31}P IR X-ray	213
4-204* $[(OC)_{10}(\mu\text{-}H)_2Os_3\{SiMe_2(2\text{-}py)\}_2]$	[5w] (—)	dk. orange —	Y	X	-19.60	—	IR X-ray	57
4-205* $[(OC)_{10}(\mu\text{-}H)(CH_3CN)Os_3\{SiMe_2CH_2C_6H_4Br\text{-}o\}]$	Y (98)	orange —	Y	—	-16.23	—	IR X-ray	57
4-206* $(OC)_{10}(MeCN)(\mu\text{-}H)Os_3[Si(OEt)_3]$ [5x]	Y (84)	yellow —	Y	X	-16.40 (s)	—	IR X-ray	211, 214
4-207 $(OC)_9(\mu\text{-}H)_3Os_3(SiPh_3)$	[5w] (53)	yellow-orange 150-152	Y	T	[5y]	—	IR, MS X-ray	215
4-208 $(OC)_9(\mu\text{-}H)_3Os_3(SiCl_3)_3$	M (68)	white 198-199	Y	X	-17.20	-15.8	^{13}C IR	148a, 185
4-209 $(OC)_9(\mu\text{-}H)_3Os_3(SiMeCl_2)_3$	M (62)	lt. yellow 158	Y	X	-16.59	—	^{13}C IR X-ray	185

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-210 $(OC)_8(\mu\text{-}H)_3Os_3(o\text{-}Me_2SiC_6H_4CH_2PPh_2)$ [5z]	[5z] (—)	—	Y	X	-12.70 (s) -11.62 (s) -7.85 (s)	—	^{13}C IR X-ray	213
Co Triad								
4-211* $(OC)_4Co\text{-}[Si(Me)\text{-}(CH_2)_4CH_2]$ [6a]	Z (55)	white 31-32	Y	X		—	^{1}H, ^{13}C IR	216
4-212 $(OC)_4Co(Si_8H_7O_{12})$ [6b]	Z (10)	colorless —	Y	X [6c]		-46.0 (*Si*-Co) -84.5 -84.6 -86.4	^{1}H, ^{13}C IR, MS X-ray	217
4-213 (OC)$_4$Co(Si[S]) [6d]	Z (—)	—	Y	—		—	IR UV-vis	218
4-214 $(OC)_3(Ph_2MeP)Co\text{-}SiMe_2Et$ [6e]	2A (100)	brown oil	Y	S		42.2 (d)	^{1}H, ^{13}C ^{31}P IR	219
4-215 $(OC)_3(Ph_2MeP)Co\text{-}SiMe_2Ph$ [6e]	2A (97)	dk. red 134-135	Y	S		32.3 (d)	^{1}H, ^{13}C ^{31}P IR	219
4-216 $(OC)_3(Ph_2MeP)Co\text{-}SiPh_3$ [6e]	2A (100)	lt. yellow 210-212 (d)	Y [1e]	S		29.8 (d)	^{1}H, ^{13}C ^{31}P IR	219
4-217 $(OC)_3(Ph_2MeP)Co\text{-}SiF_3$ [6f]	2B (—)	yellow —	Y	—		—	IR	220
4-218 $(OC)_3(Ph_2MeP)CoSiEt_3$ [6e]	2A (100)	brown oil	N	S		51.9 (d)	^{1}H, ^{13}C ^{31}P IR	219
4-219 $(OC)_3(Ph_3P)CoSiPh_3$ [6g]	2C [6h] (—)	white —	Y [1e]	—		—	IR	220
4-220 $(OC)_3(H)Co(SiEt_3)_2$ [6i]	2D (—)	—	N	[6j] (-77)	-9.8	—	IR	221
4-221 $(OC)_2(Ph_3P)_2Co\text{-}SiMePh_2$ [6k]	2E (73)	yellow 131 (d)	Y [1e]	S		—	^{1}H, ^{31}P IR X-ray	222, 223
4-222 $(OC)_2(Ph_3P)_2CoSiF_3$ [6l]	2F (—)	yellow —	Y	—		—	IR	220
4-223 $(OC)(Ph_3P)_3CoSiF_3$	2G (—)	yellow —	Y	—		—	IR	220
4-224 $Cp(\eta^2\text{-}C_2H_4)(H)Rh\text{-}SiEt_3$ [6m]	2H [6n] (—)	yellow oil	N	T	-14.85 (d) $^1J_{RhH}$ = 33.2 $^2J_{HSi}$ = 12.0	41.6 (d) $^1J_{RhSi}$ = 22.2	VT-NMR ^{13}C, ^{103}Rh IR, MS UV-vis	224 225
4-225 $Cp(\eta^2\text{-}C_2H_4)(H)Rh\text{-}Si(i\text{-}Pr)_3$ [6o]	2H (—)	white —	N	T	-14.85 (d) $^1J_{RhH}$ = 31.6 $^2J_{HSi}$ = 15.6	49.3 (d) $^1J_{RhSi}$ = 25.6	^{13}C, ^{103}Rh IR, MS UV-vis	225
4-226 $Cp(H)_2Rh(SiEt_3)_2$ [6m]	2H (95)	white 29-30	Y	T	-14.16 (d) $^1J_{RhH}$ = 38.3 $^2J_{HSi}$ = 6.8	40.1 (d) $^1J_{RhSi}$ = 16.6	^{13}C, ^{103}Rh IR, MS UV-vis	224, 226
4-227 $Cp(H)_2Rh[Si(i\text{-}Pr)_3]_2$	2H (—)	white —	N	T	-14.46 (d) $^1J_{RhH}$ = 35.5 $^2J_{HSi}$ = 6.3	52.2 (d) $^1J_{RhSi}$ = 18.3	^{13}C IR, MS	225

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR			Other Data	Ref.
				solvent (temp.)[1b]	^1H[1c] M-H	^{29}Si[1c]		
4-228 $Cp^*(OC)(H)RhSiEt_3$ [6p]	2I (—)	yellow oil	N	S or T X	-11.56 (d) $^1J_{RhH}$ = 36 -14.1 [6q] $^1J_{RhH}$ = 37.4	—	^{13}C, ^{103}Rh IR UV-vis	227, 228
4-229 $(\eta^5\text{-}C_5H_4SiMe_3)(H)_2\text{-}Rh(SiMe_3)_2$	2J [6r] (—)	—	N	T	-13.90 (d) $^1J_{RhH}$ = 39.2 $^2J_{SiH}$ = 7.1	6.6 (d, C_5H_4Si) $^1J_{RhSi}$ = 0.4 18.44 (d) $^1J_{RhSi}$ = 15.2	^{13}C	226
4-230 $(\eta^5\text{-}C_5H_4SiEt_3)(H)_2\text{-}Rh(SiEt_3)_2$	2J [6s] (—)	—	Y	T	-14.08 (d) $^1J_{RhH}$ = 37.2 $^2J_{SiH}$ = 7.0	-0.85 (s, C_5H_4Si) 37.4 (d) $^1J_{RhSi}$ = 16.8	^{13}C, ^{103}Rh MS	226
4-231 $Cp^*(\eta^2\text{-}C_2H_4)(H)Rh\text{-}SiEt_3$ [6t]	2K (25)	—	N	S	-13.75 (d) $^1J_{RhH}$ = 35	-38.2 $^1J_{RhSi}$ = 17	^{13}C, ^{103}Rh IR	227
4-232 $Cp^*(\eta^2\text{-}C_2H_4)(H)Rh\text{-}Si(OEt)_3$ [6t]	2K (38)	lt. yellow oil	Y [1e]	S	-13.61 (d) $^1J_{RhH}$ = 35.5	-9.9 $^1J_{RhSi}$ = 45	^{13}C, ^{103}Rh IR, MS	227
4-233 $Cp^*(H)_2Rh(SiMe_3)_2$ [6u]	2L [6v] (57)	colorless —	Y	S	-13.54 (d) $^1J_{RhH}$ = 38.6	—	^{13}C, ^{103}Rh IR	229
4-234 $Cp^*(H)_2Rh(SiEt_3)_2$	2L (94) [6w]	colorless 95 (d)	Y	S	-13.85 (d) $^1J_{RhH}$ = 36.9 $^1J_{SiH}$ = 7.9	38.3 (d) $^1J_{RhSi}$ = 15.9	^{13}C, ^{103}Rh IR UV-vis X-ray N. D.	230 231
4-235 $Cp^*(H)_2Rh(SiPh_3)_2$	2L (—)	white —	Y	X	-11.50 (d) $^1J_{RhH}$ = 34	—	IR	232
4-236 $Cp^*(H)_2Rh(SiPh_3)\text{-}(SiPh_2Cl)$	2L (—)	white —	Y	X	-11.17 (d) $^1J_{RhH}$ = 35	—	^{13}C IR	232
4-237 $Cp^*(H)_2Rh(SiEt_3)\text{-}[Si(OEt)_3]$ [6x]	2M [6y] (40)	—	Y	—	—	—	—	233
4-238 $Cp^*(H)_2Rh[Si(OEt)_3]_2$	2K [6z] (65)	—	Y	—	—	—	—	233
4-239a $(Me_3P)_3RhSiPh_3$	2N (67) or 2O [7a]	red —	Y	S		—	^1H, ^{31}P X-ray	234, 235
4-239b *mer*-$(Me_3P)_3(PhS)(H)\text{-}RhSiPh_3$ [7b]	2P (80) [7c]	yellow —	Y [1e]	U (-50)	-8.79 (ddt) $^1J_{RhH}$ = 17	—	^{31}P IR X-ray	112
4-239c *mer*-$(Me_3P)_3[(p\text{-}Tolyl)S](H)RhSiPh_3$ [7b]	2P (84) [7c]	yellow —	Y [1e]	U (-50)	-8.74 (ddt) $^1J_{RhH}$ = 16	—	VT-NMR ^{31}P IR X-ray	112
4-239d *mer*-$(Me_3P)_3(PhS)(H)\text{-}RhSi(OMe)_3$ [7b]	2P (26)	yellow —	Y	S	-9.33 (ddt) $^1J_{RhH}$ = 18	—	^{31}P IR X-ray	112
4-240 *mer*-$(Me_3P)_3(C_6F_5)\text{-}(H)RhSi(OEt)_3$	2O (—)	—	—	—	—	—	^1H, ^{19}F ^{31}P X-ray	235 [1j]
4-241 *mer*-$(Me_3P)_3(C_6F_5)\text{-}(H)RhSi(SEt)_3$ [7d]	2O (93)	yellow	N	S	-9.77 (dm)	—	^{19}F, ^{31}P	236
4-242 *fac*-$(Me_3P)_3(H)Rh\text{-}[SiMe_2(CH_2)_2SiMe_2]$	2P (41)	colorless —	N	S	-11.12 (ddt)	—	^{13}C X-ray	237

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-243a (i-$Pr_3P)_2Cl(H)Rh$-$Si(CH_2CH_2Ph)_3$ [7e]	2Q (—)	yellow —	N	S	-16.63 (td) $^1J_{RhH}$ = 22	—	^{31}P	238
4-243b (i-$Pr_3P)_2Cl(H)Rh$-$Si(C{\equiv}CPh)_3$ [7f]	2Q (64)	yellow —	Y [1e]	S	-16.50 (dt) $^1J_{RhH}$ = 21	—	^{31}P X-ray	239
4-243c (i-$Pr_3P)_2Cl(H)Rh$-$SiPh_3$ [7f]	2Q (58)	yellow —	Y	S	-16.20 (dt) $^1J_{RhH}$ = 21	—	^{31}P X-ray	239
4-243d $(Ph_3P)_2Cl(H)Rh$-$SiPhMe_2$ [7e]	2R (—)	—	N	X (-20)	-15.33 (dt) $^1J_{RhH}$ = 22.7	—	^{31}P	240
4-244 $(Ph_3P)_2Cl(H)Rh$-$(SiMe_2CH_2CH_2SiPh_2H)$ [7e]	2R (—)	—	N	X (-20)	-15.54 (dt) [7g] $^1J_{RhH}$ = 23.5	—	^{31}P	240
4-245 $(Ph_3P)_2(H)_3Rh$-$(SiMe_2CH_2CH_2SiPh_2)$ [7h]	2R (—)	—	N	T (-60)	-10.8 (br d) -7.3 (br s) -6.7 (br s)	—	VT-NMR ^{31}P	240
4-246 $(Ph_3P)_2(H)_3Rh$-$(SiPh_2CH_2CH_2SiPh_2)$ [7h]	2R (—)	—	N	T (-60)	-10.9 (br d) -6.3 (br s)	—	VT-NMR ^{31}P	240
4-247 $(Ph_3P)_2Cl(H)Rh$-$(SiPh_2CH_2CH_2SiPh_2H)$ [7e]	2R (—)	—	N	X (-20)	-15.18 (dt) [7i] $^1J_{RhH}$ = 22.0	—	^{31}P	240
4-248 $Cl(H)Rh[Si(CH_2$-$CH_2PPh_2)_3]$ [7j]	2S [7k] (—)	orange —	Y	—	-8.84 (dq) $^1J_{RhH}$ = 11.9	—	^{13}C ^{31}P IR	241
4-249 $Me_3P(dtbpm)Rh$-$Si(OEt)_3$	2T [7l] (80-90)	red —	Y [1e]	T (0)		—	^{1}H, ^{13}C ^{31}P X-ray	242
4-250 $(Cl)Rh(SiMe_2CH_2$-$CH_2PPh_2)_2$	2S (81)	yellow —	Y	S		—	^{1}H, ^{31}P IR	243
4-251 $(OEP)RhSiEt_3$	2U (54)	purple —	HRMS	X		51.9 (d) $^1J_{RhSi}$ = 29.3	^{1}H, ^{13}C IR, MS UV-vis X-ray	244
4-252 $(OEP)RhSiMe_2Ph$	2U (44)	—	HRMS	S		28.3 (d) $^1J_{RhSi}$ = 30.2	^{1}H IR, MS UV-vis	244
4-253 $(OEP)RhSiPh_3$	2U (65)	—	HRMS	X		11.6 (d) $^1J_{RhSi}$ = 35.7	^{1}H IR, MS UV-vis	244
4-254 $(OEP)RhSiMe_2OEt$	2U (42)	—	HRMS	X		37.2 (d) $^1J_{RhSi}$ = 30.5	^{1}H IR, MS UV-vis	244
4-255a *fac*-(dmesiqn)$_3$Rh	2V (50)	yellow —	N	X		23.6 $^1J_{RhSi}$ = 41.7	^{1}H MS UV-vis X-ray	245, 246
4-255b $(DAD)Cl(H)Rh$-$Si(OEt)_3$	2W (—)	green-yellow —	Y [1e]	X	-13.58 (d) $^1J_{RhH}$ = 19.7	—	IR	247
4-256 $(nbd)(H)_2RhSiEt_3$	2X [7m] (—)	—	N	S	-13.88 (d) $^1J_{RhH}$ = 42	—	^{31}P	248
4-257 $Cp^*(Me_3P)Ir$-$(\eta^2$-$SiPh_2CH_2)$ [7n]	2Y [7o] (—)	yellow —	—	S T: (^{31}P)		—	^{1}H, ^{13}C ^{31}P MS X-ray	249 [1j]

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR			Other Data	Ref.
				solvent (temp.)[1b]	^{1}H [1c] M-H	^{29}Si [1c]		
4-258 $Cp^*(Me_3P)(Me)Ir-SiMe_2OTf$ [7p]	2Z (88)	—	—	—		—	—	113 [1j]
4-259 $(\eta^5-C_5Me_4Et)Me_3P-(Ph)IrSiMe_2F$ [7q]	3A (82)	colorless —	Y	S		—	^{1}H, ^{13}C ^{19}F, ^{31}P IR, MS	250
4-260 $Cp^*(\eta^2-C_2H_4)(H)Ir-Si(OEt)_3$ [7r]	3B (—)	—	N	S or T	-17.29	—	^{13}C IR	227
4-261 $Cp^*Cl(H)_2IrSiEt_3$ [7s]	3C (70) [7t]	colorless —	Y [1e]	Y	-12.60 (s)	—	IR	232, 251
4-262 $Cp^*(H)_2Ir(SiEt_3)_2$	3D [7u] (40)	colorless —	Y	X	-17.40 (s)	—	^{13}C IR, MS UV-vis N. D.	231, 232, 251, 252
4-263 $(OC)_3(Cy_3P)IrSiPh_3$ [7v]	3E (59)	white —	Y	S		—	^{1}H, ^{31}P IR	58
4-264 $(OC)_2Cy_3P(CH_3OCO)-(H)IrSiPh_3$ [7v]	3E (—)	—	—	S	-6.8 (d)	—	^{31}P IR	58
4-265 $(OC)_2Cy_3P(H)_2Ir-SiPh_3$ [7v]	3E (65) [7w]	white —	Y	S	-10.3 (d)	—	^{31}P IR	58
4-266 $OC(Ph_3P)_2(H)Ir-(SiMePhOSiMePh)$ [7x]	3F (87)	white 165-170	Y	S	-7.15 (t) [7y] -7.55 (t) -7.68 (t)	—	IR	253
4-267 $OC(Ph_2MeP)_2Cl(H)Ir-Si(OEt)_3$ [7z]	3G (—)	white —	Y	[8a]	-15.32 (t)	—	IR	254
4-268 $OC(Ph_3P)_2Cl(H)Ir-(2-SiMe_2C_5H_4N)$	3F (—)	yellow —	Y	—	—	—	IR	149
4-269 *cis*-$OC(Ph_3P)_2(H)_2Ir-Si(SEt)_3$ [8b]	3H (—)	—	Y	S	-10.21 (ddd) $^2J_{HH} = 4.4$ -9.23 (ddd)	—	^{31}P, ^{13}C	236
4-270 $OC[(p-Tol)_3P]_2(H)_2Ir-SiMe_2Ph$ [8c]	3I [8d] (75-85)	colorless —	Y	—	-9.98 (ddd) $^2J_{HH} = 4.5$ -9.25 (td) $^2J_{HH} = 4.5$	—	^{31}P, ^{13}C IR X-ray	255
4-271 $OC(Ph_3P)Cl(H)Ir-(SiMe_2CH_2CH_2PPh_2)$ [8e]	3F (73)	white 160-161	Y	X	-7.38 (t) [8f]	—	^{31}P IR X-ray	114, 256, 257
4-272 *cis*-$OC(Ph_3P)(H)_2Ir-(SiMe_2CH_2CH_2PPh_2)$	3H [8g] (71)	colorless —	Y	X	-10.64 (dd) -10.59 (app t)	—	^{31}P IR	257, 114
4-273 $OC(dppe)(NC)(H)Ir-SiEt_3$ [8h]	3J (—)	—	Y	W	-10.05 (~t)	—		258
4-274 $OC(dppe)Br(H)Ir-SiEt_3$ [8i]	3K (—)	white —	Y	S	-16.64 (dd)	—	^{31}P IR	258
4-275 $OC(dppe)Br(H)Ir-SiMeCl_2$ [8i]	3K (—)	white —	N	S	-8.77 (~ t)	—	^{13}C, ^{31}P IR	258

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-276 OC(chiraphos)Br(H)-IrSiPh$_3$ [8j]	3L (99)	—	N	W	-7.93 (dd), -8.49 (dd) (minor) -16.04 (dd), -16.34 (dd) (major)	—	—	259
4-277 OC(dppe)(H)$_2$IrSiEt$_3$ [8k]	3M (—)	colorless —	N	S or T	-10.06 (dd) -10.69 (t)	—	^{31}P IR	60, 258
4-278 OC(dppe)(H)$_2$Ir SiMeCl$_2$ [8k]	3M (—)	colorless —	N	S or T	-9.71 (dd) -10.34 (t)	—	^{31}P IR	60
4-279 OC(dppe)(H)$_2$IrSiPh$_3$ [8k]	3M (—)	colorless —	N	S or T	-9.43 (dd) -10.20 (t)	—	^{31}P IR	60
4-280a OC(dppe)(H)Ir-(SiMe$_2$Cl)$_2$ [8k]	3M (90)	colorless —	Y	S or T	-9.56 (t)	—	^{31}P IR X-ray	60
4-280b OC(Cl)(H)Ir[SiMe-(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$ [8l]	3F (66)	white —	Y	X	-17.2 (t) (major) -6.09 (t) (minor)	—	^{13}C, ^{31}P IR	186
4-281 *cis*-OC[(*p*-Tol)$_3$P]$_2$-(H)Ir(SiMe$_2$Ph)$_2$ [8m]	3N (—)	burnt orange —	N	S	-10.28 (dd)	—	IR	260
4-282 *fac*-(Me$_3$P)$_3$Me(H)Ir-SiEt$_3$ [8n]	3O (92)	colorless —	Y	S	-12.15 (dt)	—	^{31}P X-ray	261, 262
4-283 *fac*-(Me$_3$P)$_3$Me(H)Ir-SiPh$_3$ [8n]	3O (98)	colorless —	Y	S	-11.79 (dt)	—	^{31}P X-ray	261, 262
4-284 *fac*-(Me$_3$P)$_3$Me(H)Ir-Si(SEt)$_3$	3O (80)	colorless —	Y	S	-12.35 (ddd)	—	^{31}P	236
4-285 *mer*-(Me$_3$P)$_3$(C$_6$F$_5$)(H)-IrSi(SEt)$_3$	2O (95)	colorless —	N	S	-12.0 (app dq)	—	^{19}F, ^{31}P MS	236
4-286 *fac*-(Me$_3$P)$_3$(H)$_2$IrSiEt$_3$	3P (96)	yellow liq. —	Y	S	-12.60 (m)	—	^{31}P	262
4-287 (Me$_3$P)$_3$(H)$_2$Ir-[Si(*t*-Bu)$_2$Cl]	3P (71)	colorless —	Y	S	-13.16 (dd)	—	^{13}C, ^{31}P IR X-ray	118
4-288 (Me$_3$P)$_3$(H)$_2$IrSiPh$_3$	3P (81)	colorless —	Y	S	-12.16 (dd)	0.09 (dt)	^{13}C, ^{31}P IR X-ray	118
4-289a *mer*-(Et$_3$P)$_3$Cl(H)Ir-Si(OEt)$_3$	3Q (97)	off-white —	N	S	-11.27 (dt)	—	^{31}P IR, MS	236
4-289b (Me$_3$P)$_2$Cl(H)Ir[η^2-SiMe$_2$(CH$_2$)$_2$PPh$_2$]	3R (73)	colorless —	Y	S	-10.04 (dt)	5.8 (ddd)	^{13}C, ^{31}P IR, MS	263
4-289c *fac*-(Me$_3$P)$_2$(H)Ir-(SiMe$_2$SiMe$_3$)[η^2-SiMe$_2$(CH$_2$)$_2$PPh$_2$] [8o]	3S (89)	colorless —	Y	S	-12.78 (dt)	-51.3 (ddd) Ir*Si*Me$_2$SiMe$_3$ -13.6 (t) SiMe$_3$ 10.5 (ddd) IrSiMe$_2$CH$_2$	^{31}P	264
4-290 *trans*-(Et$_3$P)$_2$Cl(H)Ir-[Si(*i*-Pr)$_2$(OH)] [8q]	3T (94)	yellow —	—	—	—	19.6	^{1}H, ^{13}C ^{31}P X-ray	265 [1j]
4-291a *trans*-(Et$_3$P)$_2$Cl(H)Ir-Si(OEt)$_3$	3T (96)	yellow-brown oil	N	S	-21.62 (t)	—	^{13}C, ^{31}P IR, MS	236

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^1H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-291b $Me_3P(H)Ir$-$(SiMe_2{\cdots}OMe{\cdots}SiMe_2)$$(\eta^2$-$SiMe_2(CH_2)_2PPh_2)$	3S[8r] (—)	—	HRMS	S	-9.88 (dd)	12.5 (dd) $IrSiMe_2CH_2$ 62.8 (dd) $Ir{=}SiMe_2$ 63.1 (dd) $Ir{=}SiMe_2$	^{31}P	264
4-292 $(Ph_3P)_2Cl(H)Ir$-$Si(OEt)_3$[8s]	3U (—)	[8t]	Y	X	-18.6 (t)	—	IR	254, 266
4-293 $(Ph_3P)_2(H)_4Ir$-$SiPh_3$[8u]	3V (89)	off-white —	Y	Y (25) Y(-80)	-10.18 (t) -10.58 (br s)	—	VT-NMR ^{31}P IR	267
4-294 $(Ph_3P)_2(H)_3Ir(disil)$	3V (78)	white —	Y	Y (25) Y (-80)	-9.12 (br s) -13.5 (br d) -9.18 (br t) -13.3 (dd) -13.7 (dd)	—	VT-NMR ^{31}P IR X-ray	267
4-295 $(Ph_3P)_2(H)_3Ir$-$[(i$-$Pr)_2SiOSi(i$-$Pr)_2]$	3V (50)	lt. yellow —	Y	Y	-11.20 (br s)	—	^{31}P IR	267
4-296a $Cl(H)Ir[SiMe(CH_2$-$CH_2CH_2PPh_2)_2]$[8v]	3W (95)	orange —	Y	X	-22.38 (t)	—	^{13}C, ^{31}P IR X-ray	186
4-296b $(Cl)Ir(SiMe_2CH_2$-$CH_2PPh_2)_2$	3W (35)	chrome yellow —	Y	S		—	^1H, ^{31}P IR X-ray	243 256
4-297a $Cy_3P(cod)(H)_2Ir$-$SiEt_3$[8w]	3X (66)	white —	Y	X	-13.52 (d)	—	IR	268
4-297b $Cy_3P(acac)(H)IrSiEt_3$[8x]	3Y (93)	yellow —	Y	S	-23.43 (d)	—	^{31}P IR X-ray	61
4-298 $Ph_3P(TFB)(H)_2Ir$-$SiEt_3$[8y]	3Z (67)	white —	Y[1c]	X	-14.84 (d)	—	^{31}P IR	121
4-299 $Ph_3As(cod)(H)_2Ir$-$SiEt_3$[8z]	4A (80)	white —	Y	X	-12.60	—	^{31}P IR X-ray	269, 270
4-300 $(cod)Cl(H)Ir$-$(SiMe_2CH_2CH_2PPh_2)$	3V (67)	ivory —	Y	S	-16.91	—	^{31}P IR X-ray	243, 256
4-301 *fac*-$(dmesiqn)_3Ir$	3H (60)	orange —	N	X		-10.1	^1H MS UV-vis X-ray	245, 246
4-302 $(triso)(H)_2Ir$-$(SiMePh_2)_2$[9a]	4B (48)	white —	Y	S: (^1H, ^{13}C) T: (^{31}P)	-20.96 (s)	—	^{13}C, ^{31}P IR	271
4-303 $(triso)(C_2H_4)(H)Ir$-$SiPh_3$	4B (42)	yellow —	Y	T: (^1H) X: (^{13}C, ^{31}P)	-24.78 (s)	—	^{13}C, ^{31}P IR	271
Co Triad MM' Non-Interacting[9b]								
4-304* $(OC)_4Co$-$[SiMe_2C_6H_5$-η^6-$Cr(CO)_3$	Z (73)[9c]	— 145-148 (d)	N	X		—	^1H IR, MS	272

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-305 $(OC)_4Co[SiMe_2\text{-}\eta^5\text{-}C_5H_4\text{-}Mn(CO)_3]$	Z (67)	— 90-93	N	S		—	^{1}H IR, MS	272
4-306 $(OC)_4Co[SiMe_2\text{-}\eta^5\text{-}C_5H_4\text{-}Fe(\eta^5\text{-}C_5H_5)]$	Z (87)	— 90-92	N	S		—	^{1}H IR, MS	272
4-307* $[(\eta^5\text{-}C_5H_4SiMe_2Co(CO)_4]_2Ru$	Z (35)	— 63 (d)	N	X		—	^{1}H IR, MS	272
4-308 $(OC)_4CoSiCl_2\text{-}FeCp(CO)_2$	Z (62)	brt. yellow 88-89 (d)	Y	S		101.3	^{1}H IR, MS	64
4-309* 1,4-$[(OC)_4CoSiMe_2]_2\text{-}C_6H_4$	Z (45)	off-white —	Y [1e]	X		—	^{1}H IR	273
4-310* $(OC)_3Cr\{[1,4\text{-}(OC)_4CoSiMe_2]_2C_6H_4\}$	Z (32)	brt. yellow 102 (d)	Y	X		—	^{1}H IR	273
4-311 $(OC)(Ph_3P)_2(H)_2Ir\text{-}[SiMe_2\text{–}\eta^6\text{-}C_6H_5\text{-}Cr(CO)_3]$	3H (66) [9c]	— 78-81	N	S	-8.47 (ddd) -9.87 (ddd)	—	IR, MS	272
4-312 $(OC)(Ph_3P)_2(H)_2Ir\text{-}[SiMe_2\text{-}\eta^5\text{-}C_5H_4\text{-}Mn(CO)_3]$	3H (69)	— 80-82	N	S	-9.70 (ddd) -11.03 (ddd)	—	IR, MS	272
4-313 $(OC)(Ph_3P)_2(H)_2Ir\text{-}[SiMe_2\text{-}\eta^5\text{-}C_5H_4\text{-}Fe(\eta^5\text{-}C_5H_5)]$	3H (8)	— 121-122	N	S	-9.32 (ddd) -10.12 (ddd)	—	IR, MS	272
4-314a* $[(OC)_4CoSiMe_2\text{-}(CH_2)_3]_4Si$	Z (—)	—	N	S		—	^{1}H IR, MS	274
4-314b* $\{[(i\text{-}Pr)_3P](Cl)HRh\text{-}[Si(CH_2Ph)_3]\}_2$ [9d]	2Q (40)	yellow —	Y	S	-19.17 (dd) J = 25, 28	—	^{31}P X-ray	238
4-315* $(H)_2Rh_2(SiMe_2C_6H_5)_4$	4C [9e] (85)	colorless —	Y	X	-13.7 (d) $^1J_{RhH} = 42$	—	IR X-ray	275
4-316 $(H)_2Ir_2(Me_2SiC_6H_5)_4$	4D (72)	white —	Y	[9f]		—	IR	275
Co Triad M_2 Interacting [9g]								
4-317* $(OC)_6Co_2\text{-}[\eta^2\text{-}(HMe_2Si)C{\equiv}C\text{-}SiMe_2Co(CO)_4]$ [9h]	Z (48)	dark red 45-47 (d)	Y [1e]	S	[9i]	—	^{1}H, ^{13}C IR UV-vis	276
4-318 $(OC)_6Co_2\text{-}[\eta^2\text{-}PhC{\equiv}CSiMe_2\text{-}Co(CO)_4]$	Z [9j] (84) [277, 278] (50) [276]	black 88-89 [278] dark red 91-93 (d) [276]	Y	S [276, 278] X: (^{29}Si) [278]		32.8	^{1}H, ^{13}C IR, MS UV-vis	276, 277, 278, 279
4-319 $(OC)_6Co_2\text{-}[\eta^2\text{-}PhC{\equiv}CSiMeEt\text{-}Co(CO)_4]$	Z [9k] (89)	red-brown 58	Y	X		—	^{1}H, ^{13}C IR, MS	122
4-320 $(OC)_6Co_2\text{-}[\eta^2\text{-}PhC{\equiv}CSiMeCl\text{-}Co(CO)_4]$	Z [9l] (92)[280] (85)[281] (80)[278]	black 92 [280, 281] 70-72 [278]	Y	X [280, 281] S: (^{1}H) [278]		—	^{1}H, ^{13}C IR, MS X-ray	278, 280, 281, 282
4-321 $(OC)_6Co_2\text{-}[\eta^2\text{-}PhC{\equiv}C\{SiMe\text{-}(OMe)Co(CO)_4\}]$	Z (63)	black 49-51	Y	X: (^{13}C) S: (^{1}H)		—	^{1}H, ^{13}C IR, MS	278
4-322 $(OC)_6Co_2\text{-}[\eta^2\text{-}PhC{\equiv}CSiCl_2\text{-}Co(CO)_4]$	Z [9m] (90)	— 110	Y	X		—	^{1}H, ^{13}C IR, MS	280

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^{1}H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-323a*$(OC)_6Co_2[\eta^2\text{-}(OC)_4\text{-}CoSiMe_2C{\equiv}CSiMe_2\text{-}Co(CO)_4]$ [9h]	Z (27)[276]	dark red 117-119 (d)	Y	S		—	^{1}H IR, MS UV-vis	276, 278
4-323b*$[(i\text{-}Pr_3P)(H)_2Rh][\mu\text{-}Si(CH_2CH_2Ph)_2]\text{-}[Rh(H)_2(i\text{-}Pr_3P)]$	2Q (22)	yellow —	Y	S	-7.09 (dd) $J_{RhH} = 24$	—	^{31}P X-ray	238
4-323c*$\{[(i\text{-}Pr)_3P](H)Rh\text{-}SiAr_3\}_2(\mu\text{-}H)(\mu\text{-}Cl)$ Ar = $C_6H_4OCF_3$-*p* [9n]	2Q [9o] (—)	orange —	Y [1e]	S	-16.12 (m) -12.62 (tt) $J_{RhH} = 57$	—	^{31}P X-ray	239
4-323d*$\{[(i\text{-}Pr)_3P](H)Rh\}_2(\mu\text{-}H)(\mu\text{-}Cl)[\mu\text{-}(i\text{-}Pr)_2Si\text{-}O\text{-}Si(i\text{-}Pr)_2]$ [9n]	2Q [9o] (26)	yellow —	Y	S	-14.67 (m) -12.90 (tt) $J_{RhH} = 56$	—	^{13}C, ^{31}P X-ray	239
4-324* $(OC)_2(H)Ir(SiPh_3)\text{-}(\mu\text{-}CH_2)_2TaCp_2$ [9p]	4E (55)	white —	Y	S	-14.3 (br s)	—	^{13}C, ^{31}P IR,UV-vis	283, 284
Ni Triad								
4-325 $(\eta^6\text{-}C_7H_8)Ni(SiCl_3)_2$ [9q]	4F (83)	yellow-orange 138-140	N	—		—	—	285
4-326 $(\eta^6\text{-}C_{10}H_8)Ni(SiCl_3)_2$ [9r]	4F (25)	rust 130-140	Y [1e]	X		—	^{1}H IR	286
4-327 $Pd(SiMe_2CH_2\text{-}CH_2PPh_2)_2$	4G (42)	yellow 43 (d)	Y	Y		—	^{1}H, ^{31}P	126
4-328 $(Ph_2MeP)_2Pd(SiCl_3)_2$	4H (32)	colorless 102 (d)	N	S		17.0	^{1}H, ^{13}C ^{31}P	126
4-329a $(dcpe)Pd(SiHMe_2)_2$	4I [9s] (—)	colorless 124	Y	S	[9t]	—	^{1}H, ^{13}C ^{31}P IR, MS X-ray	73
4-329b $[(Ph_3P)(phen)Pd\text{-}SiEt_3]^+[BAr'_4]^-$ [9u] Ar' = $3,5\text{-}(CF_3)_2C_6H_3$	4J (48)	orange —	Y	Y		—	^{31}P	287
4-329c $[(phen)(\eta^2\text{-}CH_2{=}CH_2)\text{-}PdSiEt_3]^+[BAr'_4]^-$ Ar' = $3,5\text{-}(CF_3)_2C_6H_3$ [9v]	4K (—)	—	N	Y (-90)		—	—	287
4-330 *cis*-$(Me_3P)_2(H)PtSiPh_3$	4L (51)	white —	Y [1e]	W	-3.05 (dd) $^{1}J_{PtH} = 892$	—	^{31}P IR	288
4-331a *cis*-$(Et_3P)_2(H)PtSiEt_3$ [9w]	4M (—)	brown oil	N	T (-30)	-2.29 (dd) $^{1}J_{PtH} = 942$	—	^{31}P	289
4-331b *cis*-$(Et_3P)_2(H)PtSiPh_3$ [9x]	4N (65)	colorless —	Y	S	-2.43 (dd) $^{1}J_{PtH} = 873$	—	^{31}P X-ray	290
4-332 *cis*-$(Cy_3P)_2(H)Pt\text{-}Si(SEt)_3$ [9y]	4O (—)	—	—	S	—	—	^{1}H, ^{31}P IR	291 [8a]
4-333 *cis*-$(Ph_3P)_2(H)PtSiPh_3$	4P (80)	lt. yellow 118	Y [1e]	X (-30)	-2.38 (dd) $^{1}J_{PtH} = 933$	—	^{31}P IR X-ray	292
4-334 *cis*-$(Et_3P)_2Pt(SiHMe_2)_2$	4Q [9z] (90)	lt. yellow 63-65	Y	X: (^{1}H, 0) T: (^{31}P)	[10a]	—	^{1}H, ^{31}P IR	293

Table 4 (Continued)

Complex	Prep.[1a]	Color m.p. (°C)	Anal.	NMR solvent (temp.)[1b]	NMR ^1H[1c] M-H	NMR ^{29}Si[1c]	Other Data	Ref.
4-335 $(Ph_3P)_2Pt$-$[SiPh_2SiPh_2SiPh_2]$	4P (35)	lt. yellow 140 (d)	Y	—		—	IR, MS UV-vis	294
4-336 $(Ph_3P)_2Pt$-$[SiMePhOSiMePh]$ [10b]	4P (80)	cream 214-216 (d)	Y [1c]	S		—	^1H IR	253
4-337 (dmpe)Pt-$[Si(t\text{-}Bu)_2(OH)](OTf)$ [10c]	4R (—)	colorless —	N	W		—	^1H, ^{31}P X-ray	295 [1j]
4-338 $(dcpe)(H)PtSiPh_3$ [10d]	4S (68)	white 172-174	Y	S (20)	-2.51 (dd) $^1J_{PtH} = 867$	—	^{31}P X-ray	296
4-339 (dcpe)Pt-$(\eta^2\text{-}SiPh_2SiPh_2)$ [10e]	4T (12)	yellow —	Y [1c]	S+Y: (^1H) T: (^{29}Si, ^{31}P)		-7.84 (dd) $^1J_{PtSi} = 1125$	^1H, ^{31}P IR, MS	297
4-340 (dppe)Pt-$(SiMe_2CH_2CH_2SiMe_2)$	4U (60)	brt. yellow 212 (d)	Y	S		34.3 (dd)	^1H, ^{13}C, ^{31}P, ^{195}Pt MS	298
4-341a (dppe)Pt-$[\eta^2\text{-}Si(i\text{-}Pr)_2Si(i\text{-}Pr)_2]$	4V [10f] (55)	yellow —	Y	Y: (^1H) T: (^{29}Si, ^{31}P)		19.6 (dd) $^1J_{PtSi} = 1128$	^1H, ^{31}P MS	297
4-341b $(Cl)Pt[SiMe(CH_2CH_2CH_2PPh_2)_2]$ [10g]	4W (73)	cream —	Y	X		—	^{13}C, ^{31}P IR, MS X-ray	186
4-342 *cis*-$Pt(SiMe_2CH_2CH_2PPh_2)_2$ [10h]	4X [10i] (~ 90) 4W (48)	white —	Y	X		—	^1H, ^{31}P X-ray	129, 128
Ni Triad MM' Non-Interacting [10j]								
4-343* $(Ph_3P)_2Pt(\mu^2\text{-}SiMe_2)$-$(\mu\text{-}H)Mn(CO)_4$	4P [10k] (62)	yellow —	Y	Y	-8.56 (dd) $^1J_{PtH} = 494$	—	^{31}P IR	299
4-344 $(Ph_3P)_2Pt(\mu^2\text{-}SiPh_2)$-$(\mu^2\text{–}H)Mn(CO)_4$	4P [10k] (66)	yellow —	Y [1c]	Y	- 9.10 (dd) $^1J_{PtH} = 490$	—	^{31}P IR	299
4-345 $(Ph_3P)_2Pt(\mu^2\text{-}SiCl_2)$-$(\mu^2\text{–}H)Mn(CO)_4$	4P [10k] (60)	yellow —	Y	Y	- 9.57 (dd) $^1J_{PtH} = 460$	—	^{31}P IR	299
4-346 $[(Ph_3P)_2(Cl)Pt$-$(SiHCl)]_2O$	4P [10l] (40-60)	white >340	Y	—		—	IR, MS	300
Cu TRIAD								
4-347 $(Ph_3P)_3CuSiPh_3$	4Y (82)	ivory 204 (d)	Y [1c]	S		—	^1H, ^{31}P	301
4-348 $(Ph_3P)_3CuSiPh_2Cl$	4Y (49)	brt. yellow 150 (d)	Y	S		—	^1H, ^{31}P	301
Zn Triad								
4-349 $Hg(SiEt_3)_2$ [10m]	4Z (—)	—	—	—		—	—	302

Table 4 (Continued)

* Structural formulas for compound numbers marked with an asterisk may be found at the end of the table. † Abbreviations: Me, methyl; Et, ethyl; Pr, propyl; *i*-Pr, isopropyl; Bu, butyl; *t*-Bu, *tert*-butyl; Cy, cyclohexyl; Hex, hexyl; Ph, phenyl; *p*-Tol, p-tolyl; Bz, benzyl; py, pyridinyl; Cp, C_5H_5; Cp*, C_5Me_5; Cp′, C_5H_4Me; Fp, $CpFe(CO)_2$; dppe, $Ph_2PCH_2CH_2PPh_2$; tdppme, $MeC(CH_2PMe_2)_3$; chiraphos, (2*S*,3*S*)-bis(diphenylphosphino)butane; dcpe, $Cy_2PCH_2CH_2PCy_2$; dmpe, $Me_2PCH_2CH_2Me_2$; dtbpm, $(t\text{-}Bu)_2PCH_2P(t\text{-}Bu)_2$; ampy, 2-amino-6-methylpyridinyl; Fc, Ferrocenyl; Fp, $Cp(CO)_2Fe-$; dppf, 1,1′-bis(diphenylphosphino)ferrocene; diop, (4*S*,5*S*)-4,5-bis(diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane; dppb, (4*S*,5*S*)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane; dmesiqn, 8-(dimethylsilyl)quinoline; OEP, octaethylporphyrinato; DAD, PhN═C(Me)C(Me)═NPh; disil, 1,2-bis(dimethylsilylbenzene); TFB, tetrafluorobenzobarrelene; nbd, norbornadiene; phen, 1,10-phenanthroline; cod, cylcooctadiene; coe, cyclooctene; acac, acetylacetonate; triso, tris(diphenyloxophosphoranyl)methanide; OTf, triflate; D_4^x, $[MeSi(X)O]_4$; E.C., equivalent conductance; lt., light; dk., dark; symm., symmetrical; unsymm., unsymmetrical; Mossb., Mossbauer spectroscopy; N.D., neutron diffraction; liq., liquid.

Footnotes: [1a] Key for Metal Complexes reacted with hydrosilanes: A, $Cp_2Ti(CO)_2$; B, Cp_2MCl_2/*n*-BuLi + PMe_3; C, Cp_2M; D, $Cp_2M(H)_3$ or $Cp'_2M(H)_3$; E, $Cp_2(H)ML$ (L = olefin); F, $Cp_2(R)ML$ ($h\nu$ or Δ) (L = olefin); G, $Cp_2(H)ML$ (L = CO); H, $(ArH)Cr(CO)_3$; I, $M(CO)_4(dppe)$ or $M(CO)_4(tdppme)$; J, $Cp_2M(H)_2$; K, $Cp(LL')M(CO)$; L, $CpM(CO)_3$ or $Cp'M(CO)_3$; M, $M_x(CO)_y$ (heat or $h\nu$); N, $Re(H)_7L_2$; O, $[CpFe(CO)_2]_2 + \Delta$; P, $CpRFe(CO)_2$; Q, $Cp(OC)_2FeSnPh_3$; R, $Fe_{(vapor)} + 2ArH$; S, $M(CO)_{5-x}L_x$; S′, $[(OC)_4Fe]_2dppe$; T, $(OC)_2(H)Fe[C_6H_4OP(O\text{-}Ph)_2\text{-}o]$; U, Cp^*L_2MR or CpL_2MR; V, $Cp^*(L)Ru(OCH_2CF_3)$; W, $Cl(R)M(CO)L_2$; X, $(Ph_3P)_3RuCl_2$, $(Ph_3P)_3(H)RuCl$, or $(Ph_3P)_4Ru(H)_2$; Y, $[(OC)_{10}Os_3(NCMe)_2]$ or $[(OC)_{11}Os_3(NCCH_3)]$; Z, $Co_2(CO)_8$; 2A, $(OC)_3(R_3P)Co(OCCH_3)$; 2B, $\{(OC)_3Co(PMe_2Ph)\}_2$; 2C, $(OC)_3CoH(PPh_3)$; 2D, $(OC)_4CoSiR_3 + h\nu$ (R = Et, Me, Ph) (low temp); 2E, $(\eta^3\text{-}C_3H_5)Co(CO)_2PPh_3 + PR_3$; 2F, $CoH(CO)_2(PPh_3)_2$; 2G, $CoH(CO)(PPh_3)_3$; 2H, $CpRh(C_2H_4)_2 + h\nu$; 2I, $Cp^*Rh(CO)_2$ + heat or $h\nu$; 2J, $CpHRh(SiMe_3)_3$ + heat; 2K, $Cp^*Rh(C_2H_4)_2 + h\nu$; 2L, $[(Cp^*Rh)_2Cl_4]$ + heat; 2M, $Cp^*(H)_2Rh(SiEt_3)_2 + h\nu$; 2N, $RhMe(PMe_3)_x$; 2O, $(C_6F_5)M(PMe_3)_3$ (M = Rh or Ir); 2P, $Rh(SAr)(PMe_3)_3$ (Ar = Ph or *p*-tolyl); 2Q, $(i\text{-}Pr_3P)_2RhCl$; 2R, $(Ph_3P)_3RhCl$; 2S, $[Rh(cod)Cl]_2$; 2T, $(dtbpm)Rh(\eta^3\text{-}CH_2C_6H_5) + Me_3P$; 2U, $[(OEP)Rh]_2$; 2V, $(OC)(PPh_3)_3RhH$ + heat; 2W, (DAD)(OC)RhCl; 2X, $[(\mu\text{-}OSiMe_3)Rh(nbd)]_2$; 2Y, $Cp^*(PMe_3)IrMeCl$ (−78 °C); 2Z, $Cp^*(PMe_3)IrMe(OTf)$; 3A, $Cp'Ir(PMe_3)Ar(F)$ (Ar = Ph; Cp′ = C_5Me_5 or C_5Me_4Et); 3B, $Cp^*Ir(C_2H_4)_2 + h\nu$; 3C, $[(Cp^*Ir)_2Cl_4]$; 3D, $Cp^*(H)_2ClIr(SiEt_3)$ + heat + Et_3N; 3E, $(OC)_2(PCy_3)Ir(OCOCH_3)$; 3F, *trans*-$Ir(CO)Cl(PPh_3)_2$; 3G, $ClIr(CO)(PMePh_2)_2$; 3H, $IrH(CO)(PPh_3)_3$; 3I, *trans*-$(OC)[(p\text{-}Tol)_3P]_2Ir(OMe)$; 3J, (OC)dppeIrCN; 3K, (OC)dppeIrBr; 3L, (chiraphos)Ir(CO)Br; 3M, $IrH_3(CO)(dppe)$; 3N, $MeIr(CO)[(p\text{-}Tol)_3P]_2$; 3O, $(Me_3P)_4IrMe$; 3P, $(Me_3P)_4IrH$; 3Q, $(Et_3P)_3IrCl$; 3R, $[(Me_3P)_4IrCO]Cl$; 3S, $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$; 3T, $(Et_3P)_2ClIr(C_2H_4)$; 3U, *trans*-$IrX(N_2)(PPh_3)_2$ (X = Cl, Br); 3V, $(Ph_3P)_2H_5Ir$; 3W, $[Ir(cod)Cl]_2$; 3X, $Ir(OEt)(cod)(PCy_3)$; 3Y, $(Cy_3P)(coe)Ir(acac)$; 3Z, $(Ph_3P)(TFB)Ir(OCOCH_3)$; 4A, $[Ir(OMe)(cod)]_2$ + L (L = PPh_3 or $AsPh_3$); 4B, $(triso)Ir(C_2H_4)_2$; 4C, $(\eta^6\text{-}indenyl)Rh(C_2H_4)_2 + h\nu$; 4D, $[(cod)Ir(OMe)]_2$ + benzoyl peroxide; 4E, $(OC)_2Ir(CH_2)_2TaCp_2$; 4F, bis(methylallyl)nickel + arene; 4G, $(Ph_2MeP)_2PdMe_2$; 4H, $(Ph_2MeP)_2PdCl_2$ + KH; 4I, $[(dcpe)Pd]_2(\mu\text{-}H)_2$; 4J, $(phen)Pd(CH_3)_2 + [H(OEt_2)_2]^+ [BAr'_4]^- + PPh_3$ [Ar′ = 3,5-$(CF_3)_2C_6H_3$]; 4K, $[(phen)Pd(CH_3)(OEt_2)]^+[BAr'_4]^- + C_2H_4$ [Ar′ = 3,5-$(CF_3)_2C_6H_3$]; 4L, $(Me_3P)_2PtH_2$; 4M, $(PEt_3)_2Pt(C_2F_4)$; 4N, $Pt(PEt_3)_4$; 4O, $Pt(PCy_3)_2$; 4P, $Pt(C_2H_4)(PPh_3)_2$; 4Q, $Pt(PEt_3)_3$; 4R, (dmpe)PtMe(OTf); 4S, $(dcpe)PtCl_2 + NaC_{10}H_8$; 4T, $(dcpe)PtCl_2$ + Li (2% Na); 4U, $(dppe)Pt(SiMe_3)_2$; 4V, $(dppe)Pt(C_2H_4)$ + heat; 4W, $(cod)PtCl_2 + Et_3N$; 4X, $Pt(cod)_2$; 4Y, $[Ph_3PCuH]_6$; 4Z, Et_2Hg + heat + $h\nu$. [1b] Solvent key: R, solvent not specified; Q, CCl_4; S, C_6D_6; S′, C_6H_6; T, C_7D_8; U, THF-d_8; V, $C_2D_2Cl_4$; W, $(CD_3)_2CO$; X, $CDCl_3$; Y, CD_2Cl_2; Y′, CH_2Cl_2; Z, CD_3CN. ZZ, too insoluble to obtain data. Data for ambient temperature in °C unless specified otherwise. [1c] In ppm. Coupling constants in Hz. Assignments: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sept, septet. [1d] 90% purity. Unstable in solution. [1e] Analysis is not within calculated %C ±0.5%. [1f] $\Delta\nu_{1/2} = 45$ Hz. [1g] Mixed with $Cp_2Nb(H)_3$. [1h] Other derivatives prepared from reaction of $HSiMePh_2$ and $HSiPh_3$. [1i] Additional derivative: $Cp_2(H)Nb(SiMe_2Ph)_2$. [1j] Data in supplementary material in these references. [1k] $\Delta\nu_{1/2} = 35$ Hz. [1l] Symmetrical isomer (2 pts). Yield given is for mixture of isomers. [1m] Unsymmetrical isomer (1 pt). [1n] Yield given is for mixture of isomers. [1o] Photolysis. [1p] Other derivatives prepared similarly: $(ArH)(OC)_2Cr(SiCl_3)_2$, ArH = *p*-$C_6H_4F_2$, $C_6H_5CF_3$, *m*-$C_6H_4(CF_3)_2$. [1q] Yield is solvent dependent. [1r] Other derivatives of $(ArH)(OC)_2(H)Cr(SiCl_3)$: ArH = *p*-$F_2C_6H_4$, $C_6H_5CF_3$, and *m*-$C_6H_4(CF_3)_2$. [1s] Cocrystallite: $(C_6H_5F)(OC)_2Cr(SiCl_3)_2$. [1t] Mixture with $[\eta^6\text{-}C_6H_3Me_3](OC)_2Cr(SiCl_3)_2$ (yellow). [1u] Other derivatives prepared from $HSiMe_3$ and $HSi(t\text{-}Bu)_2Cl$. [1v] $(\eta\text{-}C_7H_7)Mo(CO)_2Cl + HSiCl_3 + Et_3N$. [1w] Other derivatives prepared from $HSiMe_3$. [1x] Too insoluble to obtain data. [1y] From reaction of $Cp_2W(CH_2{=}SiMe_2)$ + hydrosilane. Other derivatives prepared from $HSiMe_2Cl$, $HSi(i\text{-}Pr)_2Cl$, and $H_2Si(t\text{-}Bu)_2$. [1z] $Cp(OC)_2WMe + HSiMe_2SiMe_2X$ (X = OMe, NEt_2). [2a] Additional derivatives: $(OC)_3(dppe)(H)WSiCl_2R$, R = Cl, *p*-Tol. [2b] Mixed with 20% $(OC)_4(dppe)W$. [2c] Mixed with 10% $(OC)_3(tdppme)W$. [2d] $Li[C_5H_4Mn(CO)_3] + Me_2SiHCl$. [2e] Additional derivative: $Cp(Me_2PCH_2CH_2CH_2PMe_2)(H)MnSiPh_3$ and also Table 3. Most $CpLL'Mn(HSiR_3)$ [L = L′ = CO; L = CO, L′ = PR'_3 (for example ref 303)] exhibit nonclassical HSi interactions and will be found in Table 7. [2f] Deuterium analogue also reported.[144] [2g] Additional derivatives: $Cp(OC)_2(H)ReSiMePhSiHMePh$, $Cp(OC)_2(H)ReSiPh_2SiMe_3$, and $Cp(OC)_2(H)ReSiMe_2SiHMe_2$ (2 isomers). [2h] Si−H resonance appears in ^1H spectrum at 5.65 ppm ($^1J_{SiH} = 182.4$ Hz). [2i] The trans isomer of $(Cp)(OC)_2(H)ReSiPh_3$ was formed from $[Et_4N][(\eta\text{-}C_5H_5)(OC)_2ReSiPh_3] + H_3PO_4$.[93] [2j] Isolated as a mixture of $(OC)L_3(H)_2ReSiPh_3$ and THF solvate. Heating under vacuum removes the THF. [2k] Prepared from reaction of $Re(H)_3(CO)(PMe_2Ph)_2$ and Ph_3SiH. [2l] Additional derivative: $(Ph_3P)_2(H)_6ReSiHEt_2$. [2m] [(+)-diop] analogue also reported. [2n] $CD_2Cl_2/CFCl_3$ (3:2 v/v). [2o] Prepared from $Re_2(CO)_8[\mu\text{-}C(H)C(Bu)](\mu\text{-}H) + HSi(OMe)_3$. [2p] Initial product believed to be $(OC)_4(H)FeSi(NMe_2)_3$ followed by migration of H from Fe to N. [2q] From $[Fe(CO)_4\{P(OEt)_3\}]$ and $HSi(NMe_2)_3$. [2r] From $[Fe(CO)_4\{P(OMe)_3\}] + HSi(NMe_2)_3$ or $[Fe(CO)_4\{P(NMe_2)_3\}] + HSi(OMe)_3$. [2r−1] Originally reported as 34.45 ppm in C_6H_6 relative to $Me_3SiOSiMe_3$.[148b] [2s] Yields are described as excellent.[148a] [2t] Other derivatives: $SiR_3 = SiMePh_2$, $SiHPh_2$. [2u] Other products: $Cp(OC)_2FeSiCl_3$ (11%) and $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$ (53%); also reported the Cp′ analogue. [2v] Other derivatives: $(\eta^6\text{-}ArH)(H)_2Fe(SiCl_3)_2$, ArH = C_6H_6, *p*-$(CH_3)_2C_6H_4$. [2w] Hexane/C_6D_6 = 4:1. [2x] May be a rapid equilibrium between cis and trans isomers. [2y] Cis/trans in solution = 4:1. [2z] Unit cell parameters only. Trans form. [3a] Compound is fluxional at 298 K. [3b] Additional derivatives: $(OC)_3(Ph_3P)(H)FeSi(OEt)_3$ and $(OC)_3(Ph_3P)(H)FeSiMeCl_2$.[166] **4−92a** has also been prepared from $(OC)_4(H)FeSiPh_3 + PPh_3$ [similar reactions were also reported with $(PhO)_3P$ and $(MeO)_3P$].[168] $(OC)_3(Me_3P)(H)FeSiPh_3$ was prepared from $(OC)_4Fe(PMe_3)$ and $HSiPh_3$.[168] [3c] Additional derivatives: *mer*-$(OC)_3(Ph_3P)(H)FeSiR_3$, $SiR_3 = SiMePhSiHMePh$, $SiPh_2SiMe_3$. [3d] Reaction of $(OC)_3(Ph_3P)(H)FeSiMe_3$ and $HSiRR'SiHRR'$. [3e] Si−H resonance appears in ^1H NMR at 6.02 ppm (s). [3f] Additional derivatives: $(OC)_3(R'_3P)(H)FeSiR_3$, R′ = Ph, $SiR_3 = SiMePh_2$, $SiMe_2Cl$, $SiMeCl_2$; $R'_3P = Ph_2MeP$, $SiR_3 = SiMeCl_2$, $SiCl_3$; $R'_3P = PhMe_2P$, $SiR_3 = SiMe_{3-x}Cl_x$ (x = 1, 2, 3); $R'_3P = Me_3P$, $SiR_3 = SiMeCl_2$, $SiCl_3$; $R'_3P = (Bu)_3P$; $PhMe_2P$, $SiR_3 = SiCl_3$. [3g] Additional derivatives: $(OC)_3LFe(SiCl_3)_2$, L = Ph_3P, Ph_2MeP, $PhMe_2P$, Me_3P, $(Bu)_3P$; $(OC)_3LFe(SiMeCl_2)_2$, L = Ph_2MeP, $PhMe_2P$, PMe_3; $(OC)_3Ph_3PFe(SiMe_2Cl)_2$.[169] [3h] Additional derivatives with $SiMe_2Cl$ and $SiMeCl_2$. [3i] Additional derivatives from $HSi(OEt)_3$ and $HSiPh_3$ are described, but more complex product mixtures were obtained. [3j] Trans CO groups. [3k] Other derivatives include: $(OC)_2[(PhO)_3P]_2(H)FeSiR_3$, R = OEt, Ph. [3l] Other derivatives include: $(OC)_2(dppe)(H)FeSiR_3$, $SiR_3 = SiCl_3$, $SiMeCl_2$, $SiMe_2H$, $SiMe_2Ph$. [3m] Other derivative: $SiCl_3$. [3n] Additional derivatives: $(OC)(dppe)(H)_3FeSiR_3$; $SiR_3 = SiMe_3$, $SiMe_2Ph$, $SiPh_3$, $Si(OMe)_3$. [3o] $(OC)_2(dppe)(H)Fe(SiR_3) + HSiR_3$. [3p] Additional derivatives: $(Ph_2EtP)_3(H)_3FeSiR_3$; $SiR_3 = SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, $SiMe_2OSiMe_2H$. Same series with the phosphine, $PBuPh_2$. [3q] $(R'Ph_2P)_3FeH_2(H_2) + HSiR_3$. [3r] AA′A″XX′X″. [3s] Other derivatives from arene = C_6Me_6 and C_6H_6. Prepared from $[(\eta^6\text{-}arene)RuCl_2]_2$. [3t] $Cp_2Ru_2(CO)_3(\mu\text{-}CH_2) + HSiMe_3$ at 170 °C. [3u] Other derivatives include: $Cp(Me_3P)_2RuSiR_3$, $SiR_3 = SiEt_3$, $SiMe_2Cl$, $SiMeCl_2$; $Cp(Ph_3P)_2RuSiCl_3$. [3v] Additional **4−111b** was obtained but contaminated with **4−112a**. [3w] Additional derivative: $Cp^*(Me_3P)_2RuSiEt_3$; sterically hindered hydrosilanes do not react and $HSiCl_3$ gives a mixture of $Cp^*L_2RuSiCl_3$ and $Cp^*L_2RuSiHCl_2$. [3x] Reaction of $Cp^*(Me_3P)(H)Ru(SiPh_2Cl)_2 + PMe_3$. [3y] Reaction of $Cp^*(L)_2RuSH + HSi(OEt)_3$. [3z] $Cp^*(Me_3P)_2RuCH_2SiMe_3 + HSi[S(p\text{-}Tol)_3]_3$. Analogous derivatives prepared from

Table 4 (Continued)

$HSi[O(p\text{-Tol})]_3$ and $HSiMe_2[S(p\text{-Tol})]$. [4a] Mixed with $CpL_2RuSiCl_3$ (31%). Yield of each of the two products depends on the ratio of $HSiCl_3$ to CpL_2RuMe. [4b] Other derivatives with $SiMe_2OEt$, $Si(OEt)_3$. [4c] Reaction required two silanes: $ArSiH_3$ and $HSiMe_3$. [4d] Additional derivative: $Cp^*[Ph(i\text{-Pr})_2P](H)_2RuSiHPh_2$. [4e] Other derivative: $(OC)_4(H)RuSiMeCl_2$. [4f] Other $(OC)_3LRu(SiCl_3)_2$: L = ETPB = $P(OCH_2)_3CC_2H_5$, PF_3, $P(OEt)_3$, $P(OPh)_3$, PMe_2Ph, $PMePh_2$, $P(o\text{-Tol})_3$, PBu_3, PCy_3, $AsPh_3$, $SbPh_3$, $CNCMe_3$. [4g] Reaction of *cis*-$(OC)_4Ru(SiCl_3)_2$ with L. [4h] Compound has mer geometry. Additional derivative: $(OC)_2(H)Ru[SiMe(CH_2CH_2PPh_2)_2]$. See also entries **4−280b**, **4−296a**, and **4−341b** for related derivatives. [4i] Additional derivatives: $(OC)(Ph_3P)_2(Cl)Ru(SiR_3)$, $SiR_3 = SiMe_2Cl$, $SiCl_3$; osmium analogues also reported; $(OC)(Ph_3P)_2(Cl)Os(SiR_3)$, $SiR_3 = SiMe_3$, $SiCl_3$. [4j] $(OC)[(t\text{-Bu})_2MeP]_2Ru(H)_2 + HSiMe_3$. [4k] Additional derivative: $(Ph_3As)_3(H)_3RuSiMeCl_2$. [4l] Derivatives where L = $P(p\text{-Tol})_3$, $AsPh_3$ also prepared. [4m] From reaction of $RuH(CH_2{=}CH_2)[(\eta^3\text{-}C_6H_8)P(C_6H_{11})_2]PCy_3$. [4n] Other derivatives reported: $Cp^*(Me_3P)_2OsSiR_3$ ($SiR_3 = SiMeCl_2$, $SiCl_3$); $Cp(Ph_3P)_2OsSiR_3$ ($SiR_3 = SiPh_2Cl$); $Cp(Me_3P)_2OsSiR_3$ ($SiR_3 = SiPh_2Cl$, $SiMeCl_2$). [4o] Reaction of $Cp'(L)_2OsCH_2SiMe_3$ ($Cp' = C_5H_5$, C_5Me_5; L = PMe_3, PPh_3) with silane. [4p] Other derivatives reported: $Cp'(Me_3P)(H)Os(SiPh_2Cl)_2$ (Cp′ = Cp, Cp*). [4q] Additional derivative: $Cp^*(Me_3P)(H)Os[C_6H_3(3\text{-Me})(6\text{-S})Si[S(p\text{-Tol})]_2$. [4r] Additional derivative: $(OC)_4(H)OsSiMeCl_2$. [4s] Additional derivative: $SiEt_3$. [4t] Isolated as CH_2Cl_2 solvate. Additional derivative prepared from $HSiMe_3$. [4u] Less soluble diastereomer. [4v] From $OsH(\eta^2\text{-}H_2BH_2)(CO)L_2$ [L = $P(i\text{-Pr})_3$] + $HSiPh_3$ in MeOH. [4w] In Tol-d_8: −9.92 (AB portion of ABXY spin system), −9.39 (t). [4x] $OsHCl(CO)L_2 + HSiR_3$. [4y] Also prepared from $OsPhCl(CO)(PPh_3)_2 + HSiCl_3$. [4z] Formed from reaction of $Cp^*Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$ with $HMe_2SiSiMe_2H$. Disproportionation of the disilane occurs. For related derivatives see Table 3. [5a] From reaction of $Fe_2(CO)_9$ with Me_2SiHCl in the presence of R_3N. [5b] Additional derivatives: $Cp(OC)(\mu\text{-}CH_2)Ru_2(SiR_3)_2$; R = Me, Et, Pr, Ph, OMe. [5c] $Cp_2Ru_2(\mu\text{-}CH_2)(CO)_2(NCMe)$ + 2.5 equiv of $HSiR_3$. When the reaction is run with 1.2 equiv of silane, $Cp_2Ru_2(\mu\text{-}CH_2)(H)(SiR_3)(CO)_2$ formed quantitatively but isolation of pure compounds was not achieved due to thermal lability. These compounds were, however, spectroscopically characterized. [5d] Additional derivative: $Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiPh_2)(H)(SiPh_3)(CO)$. [5e] Prepared from $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ and $HSiMe_2Ph$ or $HSiPh_3$. The reaction of $Cp_2Ru_2(\mu\text{-}CH_2)_2(CO)(MeCN)$ and $HSiMe_3$ gave a similar product which was to unstable to be isolated. [5f] Structure was confirmed by X-ray crystallography but the quality of the data obtained was not considered satisfactory. See footnote 12 of ref 107. [5g] Reaction of $Cp_2Ru_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)(MeCN)$ and $HSiMe_2Ph$. Additional derivative from $HSiPh_3$. [5h] Additional derivative: $SiEt_3$, $SiPr_3$. [5i] Additional derivative: $SiMe_2Cl$. [5j] From reaction of $[Ru_3(\mu\text{-}C_4H_4N_2)(\mu\text{-}CO)_3(CO)_7]$ and $HSiEt_3$. Other derivatives prepared from $HSiPh_3$ and $HSi(OMe)_3$. [5k] From $Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(PPh_3)_n(CO)_{8-n}$. [5l] Prepared from $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9] + HSi(OMe)_3$. [5m] Prepared from $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9] + PhC{\equiv}CPh$ followed by $HSi(OMe)_3$. Provides **4−194**/**4−195**/**4−196** = 1:12:3 (NMR) which were separated by column chromatography. The reaction of $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9]$ with $PhC{\equiv}CPh$, followed by $HSiEt_3$ gives similar products. When $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9]$ was reacted with $HSi(OMe)_3$ followed by $PhC{\equiv}CPh$, the products included **4−186** as well as an isomer of **4−186**. [5n] From $Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(PPh_3)_n(CO)_{8-n}$. [5o] Prepared from $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9]$ and PPh_3 followed by $HSiEt_3$. [5p] From $Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(PPh_3)_n(CO)_{7-n}$. [5q] Isomorphous to $[Ru_2(\mu\text{-}Ph_2PCH_2SiMe_2)_2(CO)_6]$. [5r] From $[Os_3(CO)_{11}(NCCH_3)]$. Additional derivatives prepared from $ArCH_2SiMeH_2$ and $ArCH_2SiH_3$ (Ar = $o\text{-}BrC_6H_4CH_2$). [5s] Prepared from reaction of $Os_3(CO)_{11}NCMe + HSi(OR)_3$ (R = Et, Me). [5t] Reaction of $[\{Os_3(CO)_{10}(MeCN)\}_2(\mu\text{-dppe})] + HSi(OMe)_3$. Additional derivative prepared from reaction with $HSi(OEt)_3$. [5u] Additional derivative: $[Os_3(\mu\text{-}H)(CO)_{10}(o\text{-}Ph_2PC_6H_4CH_2SiMeH)]$ (X-ray). [5v] Additional derivative: $[(OC)_{10}(\mu\text{-}H)Os_3(o\text{-}HMeSiC_6H_4CH_2PPh_2)]$. [5w] From reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. [5x] Additional derivative: $Os_3(CO)_{10}(NCMe)[Si(OMe)_3](\mu\text{-}H)$. [5y] Hydride resonances at δ −8.58, −12.29, −12.42. [5z] Minor product from reaction of $o\text{-}HMe_2SiC_6H_4CH_2PPh_2$ with $[Os_3H_2(CO)_{10}]$. $[Os_3(\mu\text{-}H)_3(CO)_8(o\text{-}HMeSiC_6H_4CH_2PPh_2)]$ prepared in a similar manner. [6a] Additional derivatives: $(OC)_4Co[Si(R)(CH_2)_4CH_2]$, R = Ph and Cl. [6b] Reaction performed with the octahydrosilasesquioxane, $H_8Si_8O_{12}$ at 50 °C with added CO for 15 h. [6c] The Si−H resonances appear in the ^{1}H NMR spectrum at 4.26 (s, 4H) and 4.27 (s, 3H). [6d] [S] = inorganic oxide surfaces, either SiO_2 or Al_2O_3. Solids treated with $HSiR_3$ to generate [S]SiH [$SiR_3 = SiMe_2Cl$, $SiCl_3$, or $Si(OEt)_3$]. [6e] Additional derivatives: $(OC)_3(Ph_3P)CoSiMe_2Ph$, $(OC)_3(Ph_3P)CoSiEt_3$. [6f] Additional derivatives: $(OC)_3LCoSiR_3$, L = Ph_3P, R = F, from $(OC)_3(Ph_3P)CoH$. Other derivatives prepared from reaction of $[(CO)_3CoL]_2$ with $HSiF_3$ (L = PMe_2Ph, PBu_3, PEt_3, $AsMe_2Ph$) and with $HSi(OEt)_3$ and L = PMe_2Ph. [6g] Reaction probably proceeds via $(OC)_2Ph_3P(H)_2CoSiPh_3$. [6h] Complex **4−219** and similar derivatives prepared from reaction of $(OC)_4CoSiPh_3$ with L (L = PPh_3, $PMePh_2$, $AsPh_3$, and $SbPh_3$). [6i] Compound observed at low temperature only as intermediate in the photolysis of $(OC)_4CoSiR_3$ at 77 K in alkane matrix or at 196 K in solution. Additional derivatives reported at low temperature: $(OC)_3(H)Co(SiR_3)(SiR'_3)$, R = Et, R′ = Ph; R = Et, R′ = Me. [6j] Perdeuteriomethylcyclohexane. [6k] Additional derivatives: $(OC)_2(R_3P)_2CoSiMePh_2$; $R_3P = Ph_2MeP$ $(EtO)_3P$, $(PhO)_3P$ and $(OC)_2(Ph_3P)_2CoSiMe_2Ph$. [6l] Additional derivatives: $(OC)_2L_2CoSiPh_3$, $L_2 = (Ph_2MeP)_2$ or dppe, prepared from reaction of $(OC)_4CoSiPh_3$with L_2. [6m] Additional derivatives: $Cp(\eta^2\text{-}C_2H_4)(H)RhSiMe_3$, $Cp(H)_2Rh(SiMe_3)_2$ [see also ref 226 for alternative preparation from $Cp(\eta^2\text{-}C_2H_4)(H)RhSiMe_3 + h\nu$ or $Cp(H)Rh(SiR_3)_3 + HSiR'_3 + h\nu$], and $Cp(\eta^2\text{-}C_2H_4)(D)RhSiEt_3$. [6n] Reaction done at 213 K and product contaminated with ∼10% of $CpRh(\eta^2\text{-}C_2H_4)_2$. [6o] Isolated as mixture of products, **4−225** (98.5%), $Cp(H)_2Rh[Si(i\text{-Pr})_3]_2$ (1%), and $CpRh(\eta^2\text{-}C_2H_4)_2$ (0.5%) by ^{1}H NMR. [6p] Other derivatives were obtained with SiR_3 = Me, Ph, OEt. Complex mixtures were obtained but a more pure sample was found with R = Et. Complexes are thermally labile. [6q] Reference 228 discusses prep of $Cp(OC)(H)RhSiEt_3$ and Cp* derivative (former compound previously reported in the literature) by reaction of $CpRh(CO)_2$ (or Cp* derivative) with Et_3SiH. The data listed for $Cp^*(OC)(H)RhSiEt_3$ gives the ^{1}H NMR resonance for the Ir−H at δ 14.1 (d, $^1J_{RhH}$ = 37.4 Hz) and is probably an error and should be negative. [6r] Reaction requires a temperature of 373 K. When R = Et the reaction was done at 298 K and product could also be prepared by reaction of $CpRh(\eta^2\text{-}C_2H_4)_2 + Et_3SiH$ at 383 K. [6s] Compound also prepared by reaction of $CpRh(\eta^2\text{-}C_2H_4)_2$ with Et_3SiH at 383 K. [6t] Additional derivatives prepared: $Cp^*(\eta^2\text{-}C_2H_4)(H)RhSiR_3$; R = Ph, Me. [6u] Additional derivatives: $Cp^*(H)_2Rh(SiMe_2Ph)_2$. [6v] Also prepared with $Cp^*Rh(\eta^2\text{-}C_2H_4)_2 + h\nu$ (80%). [6w] The reaction is accelerated with added Et_3N but with lower yield (50%). Higher yield (94%) obtained by reaction of $[(Cp^*Ir)_2Cl_4] + HSiEt_3$ in toluene for 5 h at 60 °C then 3 days at 20 °C. [6x] After longer irradiation times or by using large amounts of $HSi(OEt)_3$, small amounts of $Cp^*(H)_2Rh[Si(OEt)_3]_2$ were also observed. [6y] Also isolated by reaction of $Cp^*(H)_2Rh(SiEt_3)_2$ with EtOH and $h\nu$. $Cp^*(H)_2Rh(SiEt_3)[Si(OMe)_3]$ also prepared by analogous reaction with MeOH and $h\nu$. [6z] Also prepared from $[(Cp^*Rh)_2Cl_4] + Et_3N + HSi(OEt)_3$ at room temperature in 50% yield. [7a] Reaction with $(C_6F_5)Rh(PMe_3)_3$ requires heating at 90 °C. [7b] Additional derivatives: *mer*-$(Me_3P)_3(ArS)(H)RhSiX_3$; Ar = $p\text{-}MeC_6H_4$, X = OMe; Ar = $p\text{-}MeOC_6H_4$, X = OMe; Ar = Ph, X = Cl; Ar = $p\text{-}MeC_6H_4$, X = Cl. See also (**3−62f**) for a similar derivative. [7c] Reaction done using 5:1 ratio of $HSiPh_3$ and $(Me_3P)_3Rh(SAr)$ and isolated as benzene solvate. When the reaction is run at room temperature using equimolar amounts, **4−239b** and **4−239c** are not formed. Dissolution in benzene or THF at room temperature causes reductive elimination of $HSiPh_3$. [7d] Silane exchange reaction with $HSi(OEt)_3$ gives the known compound, *mer*-$(Me_3P)_3(C_6F_5)(H)RhSi(OEt)_3$ (**4−240**). [7e] Characterized in solution only. [7f] Additional derivatives: $(i\text{-}Pr_3P)_2(Cl)(H)RhSiAr_3$, Ar = p-Tol, $p\text{-}MeOC_6H_4$, $p\text{-}ClC_6H_4$, $p\text{-}FC_6H_4$, $p\text{-}F_3CC_6H_4$. [7g] SiH resonance in ^{1}H NMR spectrum appears at 4.44 (br s). [7h] Characterized in solution only and complexes are fluxional. [7i] SiH resonance in ^{1}H NMR spectrum appears at 4.32 (br s). [7j] Additional derivatives prepared but no data given: $Rh(tripsi)(PPh_3)$, Rh(tripsi)(CO) (X-ray done). [7k] Also prepared from $HSi(CH_2CH_2PPh_2)_3$ (H-tripsi) and $(Ph_3P)_2Rh(CO)Cl$. [7l] Compound prepared at −10 °C and is unstable above room temperature. Also prepared with $(dtbpm)(Me_3P)RhMe$. [7m] Reaction requires an excess of $HSiEt_3$. Also prepared by reaction of $(Me_3SiO)Rh(nbd)(PPh_3)$ with Et_3SiH. [7n] Additional derivatives: $Cp^*(Me_3P)Ir(\eta^2\text{-}SiMe_2CH_2)$ and $Cp^*(Me_3P)Rh(\eta^2\text{-}SiPh_2CH_2)$ but they were not isolated in pure form. [7o] Product formed by reaction of $HSiPh_2CH_2MgCl$ with $Cp^*(Me_3P)IrMeCl$. Deuterated analogue prepared with $ClMgCD_2SiPh_2D$ and showed only elimination of CDH_3. [7p] Additional derivatives: $Cp^*(Me_3P)(Ph)Ir(SiPh_2OTf)$, $Cp^*(Me_3P)(Ph)Ir(SiMe_2OTf)$, $Cp^*(Me_3P)(H)Ir(SiPh_2OTf)$ (**3−63**). Reaction believed to occur by initial Si−H oxidative addition followed by rearrangement to

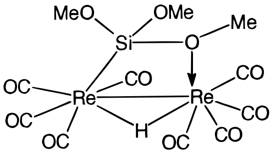
Table 4 (Continued)

give the final product. [7q] Additional derivatives: $Cp'(Me_3P)RIr(SiMe_2F)$; $Cp' = \eta^5$-C_5Me_5, R = Ph; $Cp' = \eta^5$-C_5Me_5, R = Me; and $Cp' = \eta^5$-C_5Me_4Et, R = Me. [7r] Other complexes, $Cp^*(\eta^2$-$C_2H_4)(H)IrSiR_3$, R = Et, Me, OEt, generated as part of a mixture. [7s] Additional derivative: $Cp^*(H)_2ClIrSiPh_3$ also prepared but not very stable in solution, decomposes in CH_2Cl_2. [7t] Triethylsilyl derivative can also be prepared by reaction of $[(Cp^*Ir)_2(\mu$-$H)_2Cl_2]$ with $HSiEt_3$ in refluxing C_6H_6 and Et_3N. [7u] Also prepared by reaction of $[(Cp^*Ir)_2Cl_4]$ + Et_3N and heat.[232,251] [7v] Additional derivatives (in solution only, using 1.5 equiv of $HSiR_3$): $(OC)_3(Cy_3P)IrSiEt_3$, $(OC)_2(Cy_3P)(H)_2IrSiEt_3$, and $(OC)_2(Cy_3P)(OCOCH_3)(H)IrSiEt_3$. [7w] Also prepared by reaction of **4−263** with H_2 (79%). [7x] Additional derivative: $(OC)(Ph_3P)_2(H)Ir[SiMeR'OSiMeR']$ ($R' = CH_2Ph$). When $R = CH_2Ph$ a mixture of two isomers was obtained and when $R' = Ph$ a mixture of three isomers was observed. Ir metallacycles are unstable in solution without added disiloxane. Reactions done at 55 °C in benzene with excess silane. [7y] Three triplets are seen in the Ir−H region of the ^1H NMR spectrum in ratio of 9:10:1, respectively, for the order shown in the table. [7z] Several derivatives prepared with the general formula, $(OC)L_2(X)(H)IrSiR_3$, from reaction of $HSiR_3$ (R = Me, Et, Ph, OEt, Cl, F; $SiR_3 = SiMePh_2$, $SiMeF_2$, $SiMeCl_2$) with $(OC)L_2IrX$ (X = F, Cl, Br, I, SCN; L = PPh_3, $PMePh_2$, and $AsPh_3$). [8a] Information not provided in reference. [8b] Isolated as a 1:1 mixture with PPh_3. [8c] Additional derivatives: $(OC)[(p$-$Tol)_3P]_2(H)_2IrSiR_3$ (R = Ph, OMe). [8d] Compounds also prepared by reaction of silane with *trans*-$(OC)[(p$-$Tol)_3P]_2Ir(OPh)$. [8e] Additional derivatives: $OC(Ph_3P)Cl(H)Ir(SiR_2CH_2CH_2PPh_2)$, $SiR_2 = SiPh_2$ or SiMePh. Deuterium analogues also made from $DSiR_2CH_2CH_2PPh_2$. [8f] The phosphorus atoms are trans to each other and cis to the hydride. The hydride is trans to the CO ligand. [8g] Compound also prepared by reaction of $(OC)(Ph_3P)_2IrCl$ with $HSiMe_2CH_2CH_2PPh_2$ followed by $LiAlH_4$ reduction and was structurally characterized but results unpublished. Deuterium analogues also prepared. [8h] Isomer with H trans to CO is formed initially. After several hours at room temperature a second isomer is observed with Et_3Si trans to CO. Over time these complexes begin to decompose to give $Et_3SiSiEt_3$ and isomers of $(OC)dppe(H)_2Ir(CN)$. [8i] Data given for **4−274** is for the thermodynamic (major) product (H trans to Br). The kinetic product has H trans to CO. An additional isomer is observed over time (with Et_3Si trans to CO). Similar results are obtained in acetone. Additional derivatives gave similar results: $OC(dppe)Br(H)IrSiPh_3$, $OC(dppe)Br(H)IrSi(OEt)_3$, $OC(dppe)Br(H)IrSiMe_2Cl$. Complex **4−275** is the kinetic product and no isomerization was observed. A secondary reaction is observed with **4−274** over extended periods of time (25 days or more) where a new Ir−silyl complex, $OC(dppe)(H)_2IrSiEt_3$, is observed, presumably by reductive elimination of Et_3SiBr from $OC(dppe)Br(H)IrSiEt_3$ followed by reaction with $HSiEt_3$ (13% yield). [8j] This product formed initially but then undergoes isomerization to the more stable diastereomer with H trans to Br (data listed for both isomers). Reaction of OC(chiraphos)IrBr with $HSiMeCl_2$ gave OC(chiraphos)Br(H)$IrSiMeCl_2$ but no spectroscopic data were reported. [8k] Additional derivatives: $OC(dppe)(H)_2IrSiR_3$, R = $SiMe_3$, $SiMe_2Cl$; $OC(dppe)(H)Ir(SiR_3)_2$, $SiR_3 = SiMe_3$, $SiMeCl_2$. Also prepared from secondary reaction of $HSiEt_3$ + $(OC)(dppe)X(H)IrSiEt_3$ (X = Br, CN).[258] [8l] Isolated as a 3:1 mixture of two isomers. See also entries **4−137a**, **4−296a**, and **4−341b** for related derivatives. [8m] Additional derivative: *trans*-$(OC)[(p$-$Tol)_3P]_2(H)Ir[Si(OMe)_3]_2$. [8n] Additional derivatives: $(Me_3P)_3Me(H)IrSi(OEt)_3$ and $(Me_3P)_3Ph(H)$-$IrSiEt_3$. [8o] Additional derivative: $(Me_3P)_2(H)Ir(SiMe_2SiMe_2OMe)[\eta^2$-$SiMe_2(CH_2)_2PPh_2]$. [8p] Reaction performed with 5 equiv of $HPhMeSiSiMe_3$ but with 1 equiv the simple oxidative addition product, *fac*-$(Me_3P)_2(H)Ir(SiMePhSiMe_3)(\eta^2$-$SiMe_2CH_2CH_2PPh_2)$ was observed spectroscopically as mixture of diastereomers. [8q] Additional derivative: *trans*-$(Et_3P)_2Cl(H)IrSiOH(t$-$Bu)_2$. [8r] Reaction performed with $HSiMe_2SiMe_2OMe$ at 45 °C but can also be done using $HMe(MeO)SiSiMe_3$. Room temperature reaction gives $(Me_3P)_2(H)Ir(SiMe_2SiMe_2OMe)[\eta^2$-$SiMe_2(CH_2)_2PPh_2]$ (derivative similar to **4−289b**). [8s] Additional derivatives: $L_2X(H)IrSiR_3$; L = PPh_3, PCy_3, $P(p$-$Tol)_3$, $PMePh_2$, $AsPh_3$, $SbPh_3$; X = Cl, Br; R = Et, Me, Ph, OEt, Cl, F (as well as mixed-ligand systems, SiR_2R'; R = F, Cl, R′ = Me; R = Me, R′ = F, Cl) were prepared and described in ref 254. Also prepared with *trans*-$IrCl(N_2)(AsPh_3)_2$ or $IrClL_2$ (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(p$-$Tol)_3$, PCy_3, and $PMePh_2$). [8t] Color of complexes reported as yellow or red. Decomposition temperature reported for **4−292** was 184−190 °C. [8u] Additional derivative: $(Ph_3P)_2(H)_3Ir(SiEt_3)$. [8v] See also entries **4−137a**, **4−280b**, and **4−341b** for related derivatives. [8w] Additional derivative: $(Cy_3P)(cod)(H)_2IrSiMe_2Ph$. [8x] Additional derivatives: $(Cy_3P)(acac)(H)$-$IrSiPh_3$, $(Cy_3P)_2(acac)(H)IrSiEt_3$. See also **2−60b**, **3−77a**, and **3−77b** for related derivatives. [8y] Additional derivatives: $(R_3P)(TFB)(H)_2IrSiR'_3$, R′ = Et, R = Cy, *i*-Pr; R′ = Ph, R = Ph, Cy, *i*-Pr. [8z] Additional derivatives: $L(cod)(H)_2IrSiR_3$; ($SiR_3 = SiEt_3$, $SiMe_2Ph$, L = Ph_3P; $SiR_3 = SiMe_2Ph$, L = Ph_3As). Silyl exchange reactions also reported with these complexes. [9a] Additional derivatives: $(triso)(H)_2Ir(SiEt_3)_2$, $(triso)(D)(H)Ir(SiEt_3)_2$. [9b] This section contains di- and polynuclear complexes of the Co triad where there is no M−M′ bond and M = M′ = Co, Rh, Ir; or M = Co, Rh, Ir and M ≠ M′, M′ = transition metal other than Co triad. [9c] Reaction done using $(\eta^6$-arene) Cr−silyl complex instead of $(\eta^5$-cyclopentadienyl) metal silyl complex as seen in entries **4−305** to **4−307** and **4−312** and **4−313**. [9d] Isolated as a benzene solvate. Additional derivative: $\{Rh[(i$-$Pr)_3P](SiR_3)H(\mu$-$Cl)_2RhH(SiR_3)[P(i$-$Pr)_3]$; R = $CH_2C_6H_4Me$-*p*. [9e] $[(cod)RhCl]_2$ can be used to prepare the complex in 83% yield (without $h\nu$, done in air). $[(cod)Rh(OMe)]_2$ was also used to carry out the reaction but no information given in experimental for this particular reaction (requires benzoyl peroxide). [9f] Compound too insoluble to obtain NMR data. [9g] This section contains di- and polynuclear complexes of the Co triad which contain a M−M bond where the M_2 unit is a homonuclear fragment containing an element of the Co triad. Additional metals may be present but do not interact with dinuclear unit. [9h] Reaction with 1.5 equiv of silane produces tricobalt complexes. Reaction with 2 equiv gives tetracobalt species. Reference 278 also reports reaction of $HSiMe_2{-}C{\equiv}C{-}SiMe_2H$ with 1.5 equiv of $Co_2(CO)_8$ gave $(OC)_4Co{-}SiMe_2C{\equiv}CSiMe_2{-}Co(CO)_4]Co_2(CO)_6$ (40%) where the alkyne is coordinated to cobalt in an η^2-fashion. However no data or experimental description were given in paper. [9i] The Si−H resonance appears at 4.86 ppm (br) in the ^1H NMR spectrum. [9j] Also prepared by thermolysis of $(OC)_6Co_2[\eta^2$-$Ph{-}C{\equiv}C{-}SiMe_2H]$ at 80 °C in toluene.[278,279] [9k] Can also be prepared by reaction of 0.5 equiv of $Co_2(CO)_8$ + $[\eta^2$-$PhC{\equiv}CSiHMeEt]Co_2(CO)_6$. [9l] Also prepared by reaction of 0.5 equiv of $Co_2(CO)_8$ with $(OC)_6Co_2[\eta^2$-$Ph{-}C{\equiv}C{-}SiHMeCl]$. [9m] Also prepared by reaction of 0.5 equiv of $Co_2(CO)_8$ with $(OC)_6Co_2[\eta^2$-$Ph{-}C{\equiv}C{-}SiHCl_2]$. [9n] Additional derivative: $[(i$-$Pr_3P)(H)Rh(SiPh_3)]_2(\mu$-$H)(\mu$-$Cl)$. Reaction with $DSiPh_3$ gave a partially deuterated mixture of product (with scrambling) and starting material. [9o] Reaction requires excess silane. [9p] Additional derivatives: $(OC)_2XIr(SiR_3)(CX'_2)_2TaCp_2$, (R = Et, X = X′ = D, H; R = Me, X = X′ = H; R = Ph, X = X′ = D). Derivatives containing R = Et or Me were characterized in solution only. [9q] Compounds were previously prepared by metal atom/vapor chemistry. This reference now uses classical solution phase procedure. Additional derivative prepared with SiF_3 group. [9r] Arenes investigated: $C_{10}H_8$, $C_{14}H_{10}$, 4,4′-dimethylbiphenyl, diphenylmethane, 1,2-diphenylethane, 4,4′-paracyclophane, and biphenyl. Reaction also works with SiF_3 and C_6F_5 groups. Only complexes with anthracene and naphthalene involve direct Si−H oxidative addition and others involve arene exchange reactions $[(\eta^6$-toluene$)Ni(SiCl_3)_2$ + arene)]. [9s] Prepared from $(HMe_2Si)_2$ in yields of 50−70%. See also **2−80**, **3−91**, and **3−92** for related derivatives. [9t] The Si−H resonance in the ^1H NMR spectrum appears as a multiplet at 4.84 ppm. [9u] Additional derivative: $[(Ph_2PCH_2CH{=}CH_2)(phen)PdSiEt_3]^+$ $[BAr'_4]^-$ ($Ar' = 3,5$-$(CF_3)_2C_6H_3$). [9v] Additional derivatives: $\{(phen)[\eta^2$-$CH_2{=}CH(t$-$Bu)]PdSi(i$-$Pr)_3\}^+$ $[BAr'_4]^-$; $\{(phen)[\eta^2$-$CH_2{=}CH(t$-$Bu)]PdSiEt_3\}^+$ $[BAr'_4]^-$; $[(phen)(\eta^2$-$CH_2{=}CHCH_2SiPh_3)PdSiEt_3]^+$ $[BAr'_4]^-$; $[(phen)(\eta^2$-$CH_2{=}CHCH_2SiPh_3)PdSiPh_3]^+$ $[BAr'_4]^-$; $[(phen)(\eta^2$-$CH_2{=}CHCH_2SiEt_3)PdSiPh_3]^+$ $[BAr'_4]^-$; $[(phen)(\eta^2$-$CH_2{=}CHCH_2SiEt_3)PdSiEt_3]^+$ $[BAr'_4]^-$; ($Ar' = 3,5$-$(CF_3)_2C_6H_3$). Complexes characterized in solution at low temperature only. [9w] Additional derivative: $(Et_3P)_2(H)PtSiMe_3$. Both compounds decomposed slowly. Characterized by ^1H and ^{31}P NMR only. [9x] Additional derivatives: $(Et_3P)_2(H)PtSiAr_3$; Ar = p-FC_6H_4, p-ClC_6H_4 were prepared by intermolecular silyl group exchange between $Pt(PEt_3)_4$ and $(i$-$Pr_3P)_2(Cl)(H)RhSiAr_3$. Complex **4−331b** was also prepared by this route in 60% yield. [9y] Cis isomer converted to trans upon heating or photolysis. The trans isomer was structurally characterized and is to be published. [9z] Same product formed with 1 or 3 equiv of disilane. Oligosilanes are observed with reaction using 3 equiv. Redistribution also observed with $HMe_2SiSiMe_3$ and $H_2MeSiSiMe_3$ but gave no observable Pt−Si species. [10a] The Si−H resonance appears at 4.51 (sept t) in the ^1H NMR spectrum with $^3J_{HH} \approx 4.0$

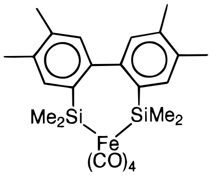
Table 4 (Continued)

Hz and $^2J_{PtH} \approx 39$ Hz. [10b] Additional derivative: $(Ph_3P)_2Pt[SiMe(Bz)OSiMe(Bz)]$. [10c] The cationic complex is not stable in solution at room temperature (half life approximately 3 h). [10d] A related derivative, (dppb)(H)$PtSiPh_3$ (dppb = $Ph_2P(CH_2)_4PPh_2$) was recently reported but only crystallographic data are available.[304] [10e] Additional derivatives: (dppe)$Pt[\eta^2$-(i-Pr)$_2$SiSi(i-Pr)$_2$] (**4−341a**) and (dppe)$Pt(\eta^2$-$Me_2SiSiMe_2$). The methyl derivative was prepared by preparative routes 4U and 4W. [10f] Also prepared from [H(i-Pr)$_2$Si]$_2$ and (dppe)$PtCl_2$ + Li (2% Na) (preparation method 4T, see **4−339**). [10g] Additional derivatives: (Cl)Pt{SiR[$(CH_2)_nPPh_2]_2$}, R = Me, n = 2; R = Ph, n = 3. (Cl)Pt{SiR[$(CH_2)_nPCy_2]_2$}, R = Me, n = 2; R = Ph, n = 2; R = Me, n = 3. (Cl)Pt[$SiPh(CH_2CH_2PPh_2)(CH_2CH_2PCy_2)$]. See also entries **4−137a**, **4−280b**, and **4−296a** for related derivatives. [10h] Additional derivatives: *cis*-$Pt(SiRR'CH_2CH_2PPh_2)_2$ R = R′ = Ph; R = Me, R′ = Ph; R = H, R′ = Me or Ph (see also **3−95**). [10i] Can also be prepared by reaction of Pt(cod)XY (X = Y = Cl or Me; X = Cl, Y = Me) with $PPh_2CH_2CH_2SiRR'H$ (NEt_3 is required when chloro ligands are used to intercept HCl formation but yields generally lower). Also prepared with $(Ph_3P)_4Pt$. [10j] This section contains dinuclear complexes with no direct M−M′ bond where M = Pt and M′ = Pt or Mn. [10k] Complexes could also be prepared with $Pt(PPh_3)_4$. [10l] Reaction requires the presence of dry air. Also prepared with $(Ph_3P)_2PtO_2$ or $(Ph_3P)_4Pt$ in the presence of dry air. [10m] *Chemical Abstracts* citation for patent (USSR) for improved yield of known compound via heating and irradiation. No data given.

Compound structures for Table 4.



4-68



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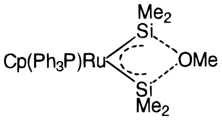

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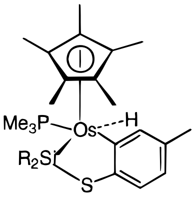
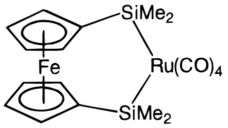


R = p-$SC_6H_4CH_3$

4-152c



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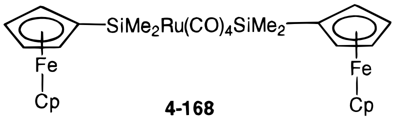

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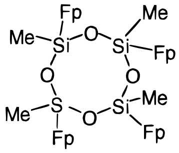

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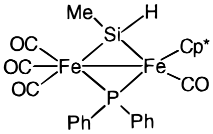

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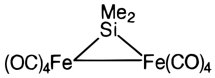

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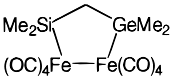

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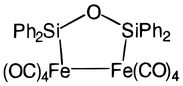

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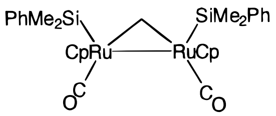
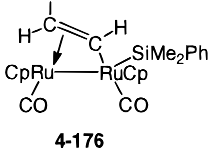


4-175a



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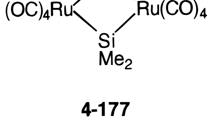

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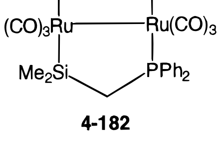

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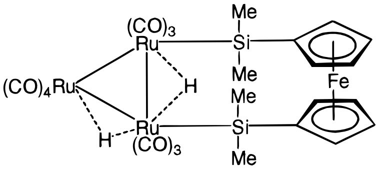

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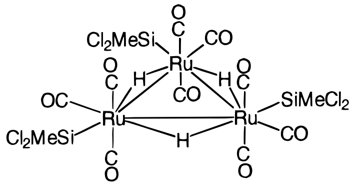

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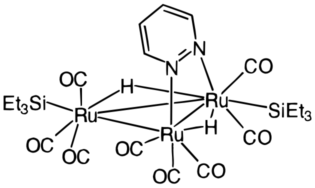

4-186

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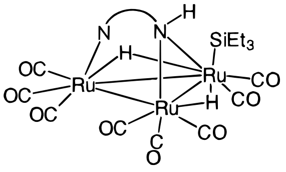
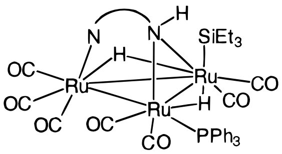


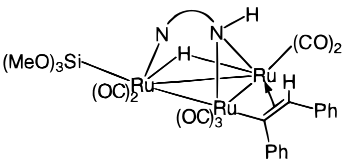
N—N—H = ampy

4-187



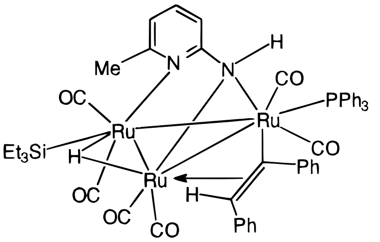
N—N—H = ampy

4-190



N—N—H = ampy

4-191



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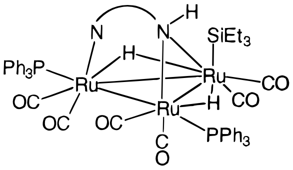

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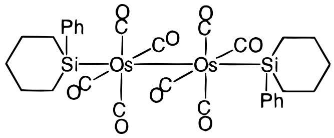

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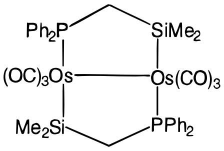

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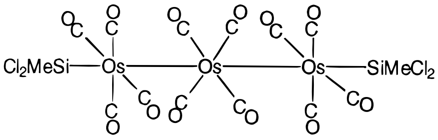

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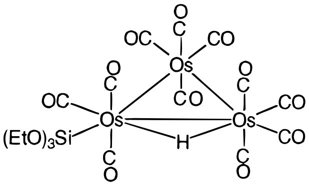

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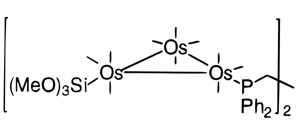

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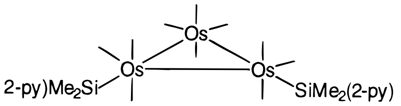
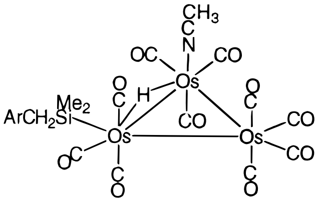


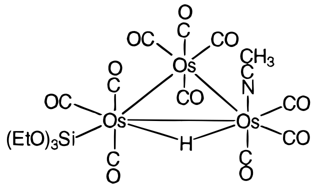
(2 bridging H's)

4-204



Ar = 2-BrC$_6$H$_4$
(1 bridging H)

4-205



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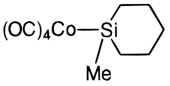

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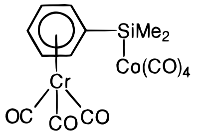

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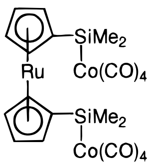

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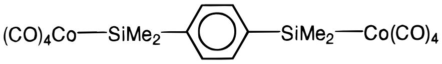

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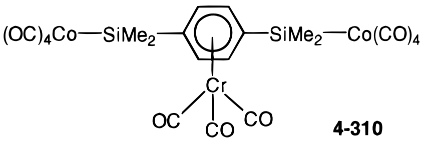

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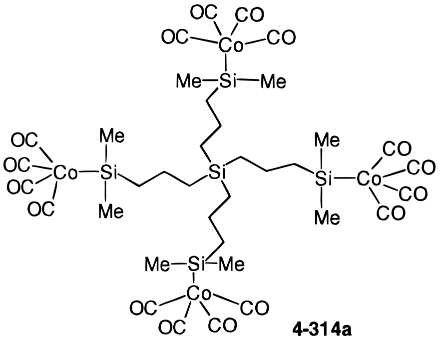
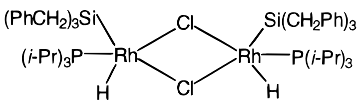


4-314a



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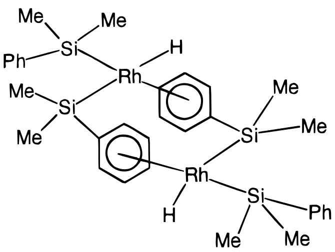

4-315

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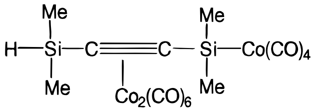

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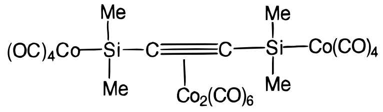

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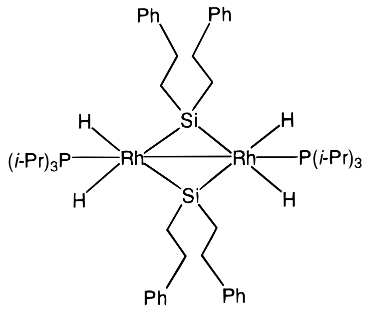
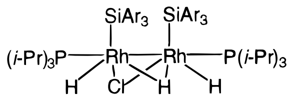
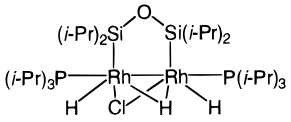


4-323b

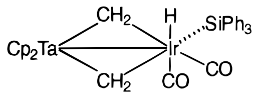


Ar = p-$(CF_3O)C_6H_4$

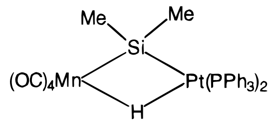
4-323c



4-323d



4-324



4-343

The Ta(V) complexes, $Cp_2Ta(H)(SiR_3)_2$ [$(SiR_3$ = $SiMe_3$ (**4−19**), $SiMe_2Cl$ (**4−20**), $Si(OMe)_3$ (**4−21**)], can be prepared from the reaction of $Cp_2Ta(L)(CH_3)$ (L = PMe_3, $CH_2{=}CH_2$) and $HSiR_3$ but not from hydrosilanes that have bulky substituents (such as *t*-Bu).[13] Within the same triad, the order of reactivity of R_3SiH with Cp_2NbH_3 was $PhMe_2SiH$ > $Me_3SiOSiMe_2H$ > Et_3SiH with the last giving only minor conversion to the niobium−silyl complex.[135] The related complex, $(C_5H_4SiMe_3)_2NbH_3$, reacts with $HSiPh_3$ but not with $HSiEt_3$ to give $Cp'_2Nb(H)_2SiPh_3$ although this could be due to an electronic effect of substituents in the tertiary silane.[39]

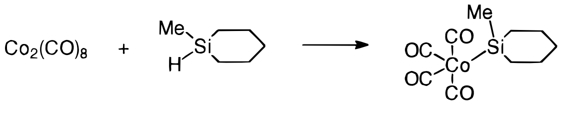
In the chromium triad, *fac*-$(OC)_3(dppe)W(THF)$ gives stable silyl derivatives on reaction with tertiary silanes but the product from a secondary silane (Ph_2SiH_2) was thermally labile.[140] It appears that there may be an upper limit in the size of the R substituents in the reaction of $HSiR_2Cl$ (R = *i*-Pr, *t*-Bu) with $Cp_2W(\eta^2\text{-}CH_2{=}SiMe_2)$. The product, $Cp_2W(SiMe_3)[Si(i\text{-}Pr)_2Cl]$, was obtained from $HSi(i\text{-}Pr)_2Cl$ but not from $HSi(t\text{-}Bu)_2Cl$.[90]

The ruthenium complex CpL_2RuMe (L = PPh_3) does not react with $HSi(SiMe_3)_3$ but does so with $HSiEt_3$ to give $Cp(Ph_3P)_2RuSiEt_3$ (**4−113**) and a similar trend is observed with the complex $CpL_2RuCH_2SiMe_3$ (L = PMe_3) which gave $Cp(Me_3P)_2RuSiEt_3$ (Table 4, footnote 3u). In the latter case, the reactivity order with tertiary silanes was observed to be $HSiCl_3$ > $HSiMeCl_2$ > $HSiMe_2Cl$.[176] The related complex, $Cp^*L_2RuCH_2SiMe_3$ (L = PMe_3) reacted neither with $HSi(SiMe_3)_3$ nor with $HSi(t\text{-}Bu)_2Cl$ even at 100 °C over 16 h.[180] Thus, the majority of the examples that suggest steric problems in the oxidative addition of silanes come from Cp derivatives in the early to middle transition-metal series.

All of the metals in the Co triad (in Table 4) are well represented with the greatest number of entries for iridium. A number of novel silyl groups and unusual ligands bound to the metal center were reported and are discussed below. There are also several entries containing bifunctional silanes which give products containing a chelating unit that involves the silyl group as part of the chelate. All of the cobalt complexes shown in Table 4 contain cobalt(I) [except **4−220** which contains Co(III)] and carbonyl ligands with several complexes also containing phosphine ligands (entries **4−211**;[216] **4−212**;[217] **4−213**;[218] **4−214** to **4−216**, **4−218**;[219] **4−217**, **4−219**, **4−222** and **4−223**;[220] **4−220**;[221] and **4−221**[222,223]). However, Rh or Ir(I) silyl complexes are rare and most of the entries listed for these metals involve a +3 oxidation state and a few examples with a formal +5 oxidation state also may be found. Complexes $(Ph_3P)_2(H)_4IrSiPh_3$ (**4−293**), $(Ph_3P)_2(H)_3Ir(disil)$ (**4−294**) and $(Ph_3P)_2(H)_3Ir[(i\text{-}Pr)_2SiOSi(i\text{-}Pr)_2]$ (**4−295**) are unusual examples of seven-coordinate iridium−silyl complexes that were prepared from the Ir(V) polyhydride, $(Ph_3P)_2IrH_5$.[267] Tertiary silanes are generally less reactive toward metal centers than are primary or secondary silanes and some trends in the reactivity of trisubstituted silanes were reported. In addition, unusual rearrangement reactions were observed with iridium and are discussed below.

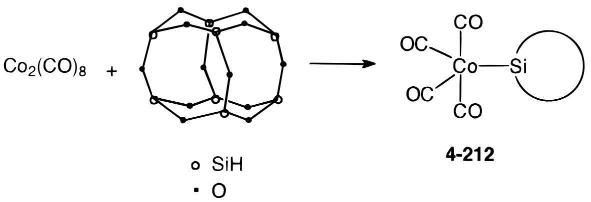
There are several complexes that were prepared from dicobalt octacarbonyl where cleavage of the Co−Co bond occurred to give mononuclear complexes (see for example, entries **4−211** through **4−213**).[216,217,218] Di- and polynuclear complexes can also be prepared such as, **4−304** through **4−310** which contain noninteracting metal sites.[64,272,273] Polynuclear cobalt complexes containing Co−Co bonds and isolated metal centers are represented by **4−317** through **4−323a** and are described in section III.E.

Some unusual silyl ligands that were investigated in combination with cobalt are illustrated in entries **4−211**,[216] **4−212**,[217] and **4−213**.[218] Dicobalt octacarbonyl reacts with silacyclohexanes, $[RHSi(C_5H_{10})]$ (R = Me, Ph, Cl; representative example given in entry **4−211**) to give complexes of the composition $(OC)_4Co[SiR(C_5H_{10})]$ in moderate yields (eq 10). Reaction of octahydrosilasesquioxane, $H_8Si_8O_{12}$, with $Co_2(CO)_8$ gave a monosubstituted complex, $(OC)_4Co(H_7Si_8O_{12})$ (**4−212**, X-ray) (eq 11). Reaction of R_3SiH [R_3SiH =



(10)

4-211



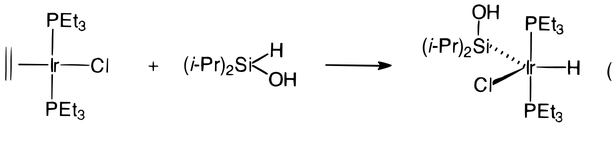
(11)

4-212

$(EtO)_3SiH$, Cl_3SiH or Me_2ClSiH] with either Al_2O_3 or SiO_2 resulted in the functionalized inorganic oxide surfaces, [S]SiH where [S] = Al_2O_3 or SiO_2. Reaction of the derivatized surface with $Co_2(CO)_8$ gave silylcobalt species, [S]$SiCo(CO)_4$ (**4−213**).[218]

A number of Ir−silyl complexes were prepared containing the $-Si(SEt)_3$ ligand. For example, the reaction of $HSi(SEt)_3$ with $HIr(CO)(PPh_3)_3$ yields *cis*-$OC(Ph_3P)_2(H)_2IrSi(SEt)_3$ (**4−269**), $MeIr(PMe_3)_4$ yields *fac*-$(Me_3P)_3Me(H)IrSi(SEt)_3$ (**4−284**), and $(C_6F_5)M(PMe_3)_3$ gives *mer*-$(Me_3P)_3(C_6F_5)(H)MSi(SEt)_3$ (M = Rh, **4−241**, and Ir, **4−285**).[236] The Ir complexes were found to have enhanced stability with respect to hydrolysis of the Si−S bonds relative to the free silane. The Rh analogue however was more reactive. Oxidative addition of $HSi(SEt)_3$ to the Pt (0) complex, $Pt(PCy_3)_2$, was also reported to give the *cis*-silylhydride complex, *cis*-$(Cy_3P)_2(H)PtSi(SEt)_3$ (**4−332**).[291] This complex can be isomerized to the trans isomer quantitatively by photolysis or heating (65 °C).

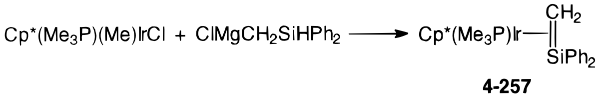
Silanols such as $(i\text{-}Pr)_2SiH(OH)$ or $(t\text{-}Bu)_2SiH(OH)$ react with $(Et_3P)_2(C_2H_4)IrCl$ to afford Ir(III) complexes such as **4−290**[265] (X-ray) (eq 12). This is the first example of a direct synthesis of a metallosilanol by oxidative addition of a Si−H bond of a silanol. The sterically hindered silanol, $(t\text{-}Bu)_2SiH(OH)$ also reacts with the platinum complex, (dmpe)PtMe(OTf) at room temperature to afford (dmpe)Pt[$Si(OH)(t\text{-}Bu)_2$](OTf) (**4−337**,[295] X-ray). The complex was found to be stable in the solid state but decomposed in solution at room temperature over a few hours.



(12)

4-290

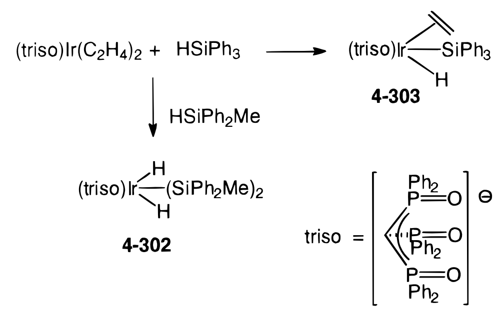
The iridium−silene complex, $Cp^*(Me_3P)Ir(\eta^2\text{-}CH_2{=}SiPh_2)$ (**4−257**[249]) was prepared by reaction of $Cp^*(Me_3P)(Me)IrCl$ with the Grignard reagent, $ClMgCH_2SiHPh_2$ at −78 °C in Et_2O (eq 13). No intermediates were observed by low-temperature ^{31}P NMR. The analogous reaction was also reported with $ClMgCH_2SiDPh_2$ in benzene-d_6 and CDH_3 was produced (no CH_4 found). Additional derivatives reported (but not isolated in pure form) were $Cp^*(Me_3P)Ir(\eta^2\text{-}CH_2{=}SiMe_2)$ and $Cp^*(Me_3P)Rh(\eta^2\text{-}CH_2{=}SiPh_2)$. The reaction to prepare complex **4−257** involves an intramolecular Si−H addition (followed by elimination of methane) where silicon is in a position β to the metal center.



$$Cp^*(Me_3P)(Me)IrCl + ClMgCH_2SiHPh_2 \longrightarrow Cp^*(Me_3P)Ir{-}\overset{CH_2}{\underset{SiPh_2}{\|}} \quad (13)$$

4-257

Scheme 17



Complex **4−303**, $(triso)(C_2H_4)HIrSiPh_3$,[271] was prepared from $(triso)Ir(C_2H_4)_2$ (triso = tris(diphenyloxophosphoranyl)methanide, Scheme 17[271]) with $HSiPh_3$ at room temperature in CH_2Cl_2, Et_2O, or $CDCl_3$. Other organosilicon and organic compounds were also formed in the reaction, namely ethyltriphenylsilane, triphenylvinylsilane, and ethane. This is a rare (alkene)silyliridium hydride and the only example of one with an O-donor ligand. The complex $(triso)(H)_2Ir(SiMePh_2)_2$ (**4−302**[271]) was prepared with the sterically less demanding silanes, Ph_2MeSiH (or Et_3SiH) and $(triso)Ir(C_2H_4)_2$ in a unique double oxidative addition. Complexes **4−302**, **4−303**, and $(triso)Ir(C_2H_4)_2$ catalyze the hydrosilylation of ethylene, whereas other olefins are isomerized but not hydrosilylated.

Several potential chelating silanes were utilized in reactions with Rh and Ir complexes some of which were described in previous paragraphs. There are two basic types of chelating silanes used, HSi⁀SiH and HSi⁀L (where L = PR_2 or NR_2). For example, a number of Rh complexes containing bifunctional silanes are represented by entries **4−244** to **4−247**.[240] Complexes $(Ph_3P)_2Cl(H)Rh(SiMe_2CH_2CH_2SiMe_2H)$ (**4−244**[240]) and **4−247** ($SiPh_2H$ analogue of **4−244**) were formed by reaction of equimolar amounts of the bifunctional silane with $RhCl(PPh_3)_3$ in $CDCl_3$ at −20 °C and are formally Rh−mono(silyl) complexes since the addition of the second Si−H bond was not observed. When the reaction was run in toluene-d_8 completely different results were obtained and complexes $(Ph_3P)_2(H)_3Rh(SiMe_2CH_2CH_2SiR_2)$ [R = Me (**4−245**) and Ph (**4−246**)] were generated. These complexes contain a Rh(V) center and are fluxional on the NMR time scale. When complex **4−244** was heated, intramolecular oxidative addition of the remaining Si−H bond occurred to give complex **4−245**. The synthesis of [*fac*-$(Me_3P)_3(H)Rh(SiMe_2CH_2CH_2SiMe_2)$] (**4−242**,[237] X-ray) was reported from reaction of $(Me_3P)_3Rh(SPh)$ and an excess of the bifunctional silane, $HMe_2SiCH_2CH_2SiMe_2H$ (a 1:1 ratio of reagents does not give complex **4−242**) at room temperature. Cyclometalladisiloxanes with the general formula, $OC(Ph_3P)_2HIr[SiMe(R)OSiMe(R)]$ (where R = Ph or CH_2Ph) were prepared by the oxidative addition of Si−H bonds in siloxanes to $(Ph_3P)_2Ir(CO)Cl$ (see entry **4−266**[253]).

Air-stable complexes $ClRh(SiMe_2CH_2CH_2PPh_2)_2$ (**4−250**[243]) and **4−296b** (Ir analogue of **4−250**)[243,256] (X-ray) were formed by reaction of $[(cod)MCl]_2$ (M = Rh, Ir) with excess $HMe_2SiCH_2CH_2PPh_2$ in THF at room temperature. When the reaction was run using slow addition of 2 equiv of $HMe_2SiCH_2CH_2PPh_2$ to $[(cod)IrCl]_2$, $[(cod)Cl(H)Ir(SiMe_2CH_2CH_2PPh_2)]$ (**4−300**,[243,256] X-ray), was obtained. Other iridium complexes such as $(OC)(Ph_3P)Cl(H)Ir(SiMe_2CH_2CH_2PPh_2)$ (**4−271**,[114,256,257] X-ray), were prepared from the rapid reaction of *trans*-$(OC)(Ph_3P)_2IrCl$ and chelating (phosphinoethyl)silyl ligands, $HSiR_2CH_2CH_2PPh_2$ (R_2 = Me_2, Ph_2, or MePh). The reactions were also performed with the deuterium analogues $DSiR_2CH_2CH_2PPh_2$. Other bifunctional complexes reported are the air-stable Rh and Ir tris(chelate) complexes, *fac*-$[(dmesiqn)_3M]$, **4−255a**[245,246] (M = Rh) and **4−301**[245,246] (M = Ir) prepared from reaction of $(OC)(Ph_3P)_3MH$ and 3 equiv of H-dmesiqn [H-dmesiqn = 8-(dimethylsilyl)quinoline]. An X-ray structure was reported for both complexes. The complex, $OC(Ph_3P)_2Cl(H)Ir(2\text{-}SiMe_2C_5H_4N)$ (**4−268**[149]), utilizes the chelating silane, 2-pyridyldimethylsilane to coordinate to Ir. The trifunctional silyl ligand, “tripsi” (tripsi = $HSi(CH_2CH_2PPh_2)_3$) was used in the preparation of $Cl(H)Rh[Si(CH_2CH_2PPh_2)_3]$ (**4−248**[241]) from reaction of $[(cod)RhCl]_2$ with (H-tripsi) in THF.

A number of Rh(V)−bis(silyl) complexes have been prepared including **4−226**,[224,226] **4−227**,[225] **4−229** to **4−230**,[226] and **4−233** to **4−238**.[229−233] Ir(V)−bis(silyl) complexes are also known and some representative examples are $Cp^*(H)_2Ir(SiEt_3)_2$ (**4−262**[231,232,251,252]) and $(triso)(H)_2Ir(SiMePh_2)_2$ (**4−302**[271]). Complexes $Cp^*Cl(H)_2IrSiEt_3$ (**4−261**[232,251]) and $[(Ph_3P)_2(H)_4IrSiPh_3]$ (**4−293**[267]) are examples of mono(silyl)−Ir(V) complexes. There are several Rh and Ir(V) complexes containing chelating silyl ligands such as **4−245** and **4−246**[240] and **4−294** and **4−295**.[267] The iridium complexes appear to be more stable than the corresponding Rh derivatives. There are very few Rh(I) and Ir(I) complexes and entries $(Me_3P)_3RhSiPh_3$ (**4−239a**[234]), $Me_3P(dtbpm)RhSi(OEt)_3$ (**4−249**[242]), and $(OC)_3(Cy_3P)IrSiPh_3$ (**4−263**[58]) are examples of this class.

Seven-coordinate Ir(V) complexes of the general formula, $IrH_3(disil)(PPh_3)_2$ [disil = 1,2-bis(dimethylsilyl)benzene, complex **4−294**[267] (X-ray)], the corresponding 1,1,3,3-tetraisopropyldisiloxyl derivative (see entry **4−295**[267]), and monodentate silyl complexes, $IrH_4(SiR_3)(PPh_3)_2$ [R = Et, Ph (**4−293**[267])], were prepared in good yield from an excess of the appropriate silane and $IrH_5(PPh_3)_2$ in THF at room temperature. The silane ligands used in complexes **4−294** and **4−295** are chelating ligands through the silicon centers. Complexes **4−293** and **4−294** are fluxional on the NMR time scale. No reaction was observed with the silanes and $IrH_5(PCy_3)_2$ and no characterizable products were obtained from reaction of silanes with $[Ir(cod)Cl]_2$, $[Ir(coe)_2Cl]_2$, $[IrH_2(Me_2CO)_2(PPh_3)_2][SbF_6]$, or $[Ir_3H_7(PCy_3)_3py_3][SbF_6]_2$.[267]

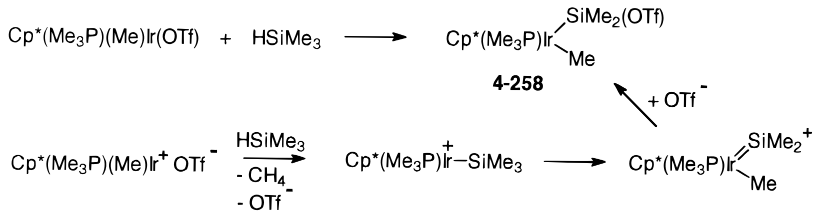
A few reports describe the reactivity or lack of reactivity of a number of silanes with the same metal precursor. For example, several cobalt complexes containing both carbonyl and phosphine ligands were reacted with a number of tertiary silanes: $(OC)_3(Ph_2MeP)CoSiF_3$ (**4−217**[220]), $(OC)_3Ph_3PCoSiPh_3$ (**4−219**[220]), $(OC)_2(Ph_3P)_2CoSiF_3$ (**4−222**[220]), and $(OC)(Ph_3P)_3CoSiF_3$ (**4−223**[220]). The cobalt dimer, $[Co(CO)_3L]_2$, (L = PMe_2Ph, PEt_3, $P(n\text{-}Bu)_3$, $AsMe_2Ph$), reacted with $HSiF_3$ (see entry **4−217**) but when L = PPh_3 no reaction occurred with $HSiF_3$, $HSi(OEt)_3$ or $HSiEt_3$. If chlorinated solvents or halosilanes such as $HSiCl_3$ or $HSiMe_2Cl$ were used decomposition products formed. The complex, $CoH(CO)_3(PPh_3)$, reacted with $HSiF_3$ or $HSi(OEt)_3$ but not the alkylsilanes $HSiR_3$ (R = Et, Me). Triphenylsilane also reacted with $CoH(CO)_3(PPh_3)$ and CO to give a mixture of products one of which was $(OC)_3(Ph_3P)CoSiPh_3$ (**4−219**). As the phosphine content increased, reactivity of the cobalt complex toward hydrosilanes decreased. Only $HSiF_3$ reacted with $CoH(CO)_2(PPh_3)_2$ and $HCo(CO)(PPh_3)_3$ to give products $Co(SiF_3)(CO)_2(PPh_3)_2$ (**4−222**) and $Co(SiF_3)(CO)(PPh_3)_3$ (**4−223**), respectively (no other silanes reacted). No tertiary silane reacted with $HCo(PR_3)_4$ (PR_3 = $PMePh_2$, $P(OMe)_3$, $P(OPh)_3$, and dppe). Thus, the starting complexes become less reactive with increasing phosphine substitution at the metal and the silanes were more reactive when electronegative substituents were present.

Several Ir(III)−silyl and −bis(silyl) complexes were prepared by reaction of the Ir−trihydride, $IrH_3(CO)(dppe)$ with tertiary silanes [entries **4−277**, $OC(dppe)(H)_2IrSiEt_3$,[60,258] through **4−280a**, $OC(dppe)(H)Ir(SiMe_2Cl)_2$,[60] X-ray; see also Tables 2 and 3 for entries with primary and secondary silanes]. The monosilyl complexes with Ph_3Si−Ir and Et_3Si−Ir do not react with additional silane to form bis(silyl) complexes possibly due to steric interactions. The Me_3Si derivative requires ethylene addition (probably as a H_2 sink) for the formation of the bis(silyl) complex (analogous to **4−280a**). It was found that only Me_3Si, Me_2ClSi, and $MeCl_2Si$ groups form bis(silyl) complexes.

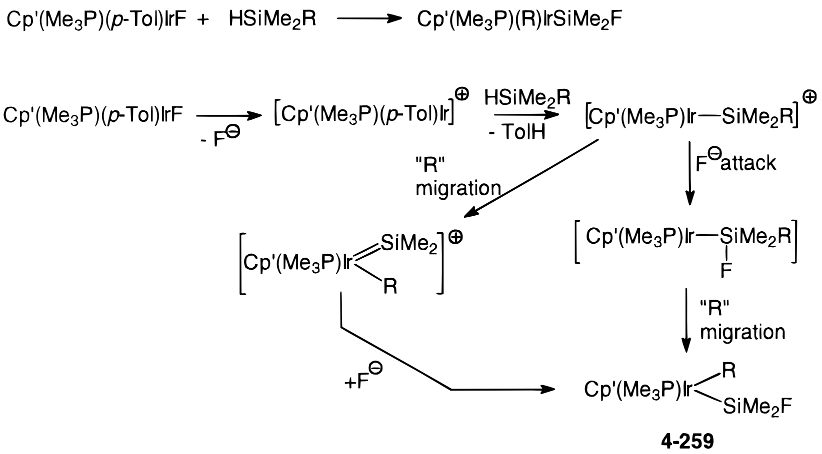
Reaction of *trans*-$(RO)Ir(CO)[P(p\text{-}Tol)_3]_2$ (R = Me, Ph) with silanes occurs at room temperature to give alkoxysilanes and dihydridoiridium−silyl complexes. A representative example is given by $(OC)[(p\text{-}Tol)_3P]_2(H)_2IrSiMe_2Ph$ (**4−270**,[255] X-ray), obtained from the reaction of $(MeO)Ir(CO)[P(p\text{-}Tol)_3]_2$ with excesss $HSiMe_2Ph$ in either benzene or THF at room temperature [other silanes investigated were $HSiPh_3$ and $HSi(OMe)_3$]. Chlorosilanes also reacted to give alkoxysilanes and Ir−Cl-containing products but probably not through an oxidative addition mechanism but through S_N2 attack of oxygen on silicon.[255]

A number of five-coordinate Ir(III) silyl complexes of the general formula, $IrHX(SiR_3)(PPh_3)_2$ were prepared from excess $HSiR_3$ (R = Et, Me, Ph, OEt, Cl, F) and *trans*-$IrX(N_2)(PPh_3)_2$ (X = Cl, Br). A representative example is $(Ph_2MeP)_2Cl(H)IrSi(OEt)_3$ (**4−292**[254,266]). Other Ir precursors were used such as *trans*-$IrCl(N_2)(AsPh_3)_2$ or $IrClL_2$ (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(p\text{-}Tol)_3$, PCy_3, and PPh_2Me). The rates of reaction followed the order $HSiCl_3 > HSiCl_2Me > HSi(OEt)_3 \approx HSiClMe_2 > HSiMe_3 \approx HSiEt_3 \approx HSiPh_3$. The ease of formation and stability with

Scheme 18



Scheme 19



respect to reductive elimination of $HSiR_3$ increased with increasing electronegativity of the groups at silicon. The corresponding Rh analogues appear to be much less stable than the Ir complexes. A number of silyliridium−carbonyl complexes were prepared with the general formula, $IrHX(SiR_3)(CO)L_2$, from $HSiR_3$ (SiR_3, R = Me, Et, Ph, OEt, Cl, F; SiR_3 = $SiMePh_2$, $SiMeF_2$, $SiMeCl_2$) and $IrX(CO)L_2$ (X = F, Cl, Br, I, SCN; L = PPh_3, $PMePh_2$, and $AsPh_3$). Most of the complexes were not sufficiently soluble to obtain NMR data. A representative example is given by $(OC)L_2Cl(H)IrSi(OEt)_3$ (**4−267**).[254]

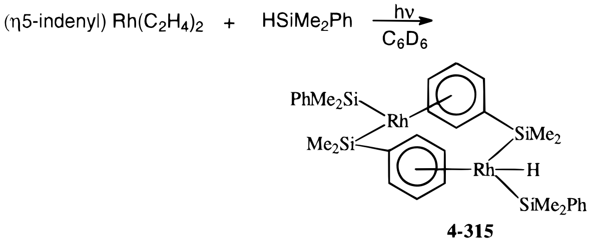
Reaction of $Cp^*(Me_3P)Ir(Me)OTf$ (OTf = OSO_2CF_3) with silanes gave rearrangement products such as **4−258**[113] (Scheme 18). The rapid reactions afforded high yields of the silyliridium complex and were believed to occur by initial oxidative addition of the Si−H bond followed by rearrangement to give the isolated product. The silanes investigated were $HSiMe_3$, $HSiPh_3$, and $HSiMe_2Ph$. NMR studies showed that the migratory aptitude of the groups on silicon favored only phenyl migration for $HSiMe_2Ph$ and hydride migration for H_2SiPh_2 (see **3−63**). The reactions probably proceed via the cationic Ir complex $[Cp^*(Me_3P)Ir(Me)][OTf]$ [through ionization of $Cp^*(Me_3P)Ir(Me)OTf$] where the Si−H bond of the silanes reacts via a σ-bond metathesis transition state or an oxidative addition/reductive elimination path. The involvement of cationic silylene intermediates also may be possible.

Reaction of $Cp'(Me_3P)Ir(Ar)F$ (Cp′ = C_5Me_5, Ar = Ph, *p*-Tol; Cp′ = C_5Me_4Et, Ar = Ph) in benzene with excess silane ($HSiMe_2Ph$ or $HSiMe_3$) at room temperature afforded (fluorosilyl)iridium complexes represented by **4−259**[250] (Scheme 19). The reaction involves the formal removal of a methyl group and the generation of a Si−F bond. The first step in the reaction is believed to be F^- ion dissociation followed by removal of the aryl group from iridium via a σ-bond metathesis reaction between the silane and $[Cp'Ir(PMe_3)(aryl)]^+$. A cationic Ir(III)−silyl complex is produced that can undergo F^- attack and then alkyl migration (or the reverse order sequence would involve a cationic iridium(V)−silylene species) to give the isolated product, **4−259**.

The silicon−hydrogen functionality in silyl-substituted cyclopentadienyl or aryl ligands complexed to metals react with dicobalt octacarbonyl to afford the heterobimetallic complexes shown in entries **4−304** through **4−307**.[272] The heterobimetallic cobalt complex $(OC)_4CoSiCl_2FeCp(CO)_2$ (**4−308**[64]) was prepared by reaction of $Cp(CO)_2FeSiHCl_2$ with $Co_2(CO)_8$.

Reaction of [η^6-1,4-bis(dimethylsilyl)benzene]chromium tricarbonyl with dicobalt octacarbonyl affords complex $(OC)_3Cr\{[1,4\text{-}(OC)_4CoSiMe_2]_2C_6H_4\}$ (**4−310**[273]). The uncomplexed (with respect to Cr) analogue, **4−309**,[273] was also synthesized by reaction of $Co_2(CO)_8$ with 1,4-bis(dimethylsilyl)benzene at room temperature. It was found that the thermal stability of 1,4-para-substituted aromatics was greater when complexed to $Cr(CO)_3$.

Reaction of Me_2PhSiH with (η^5-indenyl)$Rh(C_2H_4)_2$ under photolysis in C_6H_6 gave complex **4−315**[275] (X-ray) in good yield (eq 14). Each Rh is η^6-bonded to



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4-315

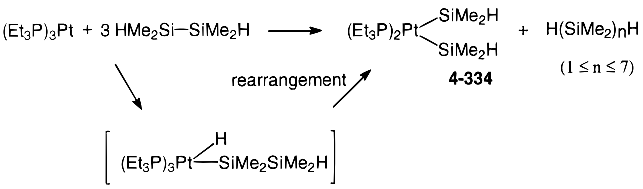
one phenyl of a Me_2PhSi group which also has a Si−Rh σ-bond to the other Rh atom. Each Rh center also has a terminal hydride and a Si−Rh σ-bond to a Me_2PhSi ligand (not involved in π-bonding). Complex **4−315** was also prepared by reaction of $[(cod)RhCl]_2$ with Me_2PhSiH in toluene at 20 °C (but in CH_2Cl_2 under N_2 no product was formed). The synthesis of **4−315**[275] could also be performed with $[(cod)Rh(OMe)]_2$ and Me_2PhSiH in CH_2Cl_2 and was promoted by benzoyl peroxide, suggesting a possible radical involvement. No reaction occurred under N_2 and a low yield was obtained when performed in air.

Entries for the nickel triad are dominated by platinum−silyl complexes with only a few nickel and palladium systems reported. The majority of the entries contain phosphine ligands (mondentate and chelating) and there are a few examples of chelating silyl ligands, $Pd(SiMe_2CH_2CH_2PPh_2)_2$ (**4−327**[126]), $(Ph_3P)_2Pt[SiMePhOSiMePh]$ (**4−336**[253]), **4−339** to **4−342**,[128,129,186,297,298] and $[(Ph_3P)_2(Cl)Pt(SiHCl)]_2O$ (**4−346**[300]).

The two reports found for nickel involve the synthesis of (π-arene)(halosilyl)nickel complexes $[(\eta^6\text{-}C_7H_8)Ni(SiCl_3)_2$ (**4−325**[285])]. Bis(2-methylallyl)nickel (or diallylnickel) reacts with $HSiCl_3$ or $HSiF_3$ in toluene to afford the $(\eta^6\text{-toluene})Ni(SiX_3)_2$ (for example, **4−325**) complex and 2-methylpropene. Other (π-arene)nickel−halosilyl complexes were prepared by arene−arene′ exchange with $(\eta^6\text{-toluene})Ni(SiCl_3)_2$ but this method was not possible for arenes such as naphthalene and anthracene. These derivatives [represented by the naphthalene complex $(\eta^6\text{-}C_{10}H_8)Ni(SiCl_3)_2$ (**4−326**[286])], were prepared in analogous manner to complex **4−325**.[285]

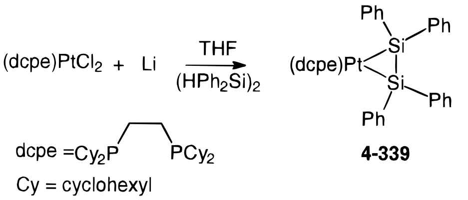
Bis(silyl)−Pd(II) complexes appear to be stable in the presence of electron-withdrawing silyl groups or if elimination of disilane (via reductive elimination of silyl groups) is prevented by use of suitable chelate ligands. The bis(chelate)−palladium complex, $Pd(SiMe_2CH_2CH_2PPh_2)_2$ (**4−327**[126]), was prepared by reaction of *cis*-$(Ph_2MeP)_2PdMe_2$ with 2 equiv of the silane, $Ph_2PCH_2CH_2SiMe_2H$. The *trans*-bis(trichlorosilyl)palladium phosphine complex $(Ph_2MeP)_2Pd(SiCl_3)_2$ (**4−328**[126]) was also reported but was prepared by a novel reaction of $(Ph_2MeP)_2PdCl_2$ with KH and $HSiCl_3$. Disproportionation was observed when the reaction was carried out with $HSiPh_3$ (only $SiMe_2Ph_2$ was observed). Chlorosilanes such as $HSiCl_3$ reacted with *cis*-$(Ph_2MeP)_2PdMe_2$ to give chloro/methyl exchange affording $(Ph_2MeP)_2PdCl_2$ and methylsilanes. A stable bis(silyl)palladium complex containing a chelating phosphine ligand was prepared from reaction of $[(dcpe)Pd]_2(\mu\text{-}H)_2$ with $HMe_2SiSiMe_2H$ (see also **2−80**,[73] **3−91**,[73] and **3−92**[73]) to afford complex $(dcpe)Pd(SiHMe_2)_2$ (**4−329a**,[73] X-ray). This reaction most probably proceeds by initial addition of the Si−H bond to the Pd center followed by silyl migration to give the observed bis(silyl) product. The enhanced stability is attributed to the ancillary dcpe ligand that lends kinetic protection via the sterically demanding cyclohexyl ligands and a stronger Pd−Si bond is expected due to the high basicity of the phosphine ligands.

Scheme 20



With 3 equiv of $HMe_2Si{-}SiMe_2H$, $Pt(PEt_3)_3$ reacted to give complex **4−334**[293] at room temperature in nearly quantitative yield along with oligosilanes $H(SiMe_2)_nH$ ($1 \leq n < 7$) (Scheme 20). Reaction with 1 equiv of $HMe_2Si{-}SiMe_2H$ also afforded complex **4−334** in 90% yield. It was proposed that the kinetically favored product was the hydrido(disilanyl)platinum complex, $(Et_3P)_3Pt(H)SiMe_2SiMe_2H$, which would be formed by oxidative addition of one of the Si−H bonds. This complex then rearranges to afford the thermodynamic product, complex **4−334**. Redistribution reactions were also observed with the disilanes, $HMe_2SiSiMe_3$ and $H_2MeSiSiMe_3$ but no Pt−Si species were detected by NMR.

Tetrasubstituted 1,2-dihydridodisilanes also reacted with Pt(0) species to afford η^2-disilene complexes, as illustrated in examples **4−339**[297] and **4−341a**[297] (eqs 15 and 16). Reaction of $(dcpe)PtCl_2$



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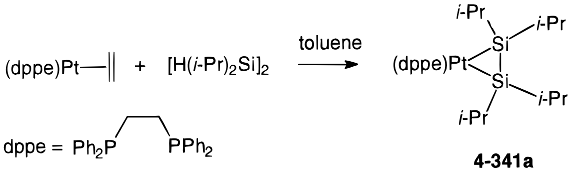


4-341a

(16)

and Li powder (2% Na) in THF in the presence of $HPh_2Si{-}SiPh_2H$ afforded complex **4−339** but in low yield. Gas evolution, (presumably H_2) was observed. An analogous reaction was also reported with $(dppe)PtCl_2$ and $HR_2Si{-}SiR_2H$ (R = Me, *i*-Pr), where yields were between 10 and 20% and significant amounts of oligomeric or polymeric silane byproducts were also observed. A higher yield was obtained for the reaction of $(dppe)Pt(C_2H_4)$ and $H(i\text{-}Pr)_2Si{-}Si(i\text{-}Pr)_2H$, yielding complex **4−339** (similar reaction also reported for $HMe_2Si{-}SiMe_2H$). The suggested mechanism involved initial oxidative addition of one of the Si−H bonds to the Pt(0) species followed by addition of the second Si−H bond to yield a six-coordinate Pt intermediate that then eliminated H_2 to give the η^2-disilene−platinum complexes.

Chelating silane ligands are also utilized with platinum. For example, the chelating bis(silyl)platinum complex, $(dppe)Pt(SiMe_2CH_2CH_2SiMe_2)$ (**4−340**) was prepared in good yield from the reaction of $HMe_2SiCH_2CH_2SiMe_2H$ with $(dppe)Pt(SiMe_3)_2$ by a silyl group exchange.[298] Cyclometalladisiloxanes, $(Ph_3P)_2Pt[SiMe(R)OSiMe(R)]$ (where R = Ph or CH_2Ph) were prepared from the oxidative addition of Si−H bonds of HMeRSiOSiRMeH in siloxanes to $(Ph_3P)_2Pt(C_2H_4)$ (entry **4−336**[253]). When a related 1,3-dihydrotrisilane, $H(Ph_2Si)_3H$ was reacted with $(Ph_3P)_2Pt(C_2H_4)$, a double 1,3-oxidative addition occurred to give the trisilaplatinacycle, $(Ph_3P)_2Pt[SiPh_2SiPh_2SiPh_2]$ (**4−335**[294]).

The *cis*-bis(chelate)−platinum complex, *cis*-Pt-$(SiMe_2CH_2CH_2PPh_2)_2$ (**4−342**,[128,129] X-ray), was prepared in moderate yield from the reaction of $(cod)_2Pt$ or $(cod)PtCl_2$ and Et_3N with the silane, $HMe_2SiCH_2CH_2PPh_2$. Several other derivatives were prepared including: *cis*-$Pt(PPh_2CH_2CH_2SiRR')_2$ (R = R′ = Ph; R = Me, R′= Ph; R = H, R′= Me or Ph). These complexes can also be prepared by reaction of Pt(cod)-XY (X = Y = Cl or Me; X= Cl, Y = Me) with $PPh_2CH_2CH_2SiRR'H$ but triethylamine was required to intercept HCl formed when Y = Cl. The oxidative addition of the Si−H bond to the platinum center occurs by a “chelate-assisted” process, i.e., initial coordination of P to Pt.

Only one reference appeared for the Cu triad and two complexes were reported, $(Ph_3P)_3CuSiPh_3$ (**4−347**) and $(Ph_3P)_3CuSiPh_2Cl$ (**4−348**).[301] These complexes were prepared by reaction of $HSiPh_3$ or $HSiPh_2Cl$, respectively with $^1/_6$ equiv of $[(Ph_3P)CuH]_6$ and 2 equiv of Ph_3P. The copper precursor serves as a source of the fragment, “$(Ph_3P)Cu$”.

An improved yield of complex **4−349**, $(Et_3Si)_2Hg$ was obtained by reaction of Et_2Hg and Et_3SiH on heating at 140−160 °C in the presence of ultraviolet irradiation (254 nm).[302]

E. Reactions of Metal–Metal-Bonded Complexes with Silanes

In the previous section the majority of the reactions of silanes that were described involved mononuclear metal complexes. These reactions tend to give products that also contain a single metal center although there are a few exceptions from the Fe triad. The reaction of $Fe(CO)_5$ with secondary silanes can provide dinuclear products with and without metal−metal bonds. Complex **3−55c**,[103,104] the dimer of “$(OC)_4Fe{=}SiPh_2$”, which contains two bridging silicon groups was formed by reaction of Ph_2SiH_2 and $Fe_2(CO)_9$ (in the presence of R_3N). However, other secondary silanes with smaller steric requirements result in Fe−Fe−bonded dimers with two bridging silylene units and a bridging CO (**3−56**[103,104] and **3−57**[105,106]). Another variation is provided on reaction with the tertiary silane, $HMe_2SiCH_2GeMe_2H$, where the product contains an Fe−Fe bond that is bridged by the $SiCH_2Ge$ unit (**4−173**[201]) which is similar to the product (**4−174**[56]) obtained from $HPh_2SiOSiPh_2H$ and $Fe_2(CO)_9$. Photolysis of $CpFe(CO)_2SiMe_3$ in the presence of primary silanes containing a bulky alkyl substitutent, produced dimer products, $Cp_2Fe_2(CO)_3(\mu\text{-}SiHR)$ (**2−46a**, R = *t*-Bu; **2−47**, R = Mes[47,53,54]), but reaction of the same silanes with $Cp^*Fe(CO)_2SiMe_3$ resulted in exchange of silyl groups to give $Cp^*(OC)_2FeSiH_2R$ (**2−36**, R = *t*-Bu; **2−37**, R = Tx[47]). With $(p\text{-}Tol)SiH_3$, $CpFe(CO)_2SiMe_3$ lost CO and oxidatively added the silane to give $Cp(OC)(H)Fe[SiH_2(p\text{-}Tol)]SiMe_3$ (**2−39**[47]), and the Cp* analogue provides a mixture of three monomers $[Cp^*(OC)_2FeSiH_2(p\text{-}Tol)$ (**2−38**), $Cp^*(OC)(H)Fe[SiH_2(p\text{-}Tol)]_2$ (**2−40**), and $Cp^*(OC)(H)Fe[SiH_2(p\text{-}Tol)]SiMe_3$ (**2−41a**)][47] plus the dimers that are analogues of **2−46a** and **2−47** as well as **2−48** and **2−49**.[47,55] A novel product was reported from $CpFe(CO)_2Me$ and secondary silanes with bulky aryl substituents. The dimer, produced from Ar_2SiH_2, $Cp_2(OC)_2Fe_2Si(Ar)_2$ [Ar = 2,4,6-C_6H_2-$(i\text{-}Pr)_3$, **3−52**] exhibited a triplet ground state.[101] Curiously, the reaction of $CpFe(CO)_2SiMe_3$ with Ar_2SiH_2 gave substantial amounts of exchange products, $CpFe(CO)_2SiAr_2H$ (Ar = 2,4,6-$C_6H_2(i\text{-}Pr)_3$, 2,6-$C_6H_3Et_2$, 2,4,6-$C_6H_2Me_3$; properties were not described) although when Ar = 2,4,6-$C_6H_2(i\text{-}Pr)_3$, a small yield of **3−52** was obtained.[101]

The purpose of the remaining part of this section is to outline the types of processes that may occur when a di- or polynuclear complex reacts with a hydrosilane and will focus on the fate of the M−M bond in the original complex. Derivatives that already contain M−M bonds and bridging groups often react with hydrosilanes to replace one of the bridging groups and the M−M bond remains intact. With $Fe_2(CO)_9$ and $PhSiH_3$ two of the bridging CO's were replaced by PhSiH units although the secondary silane Ph_2SiH_2 gave a different product that contained a Ph_2Si bridge with an agostic SiHFe interaction as well as a terminal $SiPh_2H$.[56] Many M−M-bonded derivatives interact with hydrosilanes to give products with agostic Si−H to metal interactions and such derivatives will be described in section VI. The iron dimer $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)FeCp^*(CO)$ also reacted with secondary silanes but disproportionation of R_2SiH_2 occurred to give R_3SiH and $RSiH_3$ and it is the latter that provided the RSiH unit that replaced the bridging CO to give **3−53**.[102] Ruthenium dimers have been studied and although the dimer unit remains the products are less easily classified. Examples are **3−58b**,[108] **3−59**,[108] **4−175a,b**,[107,175,202] and **4−176**.[203]

The reaction of $M_2(CO)_{10}$ (M = Mn, Re) can result in cleavage of the M−M bond to give $(OC)_5MSiR_3$ (see examples **4−52** to **4−55**,[145,146] **4−58**,[148] **4−59**,[149] and **4−60**[146]). Mn triad complexes with bridging groups can react with retention of the M−M bond as is illustrated with $Re_2(CO)_8[\mu\text{-}C(H)CBu](\mu\text{-}H)$ and $HSi(OMe)_3$, although the product **4−68**[153] also contained a SiOMe bridge between the two Re atoms that could lend additional stabilization. Another example is given by the reaction of the Mn dimer $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ ($L_2 = Ph_2PCH_2PPh_2$) which produces $[Mn_2(\mu\text{-}H_2SiPh_2)(CO)_6(\mu\text{-}L_2)]$ for which agostic SiHMn interactions have been proposed (section VI).[95]

With more metals in the reacting complex, several reaction pathways are possible. A triangular M_3 unit may react with retention of the cycle or by ring opening to give an angular M_3 system (two terminal metal centers are “cis” coordinated to the internal M). If isomerization of the central M occurs, then a linear M_3 product is possible. Additional isomers result in the linear M_3 unit if isomerization of the terminal metal centers occurs. Other pathways involving M−M cleavage are possible to give both metal dimers and metal monomer products.

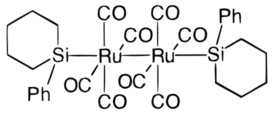
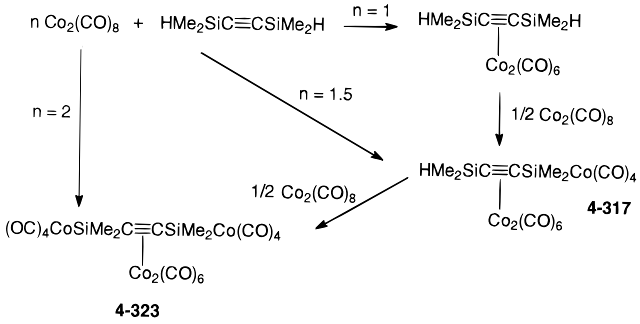


Figure 9. Structure of **4−181**.

Scheme 21

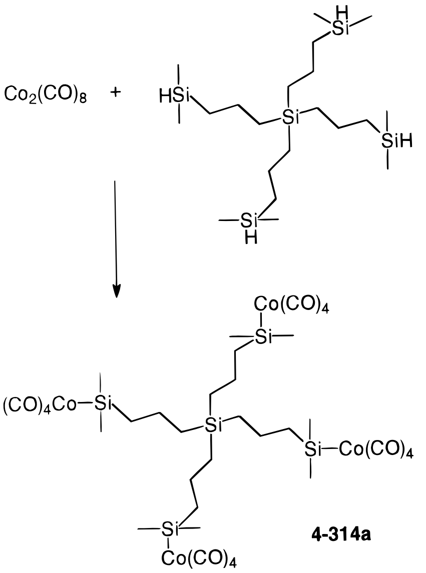


The reaction of $Ru_3(CO)_{12}$ with $HSiCl_3$ for short time periods resulted in the isolation of a silyl derivative with the trinuclear skeleton intact [$(OC)_9(\mu\text{-}H)_3Ru_3(SiCl_3)_3$ (**4−185**[148,185])] with three hydride bridges and a silicon substituent at each Ru, as well as the ring-degraded metal dimer $(OC)_8Ru_2(SiCl_3)_2$ (**4−179**[185,204]). If the reaction was conducted for prolonged periods of time the dimer disappeared and was replaced with the monomeric, *cis*-disilyl-substituted product *cis*-$(OC)_4Ru(SiCl_3)_2$ (**4−131**[148,163,184,185]). The yield of the trinuclear complex did not change over time. The trinuclear skeleton of $Ru_3(CO)_{12}$ also remained intact on reaction with $(C_5H_4SiMe_2H)_2Fe$ (see product **4−183**[206]). However, with $Ph_2PCH_2SiMe_2H$ a centrosymmetric dimer with the PCH_2Si unit bridging the two metal centers (**4−182**[205]) was obtained. In contrast, reaction of a silacyclohexane with $Ru_3(CO)_{12}$ provided a diruthenium complex with a linear Si−Ru−Ru−Si sequence (**4−180**[195] and **4−181**,[195] Figure 9).

The trinuclear osmium complex, $Os_3(CO)_{12}$, reacts with $HSiCl_3$ (and similarly with $HSiMeCl_2$) to give the osmium analogue, $(OC)_9(\mu\text{-}H)_3Os_3(SiCl_3)_3$ (**4−208**[148,185]) of the previously described Ru complex **4−185**.[148,185] However, if the reaction with $HSiCl_3$ is conducted at similar temperatures in the presence of CO, ring opening occurred to give the linear Si−Os−Os−Os−Si sequence in **4−198**.[148,194] A centrosymmetric dimer, **4−196**,[205] was also obtained from $Ph_2PCH_2SiMe_2H$ with $Os_3(CO)_{12}$ [as was also observed for $Ru_3(CO)_{12}$]. In reaction of phenylsilacyclohexane and $Os_3(CO)_{12}$, degradation to the *trans*-disilaosmium derivative $(OC)_4Os[SiPh(CH_2)_5]_2$ (**4−159**[195]) occurred. The triosmium complexes $Os_3(\mu\text{-}H)_2(CO)_{10}$, $\{Os_3(CO)_{11}\}_2(\mu\text{-dppe})\}$, and $Os_3(CO)_{10}(MeCN)_2$ have been reacted with silanes with retention of the Os_3 cyclic unit in products **4−199** to **4−206**[57,211−214] and **4−209**.[185]

Several cobalt cluster complexes were prepared from silafunctional alkynes and $Co_2(CO)_8$ including complexes **4−317** through **4−323a**,[122,276−282] and the nature of the product formed depended upon the stoichiometry of the reaction (Scheme 21[276]). For example, when 1 equiv of $Co_2(CO)_8$ was reacted with the alkyne, $HMe_2SiC{\equiv}CSiMe_2H$, coordination of two cobalt centers to the triple bond occurred to give the μ-alkyne complex, $(OC)_6Co_2\text{-}\eta^2\text{-}[HMe_2SiC{\equiv}CSiMe_2H]$. Addition of 0.5 equiv of $Co_2(CO)_8$ [or a total of 1.5 equiv of $Co_2(CO)_8$] to the μ-alkyne complex produced **4−317** where oxidative addition of one of the Si−H bonds to Co occurred.[276] Addition of 2 equiv of $Co_2(CO)_8$ to $HMe_2SiC{\equiv}CSiMe_2H$ (or 1 equiv to $(OC)_6Co_2\text{-}\eta^2\text{-}[HMe_2SiC{\equiv}CSiMe_2H]$) gave the tetracobalt species **4−323a** where both Si−H bonds are replaced with Si−Co bonds.

The silicon dendrimer, $[HSiMe_2(CH_2)_3]_4Si$, reacted with $Co_2(CO)_8$ to give a tetrametallic macromolecule, $[(OC)_4CoSiMe_2(CH_2)_3]_4Si$, complex **4−314a**[274] (eq 17). Thus, oxidative addition of the Si−H bond to the Co center allowed for modification of the periphery of the dendrimer.



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IV. Solid-State Structures

Structural data reported for silyl−transition-metal complexes prepared from hydrosilanes and that include only those derivatives with “classical” M−Si, M−H, and/or Si−H bonds are summarized in Table 5.[306−449] Complexes with “nonclassical” MHSi interactions are discussed in section VI. Additional structural data for silylmetal complexes prepared by routes other than those with hydrosilanes and reported in the Cambridge Data Base are included in the footnotes of Table 5 as are data for complexes reported before 1980.[450]

Of the 30 metals in groups 3−12, only 6 (TM = Y, La, V, Tc, Ag, and Cd) do not have silyl complexes characterized by diffraction methods. The range of silicon−transition-metal bond lengths (2c−2e interactions) that have been reported for the remaining metals are summarized in Table 6 which also includes the number of independent TM−Si bond length data (entries in Table 5 as well as the footnotes). For most of the metals, the difference (lowest value to highest value) in TM−Si bond lengths falls between 0.1 and 0.2 Å with a difference of less than 0.1 Å for six of the metals and of greater than 0.2 Å for four of the metals. The mean values are summarized in Figure 10 to illustrate the periodic

Table 5. Structural Data for Silylmetal Complexes*

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
Scandium Triad [1b]				
Titanium Triad				
$Cp_2(Me_3P)TiSiH_2Ph$ (**2-1**)		[1c]	2.650 (1) [1d]	34
$Cp_2(Et_3P)TiSiH_2Ph$ (**2-2**)		1.50 [1e]	2.634 (5)	33
$Cp_2(Me_3P)TiSiHMePh$ (**3-2**)		[1f]	2.646 (2)	34
$Cp_2(Me_3P)TiSiHPh_2$ (**3-3**)		1.50 [1g]	2.652 (1)	33
$Cp_2(Me_3P)(H)ZrSiHPh_2$ (**3-6**)		—	2.707 (5)	83
$Cp_2(Me_3P)(H)ZrSiPh_3$ (**4-2**)	1.94 (5)		2.721 (2)	82
$CpCp^*(H)Hf[SiH(SiMe_3)_2]$ (**3-7**)	[1h]	[1h]	2.744 (1)	36
Titanium Triad Dimers				
$Cp_2Zr(SiHPhMe)(\mu\text{-}H)_2(PhMe_2Si)\text{-}ZrCp_2$ (**3-13***) [1i]	1.94 (10) 1.95 (10)	—	2.806 (4)	39
$Cp_2Zr(SiHPh_2)(\mu\text{-}H)_2(Ph_2HSi)ZrCp_2$ (**3-14**)	$Zr\text{-}H_{br}$ 1.96 (3) 2.01 (2)	1.43(2)	2.7590 (8)	183
Other derivatives [1j]				
Vanadium Triad				
$(C_5H_4SiMe_3)_2(H)_2NbSiPh_2H$ (**3-16**)	1.77 (6) 1.76 (6)	2.37(6) [Si⋯HNb] 2.21(6) [Si⋯HNb] [1k]	2.616 (3)	39
$Cp_2(H)Nb(SiMe_2Cl)_2$ (**4-9**)	1.756	2.056	2.5974 (10)	136
$Cp_2(Me_3P)TaSiH(t\text{-}Bu)_2$ (**3-17**)		[1l]	2.740 (1)	137
$Cp_2(H^2)Ta(SiH^1Me_2)_2$ (**3-18**)	[1m]	1.45 [1m]	2.633 (2) 2.624 (2)	13a
	1.785 (15)	1.483 (22)($Si\text{-}H^1$) 2.189, 2.190 (17) ($Si\cdots H^2$)	2.644 (14)	13b
$Cp_2(Me_3P)TaSiMe_3$ (**4-11**)			2.639 (4)	13
$Cp_2(H)_2TaSiMe_2Ph$ (**4-16**)	[1n]		2.651 (4)	135
Other derivatives [1o]				
Chromium Triad				
$(\eta^6\text{-}C_6H_5F)(OC)_2Cr(SiCl_3)_2$ (**4-24**) [1p]			2.376 (2) 2.377 (2)	138
$(\eta^6\text{- }Me_3C_6H_3)(OC)_2Cr(SiCl_3)_2$ (**4-25**) [1q]			2.383 (3), 2.382 (3) 2.382 (3), 2.371 (3)	137
$(\eta^6\text{-}C_6H_5F)(OC)(H)_2Cr(SiCl_3)_2$ (**4-30**) [1p]	1.42 (7) 1.52 (6)	1.75 (7) 1.60 (6)	2.361 (2) 2.368 (2)	138
$(\eta^6\text{-}C_6H_3Me_3)(OC)_2Cr(H^1)(H^2)\text{-}(Si^1Cl_3)(Si^2Cl_3)$ (**4-31**)	$Cr\text{-}H^1$ 1.53 (5) $Cr\text{-}H^2$ 1.59 (4)	$Si^1\text{-}H^1$ 1.66 (4) $Si^1\text{-}H^2$ 1.87 (4) $Si^2\text{-}H^2$ 1.95 (4)	2.365 (1) $Cr\text{-}Si^1$ 2.373 (1) $Cr\text{-}Si^2$	138
$Cp_2(H)MoSiHMe_2$ (**3-21**) [1q]	1.72 (6) 1.63 (6)	1.33 (7) 1.41 (9)	2.538 (2) 2.541 (6)	90
$(C_5H_4Me)_2(H)MoSiH(t\text{-}Bu)_2$ (**3-24**)	1.68 (3)	1.42 (3)	2.604 (1)	90
$Cp_2(H)MoSiMe_2Cl$ (**4-33**)	1.83 (5)		2.513 (1)	90

Table 5 (Continued)

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
$(C_5H_4Me)_2(H)MoSiMe_3$ (**4-35**)	1.71 (4)		2.560 (1)	90
$\{H_2Mo(Si^1H_2Ph)Si^2Ph[(C_6H_4)PhP\text{-}CH_2CH_2PPh_2]_2\}$ (**2-19b**)			2.620 (2) Mo-Si^1 2.559 (2) Mo-Si^2	42
$Cp_2W(SiMe_3)SiH(t\text{-}Bu)_2$ (**3-25**)		1.42 (5)	2.599 (1) 2.644 (1)	90
$Cp_2W(SiMe_3)Si(i\text{-}Pr)_2Cl$ (**5-1**) [1r]			2.602 (1) 2.594 (1)	90
$Cp_2(H)WSiMe_3$ (**5-2**) [1s]	[1n]		2.560 (1)	90
$Cp(OC)_2W(Me_2Si\cdots OMe\cdots SiMe_2)$ (**4-44a**)			2.490 (3)	142
$Cp(OC)_2W(Me_2Si\cdots NEt_2\cdots SiMe_2)$ (**4-44b**)			2.502 (2) 2.501 (2)	142
Other derivatives [1t]				
Manganese Triad				
$[(Cp^*)(OC)_2(H)Mn]_2SiH_2$ (**1-5**)		[1u]	2.434 (3)	23
$(Cp')(OC)_2Mn(SiCl_3)_2$ (**5-3**) [1v]			2.320 (2) 2.326 (2)	331a
$(\eta^5\text{-}Cp)(Me_2PCH_2CH_2PMe_2)(H)Mn(SiHPh_2)$ (**3-33**)	[1w]	[1w]	2.319 (4)	45
$(OC)_5MnSiPh_3$ (**5-4**) [1x, 1q]			2.509 (2) 2.498 (2)	331c
$(Cyp_3P)_2(H)_5Re(SiH_2Ph)_2$ (**2-29**)	[1y]	[1y]	2.501 (2) 2.490 (2)	46
$[Ph(i\text{-}Pr)_2P](H)_5Re(SiHPh_2)_2$ (**3-37**) [1z]	1.704 (14) 1.707 (13) 1.676 (12) 1.684 (13) 1.698 (11)	2.048 (12) 2.065 (14) 2.146 (12) 1.510 (12) 1.493 (11)	2.500 (8) 2.510 (9)	46
$(OC)(PhMe_2P)_3(H)_2Re(SiPh_3)$ (**4-61**)	[1n]		2.451 (3)	150
$(OC)(PhMe_2P)_3(H)_2Re(SiPh_3)\cdot THF$ (**5-5**)	[1n]		2.434 (2)	150
$(Ph_3P)_2(H)_6Re(SiPh_3)$ (**4-63**)	[2a]		2.474 (4)	94
$(Ph_3P)_2(H)_6Re(SiPh_3)\cdot CH_2Cl_2$ (**5-6**)			2.475 (4)	94
$(Ph_3P)_2(H)_5Re(disil)$ (**4-67**)	1.60 (6) [2b] 1.52 (7) [2b] 1.52 (9) [2b]		2.495 (2) 2.489 (3)	152
Manganese Triad Dimers				
$(OC)_8Re_2[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (**4-68***)	1.9 (1), 1.8 (1)		2.477 (3)	153
Other derivatives [2c]				
Fe Triad: Mononuclear				
$(OC)_4Fe{=}SiArPh$ (**3-41**) $Ar = C_6H_4CH_2NMe_2\text{-}2$			2.259 (1)	91
$(OC)_3[EtO(Me_2N)_2P]Fe{=}Si(OEt)_2 \leftarrow HNMe_2$ (**4-70**)			2.218 (2)	154
$Cp(OC)_2FeSiCl_3$ (**4-75**)			2.216 (1)	157

Table 5 (Continued)

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
$(\eta^6\text{-}C_6H_6)(H)_2Fe(SiCl_3)_2$ [2d] **(5-7)**	1.45 (7)		2.210 (3) 2.207 (3)	162
$(\eta^6\text{-}C_6H_5CH_3)(H)_2Fe(SiHCl_2)_2$ **(3-45b)**	1.1 (1) 1.31 (8)	1.538 (8) 1.5 (1)	2.219 (4) 2.222 (4)	48
$(\eta^6\text{-}C_6H_5CH_3)(H)_2Fe(SiF_3)_2$ **(4-79)**	[1n]		2.251 (5) 2.261 (5)	160
$(\eta^6\text{-}C_6H_5CH_3)(H)_2Fe(SiCl_3)_2$ **(4-80)**	1.50 (6) 1.72 (9)		2.222 (2) 2.218 (2)	161, 162
$[\eta^6\text{-}p\text{-}C_6H_4(CH_3)_2](H)_2Fe(SiCl_3)_2$ **(5-8)** [2d]	1.40 (7); 1.24 (8)		2.226 (2) 2.222 (2)	162
$(OC)_3(Ph_3P)(H)Fe(SiPh_3)$ **(4-91)** [2e] (*trans-mer*)			2.343 (12)	167
$[(OC)_3(Ph_3P)Fe(SiCl_3)]PPN$ **(5-9)** [2f]			2.197 (3)	171
$\{(OC)_3[(PhO)_3P]Fe(SiCl_3)\}PPN$ **(5-10)** [2f]			2.206 (4)	171
$(OC)_2(dppe)(H)FeSiMe_3$ **(4-104)**	1.52 (5)		2.360 (2)	172
$(OC)(dppe)(H)_3FeSi(OEt)_3$ **(4-108)**			2.250 (4) [2.246 (4)]	49 [173]
$Cp(Me_3P)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ **(4-112b)**			2.335 (1)	177
$Cp(Ph_3P)Ru(SiMe_2\cdots OMe\cdots SiMe_2)$ **(4-114)**			2.333 (5) 2.333 (4)	178
$Cp^*(Me_3P)_2RuSi[S(p\text{-}Tol)]_3$ **(4-120)**			2.350 (1)	183
$Cp^*(i\text{-}Pr_3P)(H)Ru(\eta^2\text{-}CH_2{=}SiPh_2)$ **(5-11)** [1q, 2g]	[1n]		2.382 (4) 2.365 (5)	336
$Cp^*(i\text{-}Pr_3P)(H)_2RuSiHMesCl$ **(5-12)** [2h]	1.50 (9); 1.59 (7)	1.48 (8)	2.302 (3)	50
mer-$(OC)_3(Ph_3P)(H)RuSiPh_3$ **(4-134)**			2.446 (2)	167
$(OC)_2(H)Ru[SiMe(CH_2CH_2CH_2\text{-}PPh_2)_2]$ **(4-136)**	[1n]		2.457 (7)	186
$(OC)(Ph_3P)_2ClRuSiEt_3$ **(4-140b)**			2.389 (5)	188b
$Cp^*(Me_3P)(H)Os\{C_6H_3(3\text{-}Me)(6\text{-}S)\text{-}Si[S(p\text{-}Tol)]_2\}$ **(4-152c*)**	1.59 (5)		2.382 (2)	192
$(OC)(i\text{-}Pr_3P)_2(H)_3Os(SiHPh_2)$ **(3-51)**	[1n]	[1n]	2.448 (2)	52
$(OC)_2(Ph_3P)_2(H)OsSiEt_3$ **(4-160)**	[1n]		2.493 (2)	100
$(OC)_2Os(SiMe_2CH_2CH_2PPh_2)_2$ **(4-162)**			2.472 (4) 2.471 (2)	187
$OC(Ph_3P)_2(Cl)OsSiCl_3$ **(4-166b)**			2.273 (6)	197
Fe Triad: M_2 and M_3				
$Cp_2(OC)_3Fe_2[\mu\text{-}SiH(t\text{-}Bu)]$ **(2-46a*)** [2i]		1.34(4)	2.272 (1) 2.270 (1)	47
$Cp_2(OC)_2(\mu\text{-}OC)Fe_2[\mu\text{-}Si(H)CHPh_2]$ **(2-46b)**	[2j]	[2j]	2.267 (1) 2.257 (1)	54
$Cp_2(OC)_2Fe_2Si(Ar)_2$ **(3-52*)** $Ar = 2,4,6\text{-}C_6H_2(i\text{-}Pr)_3$			2.351 (3)	101

Table 5 (Continued)

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
$[(OC)_8Fe_2]_2Si$ (**1-6***) [2k]			2.348 (4), 2.345 (4), 2.352 (4), 2.342 (4)	24, 25
$[(OC)_4(Me_3P)_4(\mu\text{-}H)Fe_2(\mu\text{-}SiCl_2)]^+$ $[(OC)_4FeSiCl_3]^-$ (**5-13***) [2l]	1.77, 1.63		2.255 (3), 2.242 (3) (cation) 2.238 (3) (anion)	337
$(OC)_9Fe_3[\mu_3\text{-}Si\{Fe(CO)_2Cp\}]_2$ (**1-7***)			Si-Fe^3: 2.296 (1), 2.294 (1), 2.324 (1), 2.315 (1), 2.306 (1), 2.301 (1) Si-Fe^2: 2.246 (1), 2.255 (1)	25
$[(OC)_4Fe]_2(\eta\text{:}\eta\text{-}Ph_2SiOSiPh_2)$ (**4-174**)			2.412 (2) 2.426 (2)	56
$Cp^*{}_2Ru_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)(\mu\text{-}H)$ (**3-58c***) [1q]	[1n]		2.309 (10) 2.288 (10) 2.316 (10) 2.309 (12)	108
$Cp_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}SiMe_2)(H)\text{-}$ $(SiMe_2Ph)_2(CO)_2$ (**4-175***) [1q]			2.417 (2) 2.422 (2)	175
$Cp(OC)(Ph_3Si)Ru(\mu\text{-}CH_2)Ru(SiPh_3)\text{-}$ $(CO)Cp$ (**5-14**) [2m]			2.429 (2)	202 175
$(OC)_6Ru_2[Me_2SiCH_2PPh_2]_2$ (**4-182***)			2.465 (1)	205
$(OC)_{10}(\mu\text{-}H)_2Ru_3\text{-}$ $(SiMe_2C_5H_4FeC_5H_4SiMe_2)$ (**4-183***)	1.80, 1.93, 1.66 (5)		2.459 (4)	206
$[(OC)_8(\mu\text{-}H)_2(\mu\text{-}C_4H_4N_2)Ru_3(SiEt_3)_2]$ (**4-186***)	Ru^1-H^2, 1.77 (9) Ru^1-H^1, 1.7 (1) Ru^2-H^2, 1.7 (1) [2n] Ru^3-H^2, 1.79 (9)		2.455 (5) [2o] 2.460 (6)	207
$(OC)_8(\mu\text{-}H)_2(\mu_3,\eta^2\text{-}ampy)Ru_3SiEt_3$ (**4-187***)	Ru^1-H^2, 1.4 (1) Ru^3-H^2, 1.9 (1) Ru^1-H^1, 1.7 (1) Ru^2-H^1, 1.8 (1)		2.435 (4)	208
$[(OC)_6(Ph_3P)(\mu_3\text{-}ampy)\{\mu,\eta^1\text{:}\eta^2\text{-}$ $PhC{=}C(H)Ph\}Ru_3\{Si(OMe)_3\}]$ (**4-192***)	Ru^1-H^1, 1.86 (6) Ru^2-H^1, 1.74 (6)		2.432 (2)	209
$(OC)_6Os_2[Me_2SiCH_2PPh_2]_2$ (**4-196***)			isomorphous to 4-182	205
$(OC)_{12}Os_3(SiCl_3)_2$ (**4-198***)			2.377 (3)	194
$[(OC)_{10}(\mu\text{-}H)Os_3(o\text{-}MeHSiC_6H_4CH_2\text{-}$ $PPh_2)]$ [2p] (**5-15**)	[1n]	—	2.425 (7)	213
$(OC)_{10}(\mu\text{-}H)_2HOs_3(SiHPh_2)_2$ (**3-61***)	[2q]	—	2.455 (2)	109
$[\{(OC)_{10}HOs_3[Si(OMe)_3]\}_2(\mu\text{-}dppe)]$ (**4-201***)	[1n]		2.404 (6)	212
$(OC)_{10}(\mu\text{-}H)Os_3(o\text{-}Ph_2PC_6H_4CH_2\text{-}$ $SiMe_2)$ (**4-202***)	[2r]		2.444 (4)	213
$[(OC)_{10}(\mu\text{-}H)Os_3(o\text{-}Me_2SiC_6H_4\text{-}$ $CH_2PPh_2)]$ (**4-203***)	[2r]		2.453 (5)	213
$[(OC)_{10}(\mu\text{-}H)_2Os_3\{SiMe_2(2\text{-}py)\}_2]$ (**4-204***)	[2r]		2.434 (4), 2.431 (4)	57
$[(OC)_{10}(\mu\text{-}H)(CH_3CN)Os_3\text{-}$ $\{SiMe_2CH_2C_6H_4Br\text{-}o\}]$ (**4-205***)	[2r]		2.452 (5)	57

Table 5 (Continued)

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
$(OC)_{10}(MeCN)(\mu\text{-}H)Os_3[Si(OEt)_3]$ **(4-206*)**	[2s]		2.39 (1)	211, 214
$(OC)_9(\mu\text{-}H)_3Os_3(SiPh_3)$ **(4-207*)**	$Os^1\text{-}H^A$, 1.99 (5) $Os^3\text{-}H^A$, 1.76 (5) $Os^1\text{-}H^B$, 1.92 (7) $Os^3\text{-}H^B$, 1.82 (7) $Os^1\text{-}H^C$, 1.89 (7) $Os^2\text{-}H^C$, 1.56 (8)		2.429 (2)	215
$(OC)_9(\mu\text{-}H)_3Os_3(SiCl_3)_3$ **(4-208*)**	[1n]		2.389 (12) 2.394 (14) 2.367 (13)	194
$(OC)_9(\mu\text{-}H)_3Os_3(SiMeCl_2)_3$ **(4-209)** [1q]	[2t]		2.420 (5) 2.400 (5)	185
$(OC)_8(\mu\text{-}H)_3Os_3(o\text{-}Me_2SiC_6H_4CH_2\text{-}PPh_2)$ **(4-210*)**	[2r]		2.432 (6)	213
Other derivatives [2u]				
Cobalt Triad- Mononuclear				
$(OC)_4Co(Si_8H_7O_{12})$ **(4-212)**		[2v]	2.285 (1)	217
$(OC)_2(Ph_3P)_2CoSiMePh_2$ **(4-221)**			2.368 (1)	222
mer-$(Me_3P)_3Cl(H)RhSiHPh_2$ **(3-62a)**	[2w]		2.313 (4)	110
mer-$(Me_3P)_3Cl(H)Rh[SiH(p\text{-}MeOC_6H_4)_2]$ **(3-62b)**	[2w]		2.319 (2)	110
mer-$(Me_3P)_3Cl(H)Rh[SiH(p\text{-}FC_6H_4)_2]$ **(3-62c)**	[2w]		2.311 (2)	110
mer-$(Me_3P)_3Cl(H)Rh[SiH(p\text{-}CF_3C_6H_4)_2]$ **(3-62d)**	[2w]		2.312 (3)	110
$Cp^*(H)_2Rh(SiEt_3)_2$ **(4-234)** [2x]	1.578 (3) 1.583 (3)		2.379 (2)	230, 231
$(Me_3P)_3RhSiPh_3$ **(4-239a)** [2y]			2.317 (1)	234
mer-$(Me_3P)_3(PhS)(H)RhSiPh_3$ **(4-239b)**	1.82 [2z]		2.383 (2)	112
mer-$(Me_3P)_3[(p\text{-}Tol)S](H)RhSiPh_3$ **(4-239c)**	1.58 [2z]		2.379 (2)	112
mer-$(Me_3P)_3(PhS)(H)RhSi(OMe)_3$ **(4-239d)** [3a]	[3b]		2.229 (3) 2.293 (3)	112
mer-$(Me_3P)_3(C_6F_5)(H)RhSi(OEt)_3$ **(4-240)**	[3c]		2.325 (4)	235
fac-$(Me_3P)_3(H)Rh(SiMe_2CH_2CH_2\text{-}SiMe_2)$ **(4-242)**	1.53 (4)		2.383 (2) 2.389 (2)	237
$(i\text{-}Pr_3P)_2Cl(H)RhSi(C{\equiv}CPh)_3$ **(4-243b)**	1.22 [2z]		2.229 (3)	239
$(i\text{-}Pr_3P)_2Cl(H)RhSiPh_3$ **(4-243c)**	1.12 [2z]		2.299 (2)	239
$(Me_3P)(dtbpm)RhSi(OEt)_3$ **(4-249)** [3d]			2.325 (2)	242
$(OEP)RhSiEt_3$ **(4-251)** [3e]			2.32 (1)	244
fac-$(dmesiqn)_3Rh$ **(4-255a*)** [3f]			2.278 (1) 2.290 (1) 2.301 (1)	246

Table 5 (Continued)

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
$OC(dppe)(H)Ir(Si^1HMe_2)(Si^2Me_2Cl)$ **(3-71)**	1.49 (5)	[3g]	Ir-Si[1] 2.418 (3) Ir-Si[2] 2.394 (3)	60
$(Me_3P)_3(H)_2IrSiHPh_2$ **(3-75)**	1.218 1.215 [3h]	1.184	2.361 (3)	118
(*i*-$Pr_3P)(TFB)(H)_2Ir{=}SiPh_2(\leftarrow OTf)$ **(3-76)**	[3i]		2.337 (2)	119
$Cy_3P(acac)Ir\{C[CH(OCH_3)OSiPh_2$ **(3-77c*)** [3j]			2.264 (2)	120
$Cp^*(Me_3P)Ir(\eta^2\text{-}SiPh_2{=}CH_2)$ **(4-257)** [3k]			2.317 (2)	249
$Cp^*(H)_2Ir(SiEt_3)_2$ **(4-262)** [3l]	1.593 (3) 1.595 (3)		2.390 (1)	231, 252
$(OC)[($*p*-$Tol)_3P]_2(H)_2IrSiMe_2Ph$ **(4-270)**	1.32 (5) 1.44 (5)		2.414 (2)	255
$OC(Ph_3P)Cl(H)Ir(SiMe_2CH_2CH_2$-$PPh_2)$ **(4-271)** [3m]	[1n]		2.411 (12)	256
$OC(dppe)(H)Ir(SiMe_2Cl)_2$ **(4-280a)**	[1n]		2.397 (2) 2.396 (2)	60
fac-$(Me_3P)_3(H)MeIrSiEt_3$ **(4-282)** [3n]	[1c]		2.424 (2)	262
fac-$(Me_3P)_3(H)MeIrSiPh_3$ **(4-283)** [3n]	[1c]		2.381 (3)	262
fac-$(Me_3P)_3(H)_2IrSi($*t*-$Bu)_2Cl$ **(4-287)**	1.365 [3o] 1.244		2.291 (3)	118
fac-$(Me_3P)_3(H)_2IrSiPh_3$ **(4-288)** [3p]	[1n]		2.382 (4)	118
trans-$(Et_3P)_2Cl(H)Ir[SiOH($*i*-$Pr)_2]$ **(4-290)**	[1n]		2.313 (6)	265
$(Ph_3P)_2(H)_3Ir(disil)$ **(4-294*)**	[1n]		2.437 (1) 2.430 (1)	267
$Cl(H)Ir[SiMe(CH_2CH_2CH_2PPh_2)_2]$ **(4-296a)**	[1n]		2.287 (3)	186
$ClIr[SiMe_2CH_2CH_2PPh_2]_2$ **(4-296b)**			2.302 (7) 2.315 (8)	256
$Cy_3P(acac)(H)IrSiEt_3$ **(4-297b)** [3q]	1.44 (4)		2.307 (1)	61
$Ph_3As(cod)(H)_2IrSiEt_3$ **(4-299)**	1.65 [3r] 1.57		2.414 (2)	269
$(cod)Cl(H)Ir[SiMe_2CH_2CH_2PPh_2]$ **(4-300)**	[1n]		2.364 (5)	256
fac-$(dmesiqn)_3Ir$ **(4-301*)**			[3f]	246
Co Triad: M_2 and Higher				
$[(OC)_7Co_2]_2Si$ **(1-8*)**			Co^1-Si 2.301 (1) Co^2-Si 2.276 (1)	27
$(OC)_{20}Co_6Si_3H_2$ **(2-61*)** [3s]			Co^1-Si^1 2.282 (2) Co^2-Si^1 2.321 (2) Co^3-Si^1 2.291 (2) Co^4-Si^1 2.293 (3) Co^1-Si^2 2.298 (2) Co^2-Si^2 2.289 (3) Co^3-Si^3 2.281 (2) Co^4-Si^3 2.315 (2) Co^5-Si^2 2.374 (2) Co^6-Si^3 2.371 (2)	62

Table 5 (Continued)

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
$(OC)_{14}Co_4Si_2S$ (**2-63***) [3t]			Co^1-Si^1 2.295 (2) Co^3-Si^1 2.308 (2) Co^4-Si^1 2.291 (2) Co^2-Si^2 2.301 (2) Co^3-Si^2 2.296 (2) Co^4-Si^2 2.307 (2)	62
$(OC)_{11}Co_4[\mu^4$-Si $Co(CO)_4]_2$ (**2-67***) [3u]			Co^1-Si^1 2.330 (2) Co^2-Si^1 2.351 (2) Co^3-Si^1 2.360 (2) Co^4-Si^1 2.308 (2) Co^5-Si^1 2.347 (2)	65
$(OC)_{11}Co_4(\mu_4$-$SiMe)_2$ (**2-68***) [3u]			Co^1-Si^1 2.320 (2) Co^2-Si^1 2.303 (2) Co^1-Si^2 2.311 (2) Co^2-Si^2 2.302 (2)	66
$(OC)_6Co_2[\eta^2$-$PhC{\equiv}CSiMeCl$-$Co(CO)_4]$ (**4-320***)			2.338 (1)	280
$(OC)_2(dppm)_2(H)_3Rh_2(\mu$-$SiHEt)$ (**2-72***)		[3a]	Rh^1-Si 2.342 (1) Rh^2-Si 2.354 (2)	68
$(OC)_2(dppm)_2Rh_2(\mu$-$SiHPh)_2$ (**2-73***)		—	Rh^1-Si^1 2.347 (1) Rh^2-Si^1 2.354 (2) Rh^1-Si^2 2.368 (2) Rh^2-Si^2 2.335 (1)	67
$(dippe)_2Rh_2(\mu$-$SiHBu)_2$ (**2-74***) [3v]		1.45 (3) [3w]	2.334 (1)	70
$(OC)_2(dppm)(\mu$-$H)Rh_2$-$(Ph_2PCH_2PPhSiEt_2)$ (**3-87***) [3x]	[3a]		2.347 (3)	68
$\{[(i$-$Pr)_3P](Cl)HRh[Si(CH_2Ph)_3]\}_2$ (**4-314b***) [3x]	[1n]		Rh^1-Si^1 2.315 (5) Rh^1-Si^2 2.301 (5)	238
$(H)_2Rh_2(SiMe_2C_6H_5)_4$ (**4-315***) [3y]	—		Rh-Si^1 2.294 (6) Rh-Si^2 2.328 (6)	275
$[(i$-$Pr_3P)(H)_2Rh][\mu$-$Si(CH_2CH_2Ph)_2][Rh(H)_2(i$-$Pr_3P)]$ (**4-323b***) [3z]	[1n]		2.365 (3) 2.367 (3)	238
$\{[(i$-$Pr)_3P](H)RhSiAr_3\}_2(\mu$-$H)(\mu$-$Cl)$ (**4-323c***) Ar = $C_6H_4OCF_3$-*p*	Rh^1-H^1 1.84 [4a] Rh^2-H^1 1.77		Rh^1-Si^1 2.279 (3) Rh^2-Si^2 2.273 (3)	239
$\{[(i$-$Pr)_3P](H)Rh\}_2(\mu$-$H)(\mu$-$Cl)[\mu$-$(i$-$Pr)_2Si$-O-Si-$(i$-$Pr)_2]$ (**4-323d***)	Rh^1-H^1 1.64 [2z] Rh^2-H^1 1.67 Rh^1-H^2 1.26 Rh^2-H^3 1.17		Rh^1 – Si^1 2.286 (3) Rh^2 – Si^2 2.295 (3)	239
$(OC)_2(dppm)_2(H)_2Ir_2(\mu$-$SiHPh)$ (**2-75***) [4b]	Ir^1-H 1.67 [4c] Ir^2-H 1.72	[3a]	Ir^1-Si 2.343 (5) Ir^2-Si 2.349 (5)	71
$(OC)_2(dppm)_2(H)_2Ir_2(\mu$-$SiPh_2)$ (**3-89***) [4d]	1.63 (9)		2.371 (4)	71
Other derivatives [4e]				
Ni Triad				
$(dmpe)Pd(SiH_2C_6H_4SiH_2)_2$ (**2-79**) [4f]		[4g]	2.345 (2) 2.394 (4)	72
$(dcpe)Pd(SiHMe_2)_2$ (**4-329a**) [4h]		[3c]	2.3563 (9) 2.359 (1)	73
trans-$(Cy_3P)_2(H)PtSiH_3$ (**1-10**)	[4i]	[4i]	2.382(3)	29
$(Et_3P)_2Pt(SiH_2C_6H_4SiH_2)_2$ (**2-83**)		[3c]	2.428 (2) 2.383 (2) 2.430 (2) 2.376 (2)	75

Table 5 (Continued)

Complex	M-H[1a]	Si-H[1a]	M-Si[1a]	Ref
fac-(dmpe)(H)Pt(SiH_2Ph)$_3$ (**2-85**)	[3c]	[3c]	2.385 (5) 2.406 (5) 2.362 (5)	74
(dcpe)Pt(SiH_2SiH_3)$_2$ (**2-86**) [4j]				76
cis-(Ph_3P)$_2$(H)Pt[SiH(R_F)$_2$] (**3-93**) [4k]	1.712	1.247	2.337 (2)	127
trans-($PhMe_2P$)$_2$ClPtSiPh_3 (**5-16**) [4l]			2.321 (2)	418
cis-(Et_3P)$_2$(H)PtSiPh_3 (**4-331b**) [4m]	1.75 [2z]		2.357 (3)	290
cis-(Ph_3P)$_2$(H)PtSiPh_3 (**4-333**) [4n]	—	[1n]	2.357 (3)	292
(dmpe)Pt[Si(OH)(*t*-Bu)$_2$](OTf) (**4-337**) [4o]			2.401 (3)	295
(dcpe)HPtSiPh_3 (**4-338**)	[4p]		2.363 (4)	296
(Cl)Pt[SiMe($CH_2CH_2CH_2PPh_2$)$_2$] (**4-341b**)			2.307 (8)	186
cis-($PPh_2CH_2CH_2SiMe_2$)$_2$Pt (**4-342**)			2.342 (8) 2.368 (6)	129
Ni Triad: M_2				
[(Pr_3P)$_2$Pt]$_2$[μ–SiH(Hex)]$_2$ (**2-88***) [4q]		[1n]	2.390 (7) 2.403 (7) 2.387 (6) 2.396 (6)	77
cis-[(Et_3P)$_2$Pt]$_2$(μ-SiHCy)]$_2$ (**2-89***) [4r]		[3c]	2.395 (5) 2.405 (6)	78
trans-[(Et_3P)$_2$Pt]$_2$[(μ-SiH(*p*-Tol)]$_2$ (**2-91***)		[3c]	2.379 (9) 2.402 (6)	79
[(Et_3P)$_2$[(μ-Si$HC_6H_4SiH_2$)$_2$-Pt(PEt_3)$_2$] (**2-92***)		[3c]	Pt^1-Si^1 2.415 (9) Pt^1-Si^2 2.44 (1) Pt^1-Si^3 2.40 (1) Pt^1-Si^4 2.41 (1) Pt^2-Si^1 2.39 (1) Pt^2-Si^4 2.352 (9)	75
trans-[(Et_3P)$_2$Pt]$_2$(μ–SiXCy)(μ–SiYCy)] (**2-93***) [4s]		[3c]	2.384 (4) 2.402 (4)	78
trans-[(Et_3P)$_2$Pt]$_2$[(μ–SiXPh) (μ–SiYPh)] (**2-94***)		[3c]	2.355 (7) - 2.383 (8) [4t]	15b, 79
(dmpe)(H)Pt(μ-SiHPh)$_2$[μ-η^1,η^1-PhHSiSiHPh]Pt(H)(dmpe) (**2-95***)	[3c]	[3c]	Pt^1-Si^1 2.382 (4) Pt^1-Si^2 2.379 (4) Pt^1-Si^3 2.426 (4) Pt^2-Si^1 2.392 (5) Pt^2-Si^2 2.391 (4) Pt^2-Si^4 2.439 (4)	74
[(dcpe)Pt]$_2$(μ-SiH_2SiH_2)$_2$ (**2-97***) [4u]			Pt-Si^1 2.378 (1) Pt-Si^2 2.369 (1)	76
Other Derivatives [4v, 4w, 4x]				

* Structural formulas for compound numbers marked with an asterisk may be found at the end of the table.

Footnotes: [1a] Values are given in angstroms. [1b] There are no published examples of Sc–Si complexes prepared by Si–H addition to a Sc precursor which has been characterized by X-ray diffraction. ScSi: 2.863(2).[306] [1c] Refined but not given. [1d] Calculated value, 2.485 Å. [1e] SiH set at 1.50 Å. [1f] Me/H disorder. [1g] Si–H distance was defined. [1h] H's at Hf and Si were located at 1.76 and 1.25 Å respectively, but were not refined. [1i] Disordered structure. [1j] Si(Ti,Zr,Hf) bonds prepared by other methods or preceding 1980 and structurally characterized. SiTi: 2.159(13);[307] 2.652(2);[308] 2.67(1);[309] 2.755(7);[310] 2.759(13);[311] 2.765(8).[310] SiZr: 2.670(1),

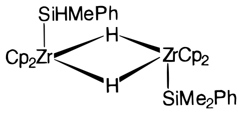
Table 5 (Continued)

2.713(1);[312] 2.753(4);[313] 2.81;[314] 2.815(1).[312] SiHf: 2.729(3);[21] 2.748(4);[315] 2.881(4).[21] [1k] Si−H hydrogen was located and refined isotropically, but bond distance data were not provided. [1l] Si−H was not refined. [1m] The Ta−H was observed in the final difference Fourier map but could not be successfully refined. The Si−H position was located and optimized at $D(\mathrm{SiH}) = 1.45$ Å. The second set of numbers for **3−18** are from a neutron diffraction study.[13b] [1n] Indicated hydrogens were not located. [1o] Si(V,Nb,Hf) bonds prepared by other methods or preceding 1980 and structurally characterized. SiTa: 2.631(2);[88] 2.642(1), 2.669(4);[316] 2.680(15);[317] 2.684(1).[88] SiNb: 2.669(1).[318] [1p] Co-crystal with $(\eta^6\text{-}C_6H_5F)(OC)_2Cr(H)_2(SiCl_3)_2$. [1q] Two molecules in the asymmetric unit. [1r] From reaction of $Cp_2W(CH_2{=}SiMe_2) + HSi(i\text{-}Pr)_2Cl$ (related to **4−43**). [1s] From reaction of $Cp_2W(CH_2{=}SiMe_2) + HSiMe_3$ (related to **4−41**). [1t] Si(Cr,Mo,W) bonds prepared by other methods or preceding 1980 and structurally characterized. SiCr: 2.409(1).[319] SiMo: 2.550(2);[320] 2.556(4);[321] 2.556(2), 2.558(2), 2.559(2);[320] 2.670(2).[322] SiW: 2.388(6);[323] 2.469(2);[324] 2.533(3);[325] 2.544(4);[326] 2.547(4);[326] 2.551(2), 2.559(4);[326] 2.559(2);[325] 2.565(4);[326] 2.591(3);[327] 2.606(2);[328] 2.633(2);[329] 2.652(2).[320] [1u] Coordinates only were published. Si−H not located. [1v] Prepared from photolysis of $(C_5H_4Me)Mn(CO)_3$ and $HSiCl_3$.[331a] [1w] Mn−H not located. Si−H was not described. [1x] Prepared from heating $Mn_2(CO)_{10}$ and $HSiPh_3$.[331b] [1y] ReH's were not located. Si−H's were assigned fixed isotropic displacement parameters. [1z] Neutron diffraction. [2a] Hydride hydrogens near the Re atom (electron density peaks of intensity 0.5 to 0.8 e/Å in the difference map) were introduced in the final refinement. [2b] Tentative assignment. [2c] Si(Mn,Re) bonds prepared by other methods or preceding 1980 and structurally characterized. SiMn: 2.453(4);[332] 2.564 (6).[331d] SiRe: 2.474(4);[333] 2.475(4);[333] 2.476(3);[334] 2.49(1).[335] [2d] From $Fe_{(v)} + ArH + HSiCl_3$ (ArH = C_6H_6, $CH_3C_6H_5$, $p\text{-}(CH_3)_2C_6H_4$).[162] [2e] The Fe and Ru compounds are isomorphous with Si and P in trans positions. The structure of the Fe derivative was not considered an accurate determination. [2f] Prepared from **4−93b** or **4−96b** by addition of PPNCl.[171] [2g] From $Cp^*Ru(L)Cl + ClMgCH_2SiHR_2$ [L = $P(i\text{-}Pr)_3$, PCy_3; R = Me, Ph].[336] [2h] Isolated as one of the products from reaction of $Cp^*[(i\text{-}Pr)_3P]ClRu$ with $MesSiH_3$. [2i] SiRR′ bridges two metal centers. [2j] Hydrogens at calculated positions. [2k] Two M_2 units. [2l] Prepared from the reaction of a 1:1:1 mixture of $Fe(CO)_5$, $HSiCl_3$, and PMe_3. [2m] Prepared as was **4−175**. Isolated as hexane solvate. [2n] One of the hydrides could not be located. [2o] Parameters for only one of the molecules in the asymmetric unit were provided. [2p] Made in similar manner as **4−203**. [2q] Os−H were calculated geometrically. [2r] Hydrogens in calculated positions. Hydrogens bridging Os centers were not located. [2s] Located in Fourier difference map but not refined. Fixed at 1.84 Å. [2t] Location of hydrides were assumed as symmetrical bridges in the plane of the Os atoms. [2u] Si(Fe,Ru,Os) bonds prepared by other methods or preceding 1980 and structurally characterized. SiFe: 2.218(2);[338] 2.222(3);[339,340] 2.224(1);[341] 2.2277(14);[341] 2.230(2);[341] 2.2330(14);[341] 2.249(1);[342,343] 2.249(3);[344] 2.252(3);[345] 2.258(1);[346] 2.260(6);[347] 2.262(2);[348,349] 2.262(1);[54] 2.263(1);[54] 2.263(2), 2.264(2);[350] 2.264(2);[351] 2.265(1);[352] 2.266(3);[349] 2.267(1);[352] 2.268(8);[353] 2.271(4);[354] 2.275(2);[350] 2.278(1);[157] 2.280(3);[351] 2.281(4);[351] 2.285(3);[353] 2.286(5);[355] 2.286(1);[356] 2.287(2);[357] 2.290(3);[353] 2.294(1);[358] 2.296(2);[359] 2.297(3);[346] 2.301(1);[358] 2.303(1);[346] 2.307(1);[360] 2.307(2);[361] 2.310(1);[362] 2.322(1);[362] 2.311(2);[360] 2.311(3);[363] 2.313(6);[347] 2.315(2);[364] 2.316(13);[363] 2.322(4);[362] 2.325(3);[365] 2.326(3);[363] 2.327(3);[366] 2.328(1);[367] 2.33(1);[366] 2.330(2);[368] 2.338(4);[362] 2.339(2);[369] 2.339(1);[365] 2.341(2);[365] 2.346;[370] 2.347(1);[371] 2.350(1);[372] 2.354(2);[365] 2.356;[368] 2.356(1);[371] 2.357(3);[373,374] 2.364(5);[356] 2.365(2);[365] 2.366(2);[195] 2.366(1);[202] 2.375(2);[375] 2.378(1);[365] 2.380(1);[374] 2.382(2);[376] 2.395(1);[377] 2.399(6);[366] 2.4049(26);[103] 2.4074(9);[378] 2.4176(16);[103] 2.421(3);[359] 2.422(2).[377,379,380] SiRu: 2.190(14);[381] 2.297(4);[188] 2.238(2);[382] 2.258(4);[381] 2.269(3);[380,381] 2.84(3);[381] 2.286(2);[307] 2.288(11);[383] 2.306(2);[336] 2.309(10), 2.309(12);[383] 2.311(4);[336] 2.316(10);[383] 2.338(1);[384] 2.387(2);[385] 2.340(1);[384] 2.349(2);[180] 2.350(1);[381] 2.360(1);[386] 2.364(1);[386] 2.365(5);[387] 2.382(4);[387] 2.387(2);[385] 2.387(1);[180] 2.396(4);[387] 2.403(4);[336,387] 2.411(2);[388] 2.414(2);[389] 2.426(1);[380] 2.43;[391] 2.432(2);[392] 2.439(4);[393] 2.452(3);[394] 2.461(2).[393] SiOs: 2.254(2);[197] 2.318(5);[395] 2.319(2);[395] 2.319(2);[197] 2.325(8);[396] 2.334(1);[192] 2.337(5);[395] 2.366(6);[397] 2.370;[188] 2.374(2);[197] 2.388(4);[397] 2.400(4);[398] 2.404(6);[398] 2.419(2);[307] 2.425(7);[213] 2.427(4);[399] 2.432(6);[400] 2.444(4);[400] 2.453(5);[400] 2.463(9);[57] 2.470(7).[188] [2v] Hydrogen atoms were geometrically idealized and the Si−H distance restrained to 1.460(5) Å. [2w] Positions of Rh−H and Si−H were determined by difference Fourier map but not refined further. [2x] Neutron diffraction done at 20 K. X-ray structure also reported.[230] [2y] Structure done at −70 °C. [2z] Positions of hydride ligands were determined by difference Fourier technique. [3a] Contains two crystallographically independent molecules in the asymmetric unit that have similar structures. [3b] Hydride position not located in final difference map. [3c] Information about hydride not provided in the indicated reference. [3d] Structure done at 203 K. [3e] Structure done at −120 °C. [3f] *fac*-(mesiqn)$_3$Ir is isomorphous to Rh analogue. X-ray structure shown only for Rh analogue in the reference. Short M−Si bond distances are seen for both complexes (2.28−2.31 Å). [3g] Si−H placed in calculated position. [3h] The hydrides were located and their approximate positions were obtained from electron density maps and were placed in ideal positions. Two independent molecules present in unit cell and arrangement of atoms in the two molecules is different but angles and distances are similar. Data for second molecule: Ir−H 1.119, 1.341 Å; Si−H 1.219 Å; Ir−Si 2.369(3) Å. [3i] Hydride located and refined isotropically but distance not given. Structure done at 153 K. [3j] Structure done at 200 K. [3k] Crystal structure contains both enantiomers which are related by an inversion center. [3l] Neutron diffraction done at 20 K. Hydrides are trans to each other. Average Rh−H 1.581(3) Å.[230] [3m] Asymmetric unit contains two molecules which differ only slightly. Data reported in reference for one molecule and the other supplied in supplementary material. [3n] Structure done at 110 K. [3o] The hydrides were located and their approximate positions were obtained from electron density maps and were placed in ideal positions. [3p] Structure was done at 130 K. [3q] Structure done at 120 K. [3r] Hydrides were not located unambiguously. Most likely positions were given from maxima in difference Fourier synthesis. [3s] Hydrogen atoms were not located. Bond lengths given for one of two independent molecules in the asymmetric unit. Structure done at 163 K. [3t] Structure done at 173 K. [3u] Structure done at 133 K. [3v] Molecule has trans geometry and exact inversion symmetry. [3w] Hydride on silicon was refined with an isotropic thermal parameter. Other hydrogens were fixed in idealized positions. [3x] Structure contained benzene as solvent of crystallization. [3y] Hydrides were located at about 1.6 Å from each Rh center from the Fourier map. Molecule is centrosymmetric. [3z] Structure contained toluene as solvent of crystallization. [4a] Positions of nonbridging hydrides were not determined unambiguously and the terminal hydrides were included in the structure calculation without further refinement of parameters. [4b] Nonbonded Si−H distances to hydrides on iridium were approximately 2.48 and 2.61 Å. Structure contained two THF solvent molecules that displayed rotational disorder. [4c] A difference Fourier map displayed peaks in the expected positions for the hydride ligand but were not refined. [4d] Molecule contains a crystallographic 2-fold axis of symmetry passing through the Si atom and the center of the Ir−Ir′ bond. Si···H nonbonded distance reported as 2.53(9) Å. [4e] Si(Co,Rh,Ir) bonds prepared by other methods or preceding 1980 and structurally characterized. SiCo: 2.209(5);[401] 2.216(1);[402] 2.217(1);[402] 2.217(2);[403] 2.221(1);[403] 2.222(1);[402] 2.226(5);[404] 2.254(3);[405] 2.281(2);[406] 2.288(1);[402] 2.291(2);[66] 2.299(2);[66] 2.307(2);[66] 2.311(2);[66] 2.313(2);[66] 2.321(2);[66] 2.324(2);[66] 2.325(2);[66] 2.381(4).[407] SiRh: 2.203(4);[408] 2.309(2);[409] 2.314(2);[110] 2.342(1);[111] 2.346(2);[409] 2.379(5);[241] 2.398(4);[410] 2.406(2).[409] SiIr: 2.235(5);[411] 2.299(5);[412] 2.344(2);[265] 2.349(7);[60] 2.352(2);[117] 2.372(7);[60] 2.399(2);[413] 2.40;[414] 2.404(3);[261,272] 2.416(2);[413] 2.42(2);[186] 2.444(2);[415] 2.447(2);[415] 2.447(5);[263] 2.454(6).[416] [4f] Structure obtained at −70 °C. [4g] Hydrogens included but not refined. [4h] Slight rotational disorder about one of the Pd−Si bonds noted but was successfully modeled by refining two conformeric structures in approxately 3:1 ratio. [4i] The positions for the H atoms bound to Si and Pt could be inferred from difference-Fourier map but were not included in the structure-factor calculations. [4j] Structural data not published. [4k] Hydrogens on Pt and Si were located and refined isotropically. Structure contains one-half molecule of $CH_3C_6H_5$ (disordered). [4l] Compound prepared previously by reaction of Ph_3SiH with *cis*-$(PhMe_2P)_2PtCl_2$ in boiling benzene−triethylamine solution.[417] [4m] A similar derivative, $(Et_3P)_2(H)Pt[Si(p\text{-}ClC_6H_4)_3]$ was characterized by X-ray crystallography, and data are available in supplementary material. [4n] Crystallized with one-half molecule of Et_2O which suffered disorder and was not accurately located. [4o] Complex isolated as acetone solvate. Acetone occupies position trans to one of the phosphines and hydrogen bonding observed between OH hydrogen and triflate group. Structure obtained at −163 °C. [4p] Hydrogen positions calculated but not refined.

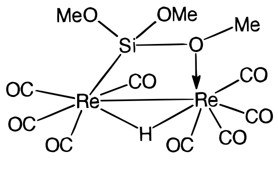
Table 5 (Continued)

[4q] Incomplete structure. [4r] Pt−Si ring adopts a butterfly arrangement (first nonplanar metal silicon four-membered ring structurally characterized). [4s] Ring is planar and contains a center of inversion. Cocrystallized mixture of X = Y = H; X = Y = Cl; X = H, Y = Cl. [4t] Trans complex with X = Y = Cl has Pt−Si distances of 2.381(2) and 2.368(2) Å.[79] [4u] Isolated as toluene solvate ($4CH_3C_6H_5$). Molecule adopts a chair conformation. [4v] Si(Ni,Pd,Pt) bonds prepared by other methods or preceding 1980 and structurally characterized. SiNi: 2.182(4);[419] 2.194(2);[420] 2.195(1);[421] 2.208(1);[421] 2.283(3);[420] 2.289(2).[420] SiPd: 2.336(1);[422] 2.356(1);[422] 2.358(5);[423] 2.367(1);[424] 2.368(1);[424] 2.368(4);[425] 2.375(4).[425] SiPt: 2.255(4);[426] 2.270(2);[491] 2.288(1);[427] 2.292;[428] 2.312(4);[429] 2.313(6);[430] 2.316(4);[429] 2.316(6);[431] 2.317(2);[432] 2.330(17);[433] 2.335(11);[434] 2.337(3);[435] 2.338(11);[434] 2.355(3);[297] 2.360(2);[436] 2.368(2);[79] 2.368(1);[437] 2.373(1);[297] 2.374(2);[297] 2.374(1);[304] 2.374(1);[437] 2.378(4);[297] 2.379(1);[291] 2.381(2);[438] 2.381(2);[79] 2.386[440a] (see footnote 4y); 2.423(2);[439] 2.444(4).[426] [4w] Si(Cu,Ag,Au) bonds prepared by other methods or preceding 1980 and structurally characterized. CuSi: 2.266(2);[441] 2.283(2);[441] 2.334(3);[442] 2.340(2);[443] 2.348(2);[442] 2.406(2).[441] AuSi: 2.291(2);[444] 2.344(10);[445] 2.352(2);[445] 2.354(4);[446] 2.356(2);[446] 2.358(1).[445] [4x] Si(Zn,Cd,Hg) bonds prepared by other methods or preceding 1980 and structurally characterized. ZnSi: 2.342(4), 2.342(4).[447] HgSi: 2.493(2);[448,449] 2.503;[448] 2.539(2);[449] 2.548(2);[449] 2.549(2).[448,449] [4y] An additional Pt−Si derivative was crystallographically characterized and reported in ref 440b, but the PtSi distance was not provided.

Compound structures for Table 5:



3-13



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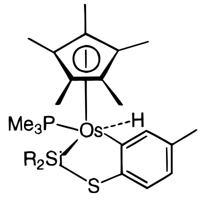
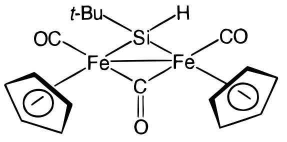
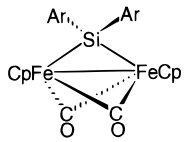


R = p-$SC_6H_4CH_3$

4-152c

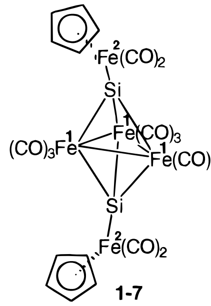


2-46a



Ar = 2,4,6-(i-Pr)$_3C_6H_2$

3-52



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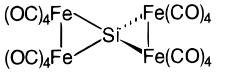

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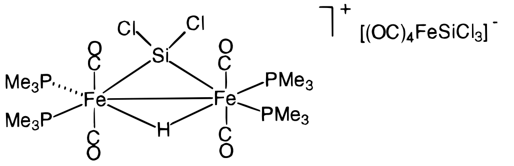

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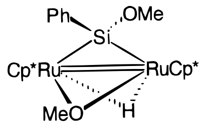
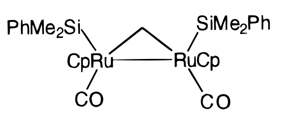


(isomer 1)

3-58c



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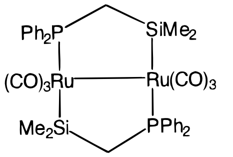

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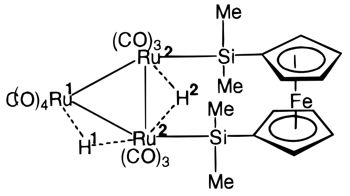

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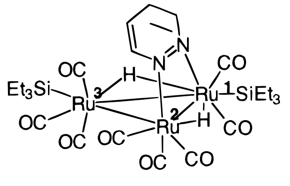

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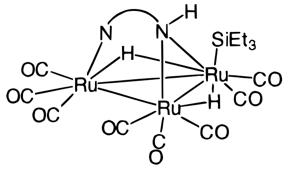
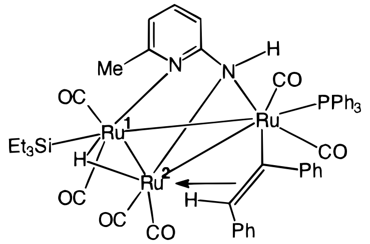


N—N—H = ampy

4-187



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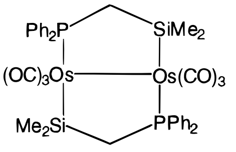

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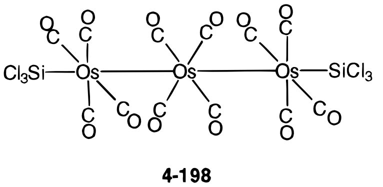

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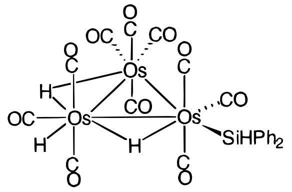

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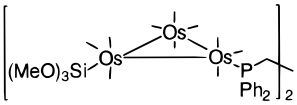

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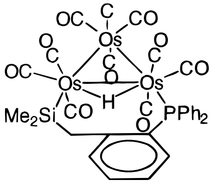

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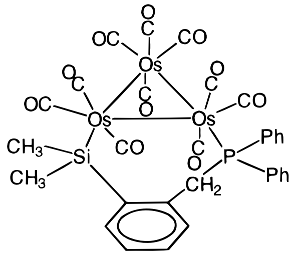
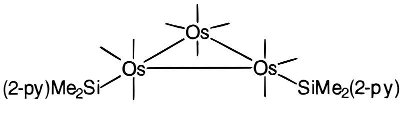


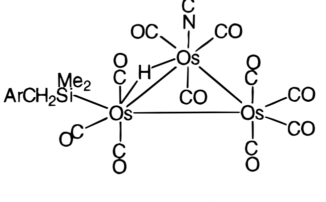
(1 bridging H)

4-203



(2 bridging H's)

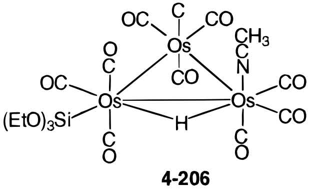
4-204



Ar = 2-BrC_6H_4

(1 bridging H)

4-205



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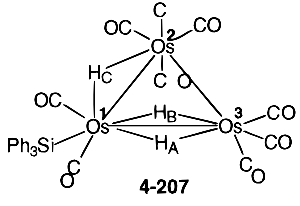

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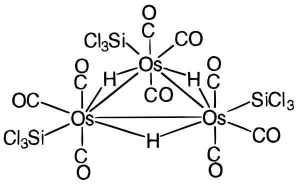

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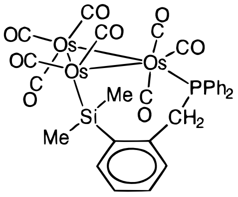
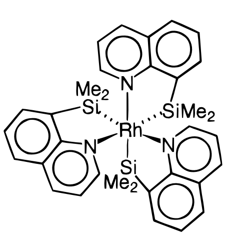
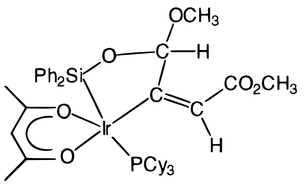


(3 bridging H's)

4-210



4-255a



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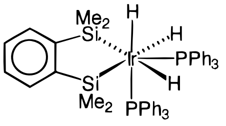

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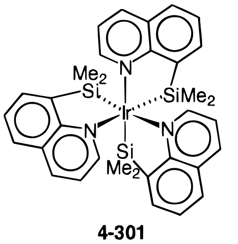

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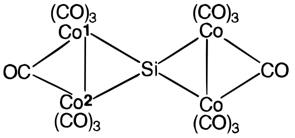

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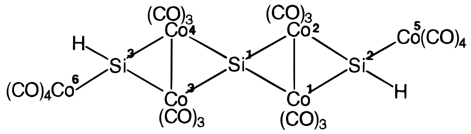

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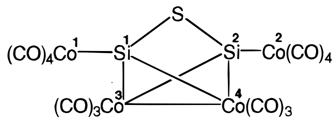

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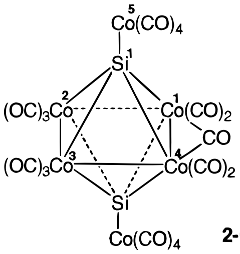

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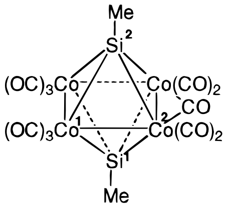

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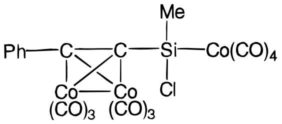

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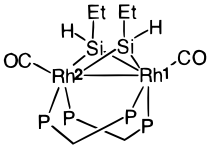

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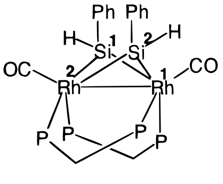

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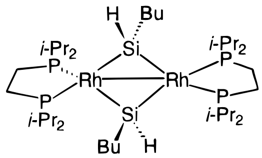

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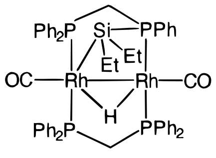

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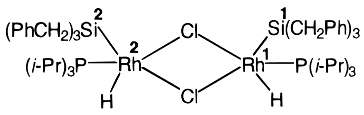

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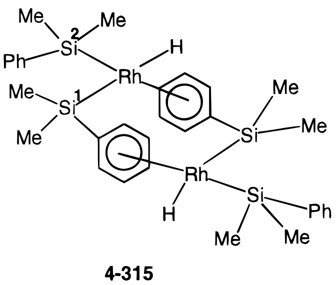

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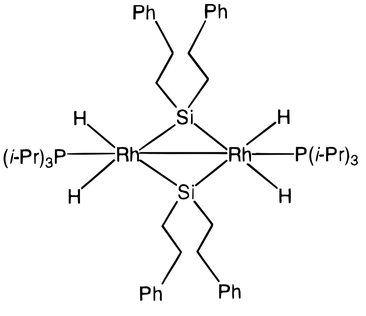

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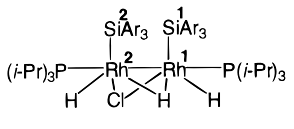

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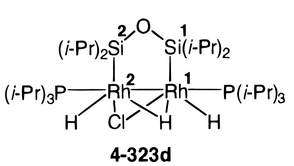

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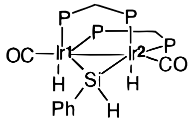

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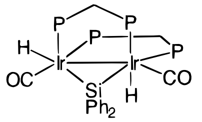

P = PPh$_2$

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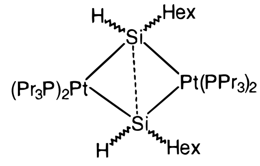

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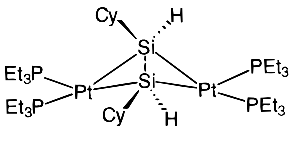

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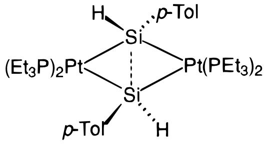

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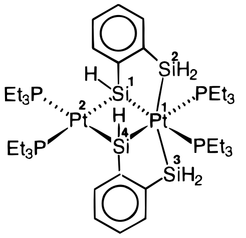

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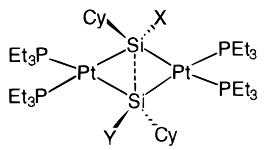

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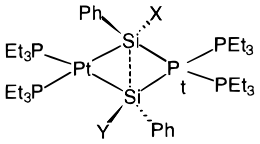

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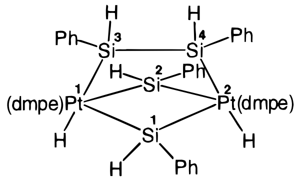

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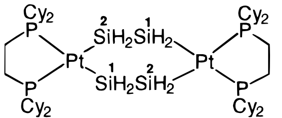
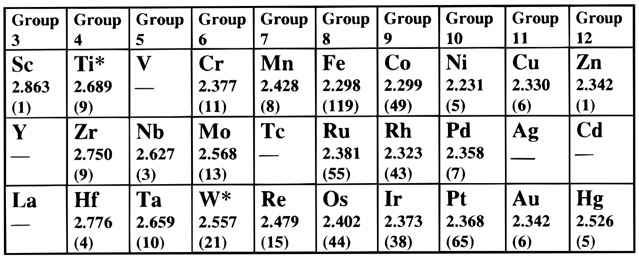


2-97

Table 6. Metal–Silicon Bond Distances

metal–silicon	range (Å) (no. of values)	difference (largest – smallest) (Å)
Sc	2.863 (1)	–
Ti	2.646–2.765 (10)[a]	0.12
Zr	2.670–2.815 (9)	0.14
Hf	2.729–2.881 (4)	0.11
V	–	
Nb	2.597–2.669 (3)	0.07
Ta	2.631–2.740 (10)	0.11
Cr	2.343–2.431 (11)	0.09
Mo	2.513–2.670 (13)	0.16
W	2.469–2.652 (21)[b]	0.18
Mn	2.319–2.564 (8)	0.13
Tc	–	
Re	2.434–2.510 (15)[c]	0.08
Fe	2.197–2.422 (119)	0.22
Ru	2.190–2.465 (55)	0.28
Os	2.254–2.493 (44)	0.22
Co	2.209–2.381 (49)	0.17
Rh	2.203–2.406 (43)	0.20
Ir	2.235–2.454 (34)	0.22
Ni	2.182–2.289 (5)	0.11
Pd	2.336–2.394 (6)	0.06
Pt	2.255–2.444 (65)	0.19
Cu	2.266–2.406 (6)	0.14
Ag	–	–
Au	2.291–2.358 (6)	0.07
Zn	2.342 (2)	0
Cd	–	–
Hg	2.493–2.549 (5)	0.06

[a] One value outside of range: 2.159. [b] One value outside of range: 2.388. [c] Si–Re distance in $H_3SiRe(CO)_5$ is 2.562 Å as determined by electron diffraction.[331e]



Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12
Sc 2.863 (1)	**Ti*** 2.689 (9)	**V** —	**Cr** 2.377 (11)	**Mn** 2.428 (8)	**Fe** 2.298 (119)	**Co** 2.299 (49)	**Ni** 2.231 (5)	**Cu** 2.330 (6)	**Zn** 2.342 (1)
Y —	**Zr** 2.750 (9)	**Nb** 2.627 (3)	**Mo** 2.568 (13)	**Tc** —	**Ru** 2.381 (55)	**Rh** 2.323 (43)	**Pd** 2.358 (7)	**Ag** —	**Cd** —
La —	**Hf** 2.776 (4)	**Ta** 2.659 (10)	**W*** 2.557 (21)	**Re** 2.479 (15)	**Os** 2.402 (44)	**Ir** 2.373 (38)	**Pt** 2.368 (65)	**Au** 2.342 (6)	**Hg** 2.526 (5)

*One value excluded from calculation.

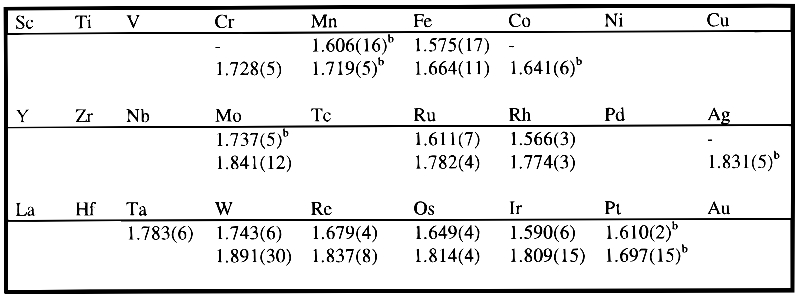
Figure 10. Mean values of silicon–transition-metal bonds. Asterisks indicate that one value was excluded from the calculation.

trends in the TM–Si distances. It is important to note however that the mean values represent all variations in substituents at both the metal and silicon centers. Just how the TM–Si distance varies with substituents has not been established. Although the ranges for TM–Si distances in Table 6 overlap from triad to triad, the mean distances decrease from Sc through Ni and increase only somewhat going down each triad. In general, the TM–Si distances for the Co and Ni triad metals are approximately 0.4 Å shorter than the early transition metals. The M–H bonds are known with less accuracy, and when refined, the distances vary from about 1.4 to 1.8 Å (exclusive of bridging hydrogen atoms) and the Si–H bond distances usually fall between 1.4 and 1.5 Å and are often set at 1.5 Å.[451] The mean values for TM–H distances determined by neutron diffraction have been summarized by Bau and are shown in Figure 11 for both terminal and M–H–M bridging cases.[452]

The majority of the complexes of the Ti, V, and Cr Triads that have been crystallographically characterized contain η^5-Cp or η^6-arene ligands. Such ligands are also found in the Mn and Fe triads but to a lesser extent. The majority of the remaining complexes contain carbonyl and phosphine ligands. The most common ligand employed with Co is CO but for Rh and Ir there are numerous examples of phosphine complexes (monodentate and chelate). All of the Pt and Pd complexes in Table 5 (formed from oxidative addition of Si–H bonds) contain phosphine ligands. The silylmetal complexes of the Co and Ni triads are also dominated by tertiary silyl groups.

As illustrated previously,[1a,b,453] metal–silicon bond distances are often shorter than expected for single TM–Si covalent bonds. The TM–Si distances are probably a function of several effects including the nature of substituents at both TM and Si centers and the oxidation state of the metal. Whether or not the observed shortening is due to a π-component between the TM and Si has not been established. With early transition metals the electronegativity values are generally less than those of silicon and the bond distance values are closer to those calculated (especially for d^0-complexes). The greatest difference between the expected and observed TM–Si bond distance occurs with late transition metals. Late transition metals are characterized by electronegativity values higher than silicon in addition to higher "d" electron counts (i.e., available π-bonding electrons). When silicon is bonded to a nonmetal center that has a lone pair, bond shortening is also observed.[454]

It is possible that a $-SiR_3$ group is simply a very strong σ-donor thus accounting for shorter bonds. The fact that $TM-SiCl_3$ bond distances tend to be the shortest is also consistent with σ-donation (Bent's rule[455]). The effect of electronegative substituents at silicon can be seen by comparing the distances for the related compounds, $(OC)_4Co-SiF_3$ (2.226 Å),[404] $(OC)_4Co-SiCl_3$ (2.254 Å),[405] and $(OC)_4Co-SiH_3$ (2.381 Å).[407] The $Mn-SiCl_3$ distance in $Cp'(OC)_2Mn(SiCl_3)_2$ (**5–3**[331a]) is on the short end of the range exhibited for Mn–Si complexes. The mean value for 10 $Cr-SiCl_3$ distances (**4–24, 4–25, 4–30, 4–31**, Table 5) is 2.374 Å and on the low end of a rather small range of distances (0.09 Å). The value of 2.374 Å is only slightly longer than that reported for the base-stabilized silylene complex, $(OC)_5Cr{=}SiCl_2(HMPA)$.[3d] The $Fe-SiCl_3$ derivatives, $Cp(OC)_2FeSiCl_3$ (**4–75**), $(\eta^6\text{-}C_6H_5CH_3)(H)_2Fe(SiCl_3)_2$ (**4–80**), $(\eta^6\text{-}p\text{-xyl})(H)_2Fe(SiCl_3)_2$ (**5–8**[162]), and $[(OC)_3LFeSiCl_3]PPN$ [L = PPh_3 (**5–9**), $P(OPh)_3$ (**5–10**)],[171] contain 10 Fe–Si distances with a mean of 2.216 Å, on the shortest end of the range exhibited for Fe. The two $Os-SiCl_3$ derivatives, **4–208** (a cluster) and **4–166b** (mononuclear complex) exhibit Os–Si distances from 2.273 to 2.394 Å. One of the few systematic studies where the substituents at Si have been varied while the metal unit is held constant is the system $Os(SiR_3)Cl(CO)(PPh_3)_2$.[197] The Os–Si distance increases in the sequence R = F < Cl [**4–166b**] < OH < Me from 2.254 Å (shortest known Os–Si) to 2.374 Å. The average F–Si–F angle in $Os(SiF_3)Cl(CO)(PPh_3)_2$ is 101.5°, consistent with a redistribution of "s" character in the orbitals of silicon resulting in an increase in the "s" character



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
			-	1.606(16)[b]	1.575(17)	-		
			1.728(5)	1.719(5)[b]	1.664(11)	1.641(6)[b]		
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
			1.737(5)[b]		1.611(7)	1.566(3)		-
			1.841(12)		1.782(4)	1.774(3)		1.831(5)[b]
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
		1.783(6)	1.743(6)	1.679(4)	1.649(4)	1.590(6)	1.610(2)[b]	
			1.891(30)	1.837(8)	1.814(4)	1.809(15)	1.697(15)[b]	

Figure 11. Average M−H terminal and μ_2-bridging distances taken from ref 452. First number is for terminal M−H bonds. Second number is for a μ_2-bridging hydride. Values with less than 3 independent determinations are noted with superscript b's.

for the orbital directed to the Os center. However, the trends are also consistent with an increasing ionic contribution to the Os−Si bond from R = Me to R = F, or with π-donation from Os→Si both of which would also contribute to bond shortening. Support for some π-acceptor ability of the silicon center is provided from IR data for the series, $Os(SiMe_{3-n}R_n)Cl(CO)(PPh_3)_2$ (R = F, Cl, OH). The ν(CO) values steadily increase with n in each sequence from $SiMe_3$ to SiR_3 and demonstrates that as more electronegative groups are added to silicon, the silyl group becomes more π-bonding (i.e., a better π-acceptor). Consequently, π-bonding from the Os to CO decreases and ν(CO) increases. The $-SiF_3$ group was estimated to have approximately one-half the π-acceptor ability of CO.[197] A similar deduction was reached for the $SiCl_3$ group in $Cp(OC)_2FeSiCl_3$ on the basis of a photoelectron spectroscopy study.[456a] However, in a UPS study of $(OC)_4CoSiCl_3$, $(OC)_5MnSiCl_3$ and *cis*-$(OC)_4Fe(SiCl_3)_2$ the authors concluded that there was no π-back-donation along the TM−Si bond. Bond shortening was attributed to charge polarization effects.[164] Ab initio calculations that illustrate π-acceptor abilities of silyl groups are described in section VII.

The shortest Rh−Si distance in Table 5 (including the CSD search) was found for $(Ph_3P)_2Cl(H)RhSiCl_3$ (as the $HSiCl_3$ solvate[415]). The shortest Ir−Si distance (2.235 Å) was observed for $[(i\text{-}Pr)_3P]_2(Cl)HIrSiMeCl_2$.[57] A related derivative, $(Me_3P)_3(Cl)_2IrSiMeCl_2$, exhibited an Ir−Si distance of 2.299 Å.[207] The authors suggested that substantial back-donation of d-electron density to an appropriate acceptor orbital on silicon could account for the bond shortening.[457a,b] The mixed bis(silyl) complex, $(OC)(dppe)HIr(SiHMe_2)(SiMe_2Cl)$ (**3−71**) shows two different Ir−Si distances: 2.394 Å ($Ir-SiMe_2Cl$) and 2.418 Å ($Ir-SiHMe_2$) in agreement with the electronegativity trend discussed earlier. All of the structures containing a Ni−Si bond in Table 5 (footnotes only) contain silyl groups with either F or Cl substituents and the shortest bond length was found for *trans*-$(Me_3P)_3Ni(SiF_3)_2$ (2.182 Å).[419] Although there are few examples, the $TM-SiF_3$ bond [see also **4−79** (Table 5), refs 403, 404, and 60] can be slightly longer than $TM-SiCl_3$ and, if π-bonding is important, would be consistent with a SiF_3 group as a weaker π-acceptor.

The TM−Si bond might be expected to have a significant π-component in the silylene complexes, $L_nTM{=}SiR_2$, but the majority of the cases isolated thus far contain a Lewis base coordinated to the silicon center.[3c] A related grouping contains a unit as shown in Figure 12 where B = OMe or NEt_2. The distances for base-stabilized TM=Si systems as well as the partial multiple bonds illustrated in Figure 12 range from 2.207 to 2.294 Å (12 values[3c,91a,154,340,349]) for Fe, 2.238 to 2.333 Å (4 values[178,181,307,382]) for Ru, and 2.325 Å[396] for Os. All of the values are on the low end of the recorded TM−Si distances. An unusual transition-metal-substituted silylene complex, $Cp^*(Me_3P)_2Ru{=}Si(STol\text{-}p)Os(CO)_4$ shows little expected π-bonding to Os and a significant π-delocalization between Si, S, and Ru.[307] The Ru−Si distance [2.286 (2) Å] falls in the range reported for base stabilized Ru=Si complexes.[1b] The Cr−Si distances range from 2.343 to 2.431 Å in $(OC)_5Cr{=}SiR_2(HMPA)$ (R = *t*-BuO, Me, Cl) and 2.490−2.502 Å in the bis(silylene)tungsten complexes (Figure 12, M = $CpW(CO)_2$; B = NEt_2, OMe).[3c,142] Thus, the values overlap the mean value for Cr and are less than the mean value for W (see Figure 10).

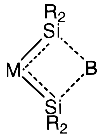


Figure 12. Donor-stabilized bis(silylene) complex.

Although base-stabilized silylene derivatives of the Co triad have been reported (**2−52**, **2−53**, and **3−76**) only **3−76** has been structurally characterized and the distance is near the midrange for Co reported in Table 6. In 1993, Tilley et al. reported the synthesis and characterization of a Pt−silylene complex, *trans*-$[(Cy_3P)_2(H)Pt{=}Si(SEt)_2]BPh_4{\cdot}CH_2Cl_2$.[291] The Pt−Si distance (2.270 Å) lies at the lower end of the Pt−Si bond range reported in Table 6 and is significantly shorter than the related derivative, *trans*-$[(Cy_3P)_2Pt(H)Si(SEt)_3]$ where the Pt−Si distance is 2.379 Å.[291] Thus, the values for both the base-stabilized silylene derivatives and the example of a base free silylene overlap with those exhibited by complexes which are presumed to have σ-bonds. Clearly, additional examples of base-free silylene complexes will be required to establish the extent of bond shortening due to an uncomplexed TM=Si bond.

Silylmetal derivatives with a $TM-SiR_2Cl$ sequence may exhibit incipient silylene character. For example, in the complex $Cp_2Mo(H)(SiMe_2Cl)$ (**4−33**), the Si−Cl length is 2.158 Å which is longer than usually found in chlorosilanes (2.023 Å). The authors suggested that the origin of this long distance may

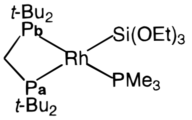


Figure 13. Structure of **4−249**.

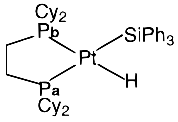


Figure 14. Structure of **4−338**.

involve π-bonding from the d^2-Mo center resulting in a contribution of the resonance structure [Mo═$SiMe_2$]-Cl.[90]

The strong trans influence displayed by silyl groups leads to longer metal−ligand distances for those groups located in a position trans to the silyl ligand.[456b] This effect is readily seen in the following examples. Complex **4−249** (Figure 13) shows steric crowding at the square-planar Rh center and the Si atom exerts a significant trans effect to the P_a center as seen by the elongated Rh−P_a distance [2.399(2) Å] vs Rh−P_b [2.315(1) Å] compared to 2.277(2) Å for the PMe_3 ligand. A reduced coupling between Rh and P_a ($^1J_{RhP}$ = 79 vs 132 Hz for P_a and P_b respectively; 150 Hz for PMe_3) is also observed.

Complex (dcpe)PtH($SiPh_3$) (**4−338**, Figure 14) also shows a substantial trans influence from the silyl ligand toward the phosphorus atom, P_a. The Pt−P_a bond (2.338(4) Å) is lengthened (marginally) compared to the *cis*-Pt−P_b distance (2.313(4) Å). Different Pt−P coupling constants were also observed ($^1J_{PtP(cis)}$ = 2471 Hz, $^1J_{PtP(trans)}$ = 1607 Hz).

M−X (X = halide) bond distances can also be affected by the trans influence of silicon. For example, an unusually long Pt−I bond [2.962(2) Å] was observed in (2,2′-bipyridyl)Me_2(I)$PtSiMe_3$ (Si is trans to I).[430] It is believed to be the longest Pt−I distance reported to date.

V. NMR Data

A. Chemical Shifts and Coupling Constants

The products produced from the reaction of hydrosilanes with metal complexes usually contain a TM−H bond and if a secondary or primary silane is involved, there are residual Si−H bonds on the silyl substituent. The effect of the nature of the solvent employed to obtain NMR data for metal hydrides has not been explored although the chemical shifts for Si−H protons can be effected by the solvent with up to 0.5 ppm difference between aromatic solvents (benzene, toluene) and halogenated solvents (chloroform and methylene chloride).[457c] With this in mind, some general observations are still useful. The ^1H chemical shifts for *mononuclear* metal hydrides are upfield of TMS although exceptions may be found in the Ti triad (**3−7**, **4−2**, and **4−3**).

For $TMSiH_xR_{3-x}$ complexes, the Si−H resonance will usually be observed between 4.0 and 5.5 ppm with some exceptions in heavy metal complexes, especially those of Ir (**2−55** and **2−57, 2−76, 3−64** to **3−66, 3−69, 3−70**, and **3−72** are examples). Another general exception includes the Si−H protons in base stabilized silylene complexes, TM═SiHAr(B) where resonances often occur between 6 and 8 ppm. The Si−H protons in silylene units that bridge two metal centers, TM(μ-SiHR)TM (dinuclear complexes; see **2−47**, **2−48** to **2−50**, **2−65**, **2−71**, **2−73** to **2−75**, **3−53**, and **3−54**) can also be found outside the range of 4.0 to 5.5 ppm. Not surprisingly, the Si−H protons in TM−SiH_3 complexes are observed in the upfield region of the range and a few are found between 3.5 and 4.0 ppm (**1−1**, **1−4**, **1−9**, and **1−10**).

It is not yet common practice to report ^{29}Si chemical shifts for silyl−metal complexes. For measurements that have been reported (Tables 1−4) the range for *mononuclear* complexes varies from −74 to −40 ppm for TM−SiH_3 (only 3 measurements), from −33 [Ta−SiH_2Me (**2−11**)] to 43 ppm [Fe−SiH_2(*p*-Tol) (**2−38**)] for TM−SiH_2R, from −120 [Y−SiH$(SiMe_3)_2$ (**3−1**)] to 68 [Mo−SiH(*t*-Bu)$_2$ (**3−24**)] for TM−$SiHR_2$ and from −86 [Fe−Si(OEt)$_3$ (**4−103**)] to 90 [Nb($SiMe_2Cl$)$_2$ (**4−9**)] for TM−SiR_3. Although Tables 1−4 do not include all silylmetal complexes that have been reported, it is probable that the range of chemical shifts, −120 to 90 ppm, a 200 ppm range, encompasses other known *mononuclear* silyl-metal complexes.

Silylene complexes tend to exhibit a downfield shift in the ^{29}Si NMR resonance although not many measurements have been reported. The base-stabilized, terminal silylenes of the type TM═SiXY(B) as well as those depicted in Figure 12 generally exhibit a ^{29}Si chemical shift >100 ppm except for TM = Fe (**2−30** to **2−33**, **3−39**, **3−40**, and **4−69** to **4−71**) and TM = Co (**2−52** and **2−53**). Dinuclear metal complexes that contain a TM−TM bond and a bridging SiR_2 unit may also be viewed as silylene complexes as outlined in a recent review by Ogino and Tobita.[458a] Although the cases where ^{29}Si resonances have been reported are primarily for the iron triad, the values tend to fall between 200 and 250 ppm for this structural grouping (examples include **2−46a**, **2−46b**, **2−47**, **2−48**, **2−49**, **2−66**, **3−53**, **3−54**, **3−58c**, and **4−171**). Electronegative substituents at silicon shift the ^{29}Si values further downfield (>260 ppm).[458a] There are few base-free, terminal silylene complexes that have been reported but those of the type [Cp*-$(Me_3P)_2RuSi(SR)_2$]BPh_4 exhibit a ^{29}Si resonance near 260 ppm thus overlapping the bridging silylene region just discussed.[1b] A single platinum example, $[(Cy_3P)_2Pt═Si(SEt)_2]^+$ has a resonance at 309 ppm.[291] In TM−(μ-SiXY)−TM complexes without TM−TM bonds, the ^{29}Si range is about 60−160 ppm.[458a] In contrast, several dimeric Pt complexes (**2−87**, **2−88**, **2−91**, and **2−94**) with bridging silylene groups (but no Pt−Pt interactions) exhibit ^{29}Si shifts (−66 to −94 ppm) markedly upfield compared to other complexes with bridging silylene groups. The Si−H resonances in the ^1H NMR spectrum for these Pt complexes also exhibited an upfield shift (3.89−4.37 ppm) compared to other (μ-SiHR) groups.

It is generally observed that $\delta(^{29}Si)$ shifts downfield from the value of the free silane when the silyl group becomes bound to a metal center (for examples see ref 90). This is clearly illustrated in $(OC)_4Co(Si_8H_7O_{12})$, **4−212**, where a nearly 40 ppm downfield shift is observed for the Si directly bound to Co (−46.0 ppm). The remaining silicon centers of the silasesquioxane moiety appear near −85 ppm. Few studies have attempted to systematically evaluate trends in ^{29}Si chemical shifts. A rare example is a study of Mo and W complexes where the ^{29}Si shifts range over 110 ppm. Four trends were identified for complexes of the type $Cp_2TM(X)SiR_3$.[90] Substituents on the Cp ring showed little effect on $\delta(^{29}Si)$ as did the other substituents (X) in the equatorial wedge. The value of the $\delta(^{29}Si)$ shifts to higher field as M changes from Mo to W (going down the triad). Substituents at Si tend to effect the $\delta(^{29}Si)$ more directly and in $TM-SiR_2X$, more electron-withdrawing X-groups cause a downfield shift, particularly when X = Cl. In a related study of the Mn system, $Cp'(OC)LMn(H)SiR_3$ the ^{29}Si chemical shifts were more influenced by substituents at Si than by changes in the L at the Mn center.[458] For example, the value of $\delta(^{29}Si)$ shift changes from 7.5 (SiR_3 = SiHPhNp) to 54.9 ($SiR_3 = SiCl_3$) but only from 13.5 (L = CO) to 26 ppm ($L = PMe_3$) in the series of ligands that were studied. The ^{29}Si resonances for several cobalt silyl complexes were reported where only the substituents at silicon differ [(Co−$SiMe_2Et$ (**4−214**), Co−$SiMe_2Ph$ (**4−215**), Co−$SiPh_3$ (**4−216**), and Co−$SiEt_3$ (**4−218**)] and the range covers about 22 ppm (29.8 ppm for **4−216** and 51.9 ppm for **4−218**).[219] Little change is seen in the ^{29}Si resonance for the related derivatives, $CpH_2Rh(SiEt_3)_2$ (**4−226**; 40.1 ppm), and $Cp^*(H)_2Rh(SiEt_3)_2$ (**4−234**, 38.3 ppm), although a slightly larger shift is observed when the groups bound to silicon are changed from Et to *i*-Pr in $Cp(H)_2Rh[Si(i\text{-}Pr)_3]_2$ (**4−227**; 52.2 ppm).[224−226,230,231]

Carbonyl derivatives of the iron triad have also been studied and include $M(CO)_4(SiMe_{3-n}Cl_n)(H)$ (M = Fe; n = 0−3; M = Ru, Os, n = 3),[148] $M(CO)_4(SiMe_{3-n}Cl_n)_2$ (M = Fe, Ru, Os; n = 0−3), $(Cl_nMe_{3-n}Si)Os_3(CO)_{12}(SiMe_{3-n}Cl_n)$($n$ = 2,3), and $M_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$ (M = Ru, Os).[148,185,194] It was also observed, in this series, that $\delta(^{29}Si)$ shifted upfield proceeding down through the triad. In the mononuclear case, $M(CO)_4(SiMe_{3-n}Cl_n)_2$, the trans isomer is found at lower field than the cis isomer. In the series $TM(SiMe_{3-n}Cl_n)$ (n = 0−3), it is the $-SiMeCl_2$ system that exhibits the lowest field ^{29}Si resonance. A plot of δ(ppm) vs n (in $TM-SiMe_{3-n}X_n$) shows the "U"-shaped curve that is often typical of silicon compounds.[459]

The $\delta(^{29}Si)$ chemical shifts are marginally dependent on the temperature as observed for $(OC)_5Cr{=}Si(H)Ar$ (Ar = $o\text{-}Me_2NCH_2C_6H_4$, **2−16**) where the value changes from +108.4 (233 K) to 112.6 (333 K).[40]

The $^1J_{SiH}$ coupling constants in free silanes tend to exhibit values near 200 Hz, although the value can be as high as 400 Hz ($HSiCl_3$[460]). The range of $^1J_{SiH}$ coupling constants in silylmetal complexes as illustrated in Tables 1−4 is from 143 to 219 Hz with approximately two-thirds of the values falling below 175 Hz. Since electronegativity values for metals are generally lower than χ_C and many fall below that of χ_H it is tempting to attribute the lowering of the value of the coupling constant in the complex to a reduction in the "s" character in the Si−H bond upon substitution of the silicon center with the more electropositive metal unit (compared to carbon). The $^1J_{SiH}$ coupling constants for base-stabilized silylene complexes, often represented in the form $TM{=}SiR_2(B)$, have values from 149 to 219 Hz which overlaps the region exhibited by the σ-bonded silyl complexes. In the base adducts, $TM{=}SiR_2{\leftarrow}B$, the Si center is pseudo-four-coordinate and this probably accounts for the similarity in values.

Due to the lack of substantial ^{29}Si chemical shift data there is little information cited for $^1J_{TMSi}$ coupling constants. The spin active isotopes of ^{103}Rh (100%, $I = {}^1/_2$) and ^{195}Pt (33.7%, $I = {}^1/_2$) and ^{183}W (14.3%, $I = {}^1/_2$) are exceptions. From the entries listed in Tables 1−4, $^1J_{RhSi}$ values lie in the range of 15 Hz [$(\eta^5\text{-}CpSiMe_3)(H)_2Rh(SiMe_3)_2$ (**4−229**)] to 45 Hz [$Cp^*(C_2H_4)(H)RhSi(OEt)_3$ (**4−232**)] while those of ^{183}W in $Cp(OC)_2W\{SiMe_2\cdots X\cdots SiMe_2\}$ (X = OMe, **4−44a**, X = NMe_2, **4−44b**) fall between 90 and 100 Hz. Pt−Si coupling constants are considerably larger and range from 659 Hz [$\{(Et_3P)_2Pt\}_2[\mu\text{-}SiH(Hex)]_2$ (**2−87**)] to 1617 Hz [$(Ph_3P)_2PtH\{SiH(R_F)_2\}$ (**3−93**)].

As a final comment, M−H bonds are usually characterized by a negative ^{1}H NMR chemical shift. The origin of this hydridic shift was studied by DFT-GIAO calculations for $H_xM(CO)_y$ (M = Mn, Tc, Re, Fe, Co, and Cr). The calculations indicate that the negative shift has its origins in a paramagnetic current localized in the metal fragment.[461]

B. Fluxional Processes

Fluxional processes that involve TM−Si bonds or exchange between silicon and hydride sites are described in this section. Additional fluxional processes have also been reported for some of the complexes but will not be summarized.

a. Restricted Rotation

Examples of restricted rotation about TM−Si (or Si−C bonds in silylmetal complexes) have been detected in metallocene derivatives of the early transition metals. The Cp* resonances in the ^{1}H NMR spectrum of $Cp^*_2Y[SiH(SiMe_3)_2]$ (**3−1**) decoalesce to two singlets at 0 °C. The Y−Si barrier to rotation was determined to be 15.6 kcal/mol.[85] Although $Cp^*_2Zr(SiPh_3)Cl$ exhibits a barrier to Zr−Si rotation ($\Delta G^\ddagger = 10.1 \pm 0.2$ kcal/mol) the related metallocene, $CpCp^*Zr(SiPh_3)Cl$ exhibits no restricted rotation.[305] The barrier to rotation about the Mo−Si bond in $Cp'_2Mo(H)[SiH(t\text{-}Bu)_2]$ ($Cp' = C_5H_5, C_5H_4Me$; **3−24**), which is a shorter bond than in the zirconium examples, is slightly greater than 20 kcal/mol. The barrier falls to 13.5 kcal/mol in the corresponding W derivative, $Cp_2W(SiMe_3)[SiH(t\text{-}Bu)_2]$ (**3−25**).[90] It was speculated that the longer TM−Si bond (compared to a carbon analog) produced an interaction between the Cp rings and the substituents on Si thus decreasing the TM−Si barrier to rotation. Barriers to rotation were also reported for $Cp_2Ta(CO)[SiH(t\text{-}Bu)_2]$ (15.4 kcal/mol) and $Cp_2Ta(PMe_3)[SiH(t\text{-}Bu)_2]$, **3−17** (10.9 kcal/mol).[90]

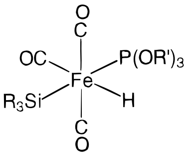


Figure 15. A fluxional, octahedral silyliron complex.

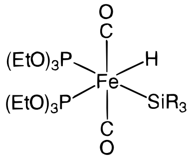


Figure 16. A fluxional, octahedral silyliron complex.

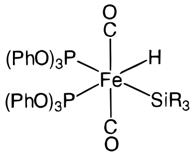


Figure 17. A fluxional, octahedral silyliron complex.

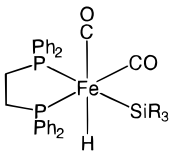


Figure 18. A fluxional, octahedral silyliron complex.

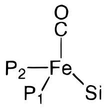


Figure 19. Structure of **4−108**.[173] P−Fe−P = 87°. P_1−Fe−Si = 127° (av). P_2−Fe−Si = 128° (av).

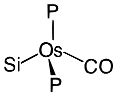


Figure 20. Structure of **3−51**.[52] P−Os−P = 146°. P_1−Os−Si = 118°. P_2−Os−Si = 91°.

b. H/Si Scrambling

Silylmetal hydrides are often fluxional in solution at room temperature, particularly those of iron as shown for the derivatives in Figures 15−18. The structures shown in Figures 15−18 are consistent with the observed low-temperature NMR data. The process which gives rise to the fluxionality was not determined.

The Fe complexes described in the previous paragraph are all considered to exhibit octahedral geometry. An interesting structural problem occurs in the metal trihydrides of the iron triad: $MH_3(CO)L_2SiR_3$ [M = Fe, L_2 = dppe, R = OEt (**4−108**); M = Os, L = $P(i\text{-}Pr)_3$, SiR_3 = $SiHPh_2$ (**3−51**); also isolated were $SiPh_3$ and $Si(OMe)_2Ph$ derivatives] and $FeH_3(PPh_2Et)_3SiPh_3$ (**4−109**). The heavy atom framework has been determined for **4−108** and **3−51** (Figures 19 and 20), and the structure of **4−109** was inferred from that of the corresponding Sn derivative with the heavy atom plus hydride framework shown in Figure 21 [hydrides are in calculated positions and were not refined[462]]. An ab initio calculation of $OsH_3(SiH_3)_3(CO)(PH_3)_2$ (a model for **3−51**) with heavy atom positions fixed at values determined by the structure study was utilized as a tool to determine the hydrogen atom positions. The hydrogens were calculated in chemically inequivalent positions consistent with the observed NMR data. T_1 measurements ruled out η^2-H_2 interactions although the possibility of η^2-$HSiR_3$ could not be excluded. The calculated parameters appear most consistent with heptacoordination at Os(IV) with a “heavily distorted” pentagonal bipyramid. Seven-coordinate complexes are usually fluxional[463] although a rare example of a rigid seven-coordinate complex was reported for $Re(H)_2(SiPh_3)(CO)(PMe_2Ph)_3$ (**4−61**). The authors seemed to favor cleavage of a residual hydrido−silyl interaction to explain the fluxional nature of **3−51** and the enthalpy of activation for the fluxional process was found to be 10.6 ± 0.2 kcal/mol. The related complex, $Ru(H)_3(CO)(SiHPh_2)[P(t\text{-}Bu)_2Me]$, has been studied only in solution[98] and is also fluxional at higher temperatures. The ^1H spectrum shows decoalescence at 173 K and the static structure exhibits mirror symmetry. Either a pentagonal-bipyramidal structure with $SiHPh_2$ and CO in axial positions or a Si-capped *fac*-octahedral structure is consistent with the observed data. No support was found for an (η^2-HSi) interaction.[98]

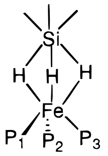


Figure 21. Structure of **4−109**.[462] P_1−Fe−P_2 = 103°. P_1−Fe−P_3 = 103°. P_2−Fe−P_3 = 102°.

The angle parameters for the related iron complexes, **4−108** and **4−109** suggest that the geometries (at least in the solid state) differ from each other as well as from **3−51**. The complex **4−108** was fluxional down to −95 °C thus the role of the hydride ligands could not be determined. However, the related complex, **4−109**, exhibited an AA′A″XX′X″ hydride signal at room temperature but two broad resonances at −60 °C in a 1:2 ratio. The $^{31}P\{^1H\}$ NMR spectrum also gave two broad signals with a 1:2 ratio at −77 °C. The authors favored a Fe−H−Si interaction (3c−2e) with an octahedral *fac*-$Fe(PR_3)_3$ unit, two terminal hydrides and the third hydride bound as η^2-$HSiR_3$. With increasing temperature, an averaging of the hydride sites with $-SiMePh_2$ occurred.[462] A seven-coordinate structure, similar to **3−51** was considered less likely due to the requirement of a high oxidation state on the Fe center [Fe(IV)], although several silyl−Fe(IV) complexes of various types have been observed (see Table 4).

An interesting case where tautomers of $Mo(H)SiH_3$ and $Mo(\eta^2\text{-}HSiH_3)$ coexist occurred in the system $(Et_2PCH_2CH_2PEt_2)_2Mo(CO)(H)(SiH_3)$ (seven-coordinate, **1−4**) and $(Et_2PCH_2CH_2PEt_2)_2Mo(CO)(\eta^2\text{-}HSiH_3)$ (six-coordinate, discussed later in section VII). The seven-coordinate oxidative addition product, **1−4**, exhibited a broad terminal hydride resonance at room temperature and a broad quintet at low temperature (−55 °C). The VT $^{31}P\{^1H\}$ spectrum was consistent

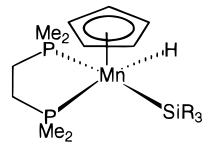


Figure 22. Proposed structure of piano-stool manganese complex, **3−32**.

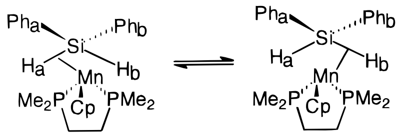


Figure 23. Windshield wiper process proposed for Cp(dppe)Mn($HSiHPh_2$).

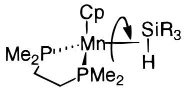


Figure 24. 3c−2e model for Cp(dppe)Mn($HSiR_3$).

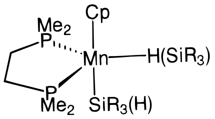


Figure 25. Five-coordinate model.

with a fluxional seven-coordinate species (no signals were observed in room-temperature spectra).

Five-coordinate complexes undergo facile pseudorotation and interchange between trigonal-bipyramidal and square-pyramidal geometries. The system, $CpMn(P_2)(H)(SiH_{3-n}Ph_n)$ (Figure 22) [P_2 = dmpe, dmpp, dmpm, $(PMe_3)_2$; $n = 1, 2$ (**3−32**), 3] are fluxional and undergo exchange of hydride and silyl positions.[45] The structure of $Cp(Me_2PCH_2CH_2PMe_2)(H)MnSiHPh_2$, **3−32**, was determined but the metal hydride was not located. The placement of the two P and Si centers suggested the location of a fourth ligand (the hydride) in the piano stool structure. Deuterium labeling of **3−32** showed that $HMnSiDPh_2$ did not exhibit H/D exchange, thus eliminating a windshield wiper motion (Figure 23). This contrasts with an exchange of H/D that was observed in labeled derivatives of $Cp'Mn(CO)_2(H)(HSiPhNp)$.[464] Since P−H coupling in **3−32** was still observed at the fast exchange limit, an intermolecular exchange process was eliminated. Two possibilities remain: (a) 3c−2e metal Si−H system (Figure 24), or (b) a pseudorotating, five-coordinate complex (Figure 25).[45]

The Ru complexes, $Cp^*Ru[P(i\text{-}Pr)_2Ph)](H)_2(SiR_3)$ [R = OMe (**4−126**), Me (**4−124**), Ph (**4−125**)][96] and $RuH(SiHPh_2)(CO)[P(t\text{-}Bu)_2Me]$[98] have been studied only in solution and both systems were fluxional. The fluxional process for **4−125** must involve a transition state (or intermediate) with a mirror plane that contains the metal center and P, Si, and the Cp centroid. The authors suggested a "tetrahedral" $Cp^*LRu(H_2)SiR_3$ or a square-pyramidal $Cp^*RuL(H)_2SiR_3$ (Cp* axial) intermediate, although a trigonal-bipyramidal intermediate with Cp* and SiR_3 in axial positions would be consistent as well. Unique to $RuH^a(SiH^bPh_2)(CO)L_2$ [**3−48**, L = $PMe(t\text{-}Bu)_2$] is an exchange of H^a/H^b protons. The suggested mechanism involved an intermediate such as shown in Figure 26 (related to Figure 23).

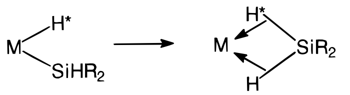


Figure 26. Proposed intermediate for the fluxional process in **3−48**.

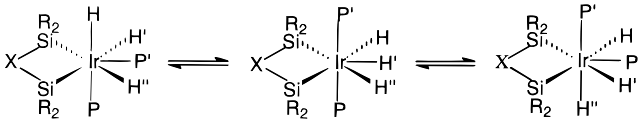


Figure 27. Turnstile rotation in seven-coordinate polyhydride complexes illustrated for **4−294**.

Polyhydride metal complexes that contain silyl substituents may contain classical 2c−2e M−H bonds or 3c−2e M-(η^2-H_2) or M-(η^2-$HSiR_3$) units. Both $ReH_6(SiR_3)(PPh_3)_2$ [SiR_3 = $SiPh_3$ (**4−63**), $SiEt_3$ (**4−62**), $SiHEt_2$ (**3−36**)] and $ReH_6(SiPh_3)L_2$ [L_2 = dppf (**4−64**), dppb (**4−65**)] appear to be classical metal hydrides with fluxional nine-coordinate metal centers. Low-temperature data were consistent with a tricapped trigonal prismatic structure, all hydrides axial. In this case, pseudorotation was not favored and rotation of a triangular face of the tricapped trigonal prism was proposed.[94,151] However, $ReH_5(Si-Si)(PPh_3)_2$ [Si−Si = 1,2-bis(dimethylsilyl)benzene (**4−67**) or 1,2-bis(dimethylsilyl)ethane (**4−66**)] appear to be eight-coordinate with an η^2-H_2 ligand but are fluxional at room temperature down to −90 °C.[152]

Seven-coordinate polyhydride complexes such as **4−245**,[240] **4−246**,[240] **4−293**,[267] and **4−294**[267] show fluxional behavior on the NMR time scale due to stereochemical nonrigidity often seen with seven-coordinate systems.[463] The barrier to fluxional exchange for **4−294** was found to be 13 kcal/mol for the hydrides and phosphines, suggesting that the positions for each become equivalent by the same fluxional process (turnstile rotation, Figure 27). The barrier to rearrangement for **4−293** was found to be lower than that of **4−294**.[267]

Exchange of H/SiR_3 has also been reported for $Cp_2Ru_2(\mu\text{-}CH_2)(H)(SiR_3)(CO)_2$ [SiR_3 = $SiMe_3$, $SiEt_3$, $Si(n\text{-}Pr)_3$, $SiPh_3$, $Si(OMe)_3$] which could not be isolated in pure form due to thermal instability. This dinuclear derivative exhibited dynamic behavior at room temperature. At low temperature the spectroscopic data were consistent with a C_s-symmetrical structure. A dyotopic rearrangement involving simultaneous hydride and silyl migration between the two metal centers was favored as shown in Figure 28. Although other processes were considered, such as conversion to η^2-HSi followed by subsequent oxidative addition, the dyotopic rearrangement provides migration through least motion of Ru substituents.[175,202] The corresponding disilyl complexes (such as **4−175a**) did not exhibit this intramolecular migration of silyl groups.

The $Cp_2Ru_2(\mu\text{-}CH_2)(H)(SiR_3)(CO)_2$[175] complexes also undergo intramolecular processes that will be described in Section VII, as will other systems where rearrangement most likely involves an agostic η^2-HSi interaction.

Several dinuclear rhodium complexes (see **2−71** and **3−86**) that contain a bridging silylene moiety

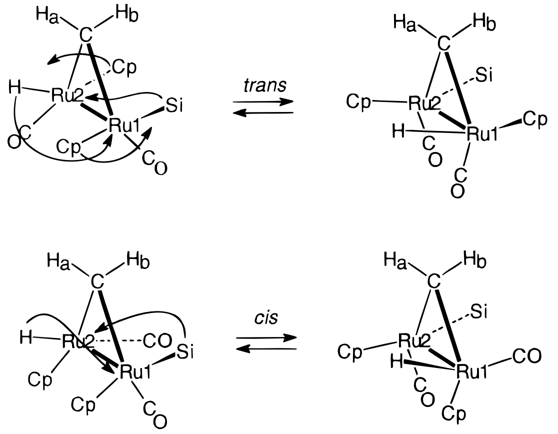


Figure 28. Dyotopic rearrangement proposed for $Cp_2Ru_2(\mu-CH_2)(H)(SiR_3)(CO)_2$.[175,202]

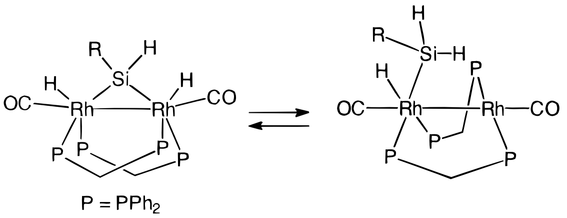


Figure 29. Intramolecular exchange through oxidative addition/reductive elimination pathway.

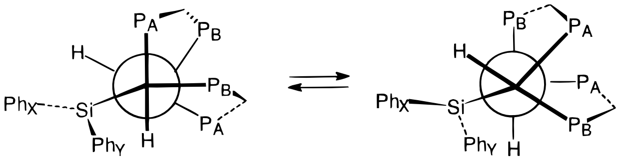


Figure 30. Fluxional process proposed for **3−89**.

show a fluxionality by NMR which involved exchange of the hydrogen atoms bound to silicon and rhodium. The $\Delta G^{\ddagger}$ for the process was calculated to be 12 ± 1 kcal/mol at both −30 and 25 °C for $(OC)_2(dppm)_2(H)_3Rh_2(\mu-SiHPh)$ (**2−71**) and suggests a $\Delta S^{\ddagger}$ near zero for the fluxional process. A similar observation was reported for the corresponding EtSi derivative. The fluxionality can be explained by a rapid reductive elimination and oxidative addition of a Si−H bond to the intermediate, $Rh_2H(SiH_2R)(CO)_2(dppm)_2$ (Figure 29).[67−69] The same fluxional process has been proposed for the μ-SiR_2 complexes $(OC)_2(dppm)_2(H)_2Rh_2(\mu-SiEt_2)$ (**3−86**). Fluxional behavior was also observed with the iridium complex $(OC)_2(dppm)_2H_2Ir_2(\mu-SiPh_2)$ (**3−89**; also the Me and Et derivatives—see footnote 3q, Table 3) but in a different manner than the rhodium counterparts.[71] The complex, $(OC)_2(dppm)(H)_2Ir(\mu-SiHPh)$ (**2−75**) was not fluxional. From the variable-temperature NMR data it appeared that the (μ-$SiPh_2$) and (μ-SiR_2) (R = Me, Et) bridged complexes had slightly different fluxional behavior. For complex **3−89** interchange of the hydride and silylene positions occurred with the hydride migrating to the opposite side of the Ir_2P_4 core concomitantly with twisting of the Ir_2P_4 core and oscillation of the silylene moiety to adopt the sterically favored position (Figure 30). The dialkylsilylene complexes appear to undero reversible migration of a (μ-SiR_2) group from a position opposite (trans) to one dppm ligand to a new position trans to the other dppm ligand (Figure 31).

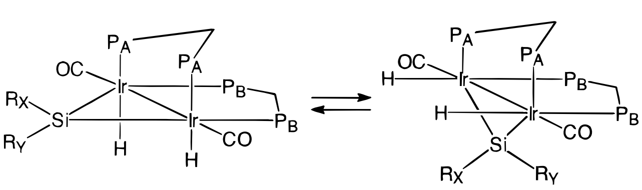


Figure 31. Proposed fluxional process for **3−89** when R = alkyl.

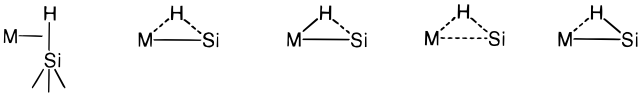


Figure 32. Representations of SiH to TM σ-interactions.

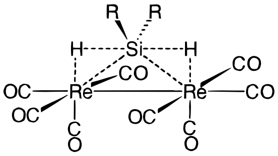


Figure 33. Earliest recognized complex with a σ SiH to TM interaction.

VI. Nonclassical Interactions

A. η^2-$HSiR_3$: σ-Interactions in TM−Si Complexes

In previous sections, complexes with 2c−2e TM−H and TM−Si bonds were described which represented an end point in the oxidative addition of a hydrosilane to an electron-deficient, coordinatively unsaturated metal substrate. However, cases are known in which the oxidative addition of the hydrosilane to the metal complex has been “arrested” at an earlier stage of the reaction. The products are described as agostic HSi interactions, η^2-HSi or as σ-complexes. The σ- (agostic) interaction has been represented in various forms some of which are shown in Figure 32.

The first recognized σ-interaction was reported by Graham and co-workers for the product obtained from the reaction of $Re_2(CO)_{10}$ with R_2SiH_2 (R = Me, Ph) (Figure 33[465a−d]). Shortly thereafter, Graham also reported the first mononuclear σ-complex, $Cp(OC)_2Mn(\eta^2$- $HSiPh_3)$.[465e]

Examples of TM(η^2-HSi) interactions are summarized in Table 7[466−490] and the available crystallographic data are presented in Table 8.[491] The early work on η^2-coordinated HSi bonds has been reviewed by Schubert[1c,d,5a] and has also been included in general reviews of σ-complexes.[7a,b] A brief summary of investigations primarily from 1990 to 1996 has also been published.[492]

When oxidative addition is incomplete it might be expected that the Si−H bond would be elongated relative to the free silane (average Si−H is usually taken as 1.48 Å[493]) and that the TM−Si bond would be longer. Schubert has proposed that a Si−H distance of 2.00 Å define the limit of any significant interaction between hydrogen and silicon.[5a] Since TM−Si distances change over a range that varies from a difference (shortest to longest) of 0.05 to 0.28 Å (see Table 6 and section IV) it is not a simple

Table 7. Derivatives with σ-Interactions*,†

Complex	Prep.[1a] (% Yd)	Color m.p.	Anal.	NMR solvent (temp.) [1b]	NMR ^{1}H [1c] M-H	NMR ^{1}H [1c] Si-H	NMR ^{29}Si [1c]	Other Data	Ref.
Titanium Triad									
7-1a [Cp$_2$Ti(μ-HSiH$_2$)]$_2$	[1d] (—)	dk. blue	N	T	-10.07 (t)	4.69 (t)	—	—	466
7-1b* [Cp$_2$Ti(μ-HSiHPh)]$_2$	A (75)	blue-black —	Y	S (20)	-8.73 (s)	5.11 (s)	—	EPR X-ray	467
7-2a [Cp$_2$Ti(μ-HSiH$_2$)(μ-H)TiCp$_2$]	[1e] (—)	dk. yellow-green	N	S (20) S (-60)	 -13.3 (m) [1f] -19.32 (m) [1f]	5.80 (br s) 5.64 (br s) 5.38 (br s)	—	—	466
7-2b* [Cp$_2$Ti(μ-HSiHPh)-(μ-H)TiCp$_2$]	A (60)	—	Y	U (-22) (-63) [1g]	~ -12 (s) ~ -12 (s) ~ -20 (s) [1g]	~ 4.3 (s)	87 J_{SiH} = 148, 58, 14	EPR X-ray	467
7-3* Cp$_2$(Me$_3$P)Ti(η^2-H^{1}SiH^{2}Ph$_2$)	B (63)	yellow —	—	S U (-55)	-3.93 (br) -4.14 (dd) J_{HH} = 11	6.36 (br) 6.03 (dd) J_{HH} = 11	J_{SiHTi} = 28 J_{SiH} = 161[1h]	IR X-ray	468
Chromium Triad									
7-4* (η^6-1,2-Me$_2$C$_6$H$_4$)(OC)$_2$Cr-(η^2-HSiHPh$_2$) [1i]	C [1j]	yellow —	Y [1k]	T (-40)	-12.09 (d)	6.47 (d) J_{HCrSiH} =5.6	17.6 $^1J_{SiH}$ = 201 $^2J_{SiCrH}$ = 80	IR	469
7-5* (η^6-C$_6$Me$_6$)(OC)$_2$Cr-(η^2-HSiHPh$_2$)	C [1j] (82)	yellow 120(d)	Y	W: (^{1}H) U: (^{29}Si)	-11.5 (d)	6.1 (d) $^3J_{HCrSiH}$ = 5.6	21.2 $^1J_{SiH}$ = 197 $^2J_{SiCrH}$ = 70.8	IR X-ray	470
7-6* (OC)[(*i*-Bu)$_2$PCH$_2$CH$_2$P-(*i*-Bu)Mo$_2$](η^2-HSiH$_3$) [1l]	D	yellow —	Y	S (25)	-7.98 (s) [1m] J_{SiMoH} = 31	4.34 (s) [1m] $^1J_{SiH}$ = 163	—	^{31}P IR X-ray	22
7-7 (OC)(dppe)$_2$Mo(η^2-HSiH$_3$)	D	yellow —	Y [1k]	S (25)	-6.87 (s) [1m] J_{SiMoH} = 50	4.46 (s) [1m] $^1J_{SiH}$ = 181	—	^{31}P IR	22
7-8 (OC)(depe)$_2$Mo(η^2-HSiH$_3$)	D	yellow —	Y	T (-5)	-8.23 (s) [1m] J_{SiH} = 35	4.56 (s) [1m] $^1J_{SiH}$ = 164	—	VT-NMR ^{31}P IR	22
7-9 (OC)(depe) Mo(η^2-HSiH$_2$Ph)	D (—)	yellow —	Y	S (25)	-8.11 (d) [1m] J_{HH} = 3.9 J_{SiH} = 39	5.86 (dd) [1m] J_{HH} = 5.7, 3.9 J_{SiH} = 169 5.75 (d) [1m] J_{HH} = 5.7 J_{SiH} = 164	—	^{31}P IR X-ray	471
7-10 (OC)(depe)Mo(η^2-HSiHPh$_2$) [1n]	D (—)	yellow —	—	S	$^2J_{SiMoH}$ = 50	$^1J_{SiH}$ = 172	—	^{31}P IR	471
7-11 (OC)(dppe)$_2$Mo(η^2-HSiH$_2$Ph) [1o]	D (—)	yellow	—	S	$^2J_{SiMoH}$ = 57	$^1J_{SiH}$ = 187, 194 [1m]	—	—	471
7-12 (OC)[(PhCH$_2$)$_2$PCH$_2$CH$_2$-P(CH$_2$Ph)$_2$]Mo(η^2-HSiH$_2$Ph)	D [1p]	yellow —	—	S	$^2J_{SiMoH}$ = 41 [1m]	$^1J_{SiH}$ = 164, 165 [1m]	—	—	471
7-13 (OC)[(PhCH$_2$)$_2$PCH$_2$CH$_2$-P(CH$_2$Ph)$_2$]Mo[η^2-HSiH$_2$ (Hex)]	D [1p]	yellow —	—	S	J_{SiMoH} = 42 [1m]	$^1J_{SiH}$ = 160, 166 [1m]	—	—	471
7-14* (OC)$_4$W(η^2-HSiPh$_2$CH$_2$CH$_2$-PPh$_2$) [1q]	E (46)	lt. yellow 47	Y [1k]	S	-6.90 (d) $^1J_{WH}$ = 37 J_{SiWH} = 98.1		11.4 (br s)	^{13}C, ^{31}P	472

Table 7 (Continued)

Complex	Prep.[1a] (% Yd)	Color m.p.	Anal.	NMR solvent (temp.)[1b]	^{1}H[1c] M-H	^{1}H[1c] Si-H	^{29}Si[1c]	Other Data	Ref.
7-15* (OC)$_3$(dppe)W[η^2-HSi-(*p*-Tol)Cl$_2$]	F [1j] (68)	— 63 (d)	Y	Y	-3.98 (dd) $^1J_{WH}$ = 46		44.6 (dd) $^2J_{SiWH}$ = 35	^{13}C, ^{31}P	140
Cr Triad: M$_2$									
7-16* {(OC)$_3$[(*i*-Pr)$_3$P]W-(μ-SiHPh$_2$)}$_2$	G (34)	orange —	Y	U (^{29}Si, -20)	-7.26 (m)		146.3 (br d) J_{SiH} = 52	^{13}C, ^{31}P X-ray	473
Manganese Triad									
7-17* Cp(OC)$_2$Mn(η^2-HSiHPh$_2$)	G [1j]							PES	474
7-18 Cp'(OC)$_2$Mn(η^2-HSiHPh$_2$)	G [1j] (75)	lt. yellow 67 (d)	Y	Q	-11.5 (br d) J_{HH} = 4.95	6.7 (d)	13.5 $^2J_{HMnSi}$ = 63.5 $^1J_{HSi}$ = 205.2	IR PES X-ray	458, 474, 475, 476
7-19 Cp*(OC)$_2$Mn(η^2-HSiHPh$_2$)	G [1j] (53)	lt. yellow 105 (d)	Y	W	-11.2 (d) $^3J_{HMnSiH}$ = 4.6	—	18.2 J_{HMnSi} = 65.4 $^1J_{SiH}$ = 200.3	IR	458
7-20 Cp'(OC)$_2$Mn(η^2-HSiHPhR) R = 1-C$_{10}$H$_7$ [1r]	G (41)	yellow 91-92	Y [1h]	S Y	-11.23 J = 4.5 -11.46 (d)	[1s]	7.5 $^1J_{SiH}$ = 208, 69	—	464, 477
7-21a Cp'(OC)$_2$Mn(η^2-HSiPh$_3$)	G (—)	lt. yellow 95-96	Y	C$_6$H$_{12}$: (^{1}H) S: (^{29}Si)	-11.5 (br) (21.5 τ)		18.5 J_{SiH} = 64.7	IR X-ray PES	144, 464, 476
7-21b Cp'(OC)$_2$Mn(η^2-HSiPh$_2$-SiHPh$_2$) [1t]	G (9)	— 76 (d)	Y	S	-10.71 (s) J_{SiH} = 57	5.69 (s) $^1J_{SiH}$ = 173	-27.4 -2.6 (MnSi)	^{13}C IR	147
7-22 Cp'(OC)$_2$Mn(η^2-HSiPh$_2$F)	[1u] (79)	yellow 99 (d)	Y	W	-11.0 (br d)		—	IR PES N.D.	458, 476, 478
7-23 Cp'(OC)$_2$Mn(η^2-HSiCl$_3$)	G (—)	—	—	S			54.9 J_{HMnSi} = 54.8	X-ray	458, 479
7-24 Cp*(OC)$_2$Mn(η^2-HSiHPh$_2$)	G [1j] (53)	yellow 105 (d)	Y	W	-11.2 (d) $^3J_{HMnSiH}$ = 4.6	5.9 (d)	18.2 J_{HMnSi} = 65.4	IR PES X-ray	458, 474
7-25 Cp'(OC)(Me$_3$P)Mn-(η^2-HSiHPh$_2$) [1v]	G [1j] (45)	— 91	Y	W	-12.0 (dd)	6.4 (dd) $^3J_{HMnSiH}$=5.2	26 $^2J_{HMnSi}$ = 38 $^1J_{SiH}$ = 188	^{31}P IR X-ray PES	303, 458, 480, 481
7-26 Cp'(OC)(Me$_3$P)(H)MnSiCl$_3$	G (—)	—		S (30)		—	59.5 $^2J_{HMnSi}$ = 20	PES	458, 480, 481
7-27 Cp'(OC)(Ph$_3$P)Mn-(η^2-HSiHPh$_2$) [1t]	G [1j] (49)	— 115 (d)	Y [1k]	W: (^{1}H) S: (^{29}Si)	-11.1 (dd)	6.3 (dd) J_{HMnSiH}= 5.0	22.8 (23.8) J_{HMnSi} = 43 (62) $^1J_{SiH}$ = 191 (200)	^{31}P IR	303, 458, 481
7-28* Cp'(OC)Mn(η^2-HSiPh$_2$CH$_2$-CH$_2$PPh$_2$)	G (40)	brt. yellow 100 (d)	Y	S: (^{1}H) S/S': (^{29}Si)	-12.8 (d)		47.2 (d)	^{31}P IR, MS X-ray	482a

Table 7 (Continued)

Complex	Prep.[1a] (% Yd)	Color m.p.	Anal.	NMR				Other Data	Ref.
				solvent (temp.)[1b]	^1H [1c] M-H	^1H [1c] Si-H	^{29}Si [1c]		
7-29a $Cp'(OC)Mn(\eta^2\text{-}HSiPh_2CH_2\text{-}CH_2PPh_2)$	G (31)	yellow 46 (d)	Y[1k]	S: (^1H) S/S': (^{29}Si)	-14.0 (d)		33.1	^{31}P	482a
7-29b $[Cp'(OC)_2Mn(H)SiMePh]_2$ [1w]	G (23)	yellow 88	Y	S	-11.2 (s) $J_{SiH} = 57$		-3.6 -2.8	^{13}C	147
Iron Triad									
7-30 * $[Cp(OC)(Et_3P)Fe\text{-}(\eta^2\text{-}HSiEt_3)]^+[BAr_4]^-$ [1x, 1y]	[1z]	—	—	Y	-16.6 (d) $J_{SiH} = 62.4$		—	^{13}C	482b
7-31 $[Cp(OC)(Et_3P)Fe\text{-}(\eta^2\text{-}H^1SiH^2Ph_2)]^+[BAr_4^-]$ [1x, 2a] $Ar = 3,5(CF_3)_2C_6H_3$	[2b]	—	—	Y	-12.9 (SiH^1) $J_{SiH} = 58$	6.5 (SiH^2) $^1J_{SiH} = 232$	—	—	482b
7-32* $[Cp(Me_3P)_2Ru(\eta\text{-}HSiCl_3)]^+[BAr_4]^-$ $Ar = 3,5(CF_3)_2C_6H_3$	[2c] (88)	tan		R	-9.87 (t) $^2J_{SiH} = 48$	30.60 (d) $^2J_{SiH} = 49$	—	—	483
7-33* $\{Cp^*Ru[\eta\text{-}HSi(SiMe_3)\text{-}C_4Me_4]\}[BPh_4]$	H (—)	amber —	Y [1k]	Y	-8.82 (s)		-144.4 *Si*$(SiMe_3)_3$ -27.1 C_4*Si*H -6.8 $^1J_{SiH} = 41$ Si(*Si*$Me_3)_3$	^{13}C X-ray	484
7-34 $L_2H_2(H_2)Ru(\eta^2\text{-}HSiPh_3)$ $L = PCy_3$	[2d]								485, 486a
7-35* $(Cy_3P)_2(H^2)_2Ru[(\mu\text{-}H^1\text{-}SiMe_2)_2C_6H_4]$	[2e] (90)	white —	Y	S (23)	-7.74 (t, H^1) -12.03 (H^2) [2f]		4.8 $J_{RuSiH} =$ 63	VT-NMR ^{31}P IR X-ray	486a
7-36 $L_2(H^2)_2Ru[(\eta^2\text{-}H^1SiMe_2)_2O]$ $L = PCy_3$	[2e] (~90)	white —	Y	S (23)	-9.48 (br)		-5.7 $J_{SiH} = 22$	VT-NMR ^{31}P $T_{1(min)}$ IR	486a
				S (-60)	-9.9 (t, H^2)	-8.5 (t, H^1)			
Iron Triad: M_2									
7-37* $[(OC)_3Fe]_2(\eta^2\text{-}HSiPh_2)_2$	[2g] (80)	yellow —	Y [1k]	S	-14.2 (s) $J_{SiH} = 23.4$		109.2	^{13}C IR X-ray	56
7-38* $[(OC)_4FeFe(CO)_3(Si^1H^1Ph_2)]\text{-}(\mu\text{-}\eta^2\text{-}H^2Si^2Ph_2)$	E (37)	red —	Y	S	-13.2 (s, FeH^2)	6.3 (s, SiH^1)	142.1 $J_{SiH} =$ 48.3 15.2 $^1J_{SiH} =$ 197.7	^{13}C X-ray	56
7-39* $(Cp^*Ru)_2(\mu\text{-}H)(H)(\mu\text{-}\eta^2\text{-}HSiMeCy)_2$	I (54)	orange-yellow 247-248	Y	S (23)	-14.1 (br s)		115.2	^{13}C IR	108
				T (-70)	-15.81 (s) -13.81 (s) -12.94 (s)				
7-40* $[\{Cp^*Ru\}_2(\mu\text{-}\eta^2\text{-}HSiEt_2)_2\text{-}(\mu\text{-}H)(H)]$ [2h]	J (—)	—	—	T (25) T (-80)	-12.81 (s) -13.54 (s) -13.90 (s) -14.50 (s)		—	^{13}C IR X-ray	386
7-41* $[Cp^*Ru(\mu\text{-}H)]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si(t\text{-}Bu)_2]$	J (89)	purple —	Y	S: (23, ^1H) T/U: 1/5 (-120, ^1H) T: (^{29}Si)	-11.12 (br) -6.15 (s) $J_{SiH} = 75$ -16.63 (s)		75.5 (quin) $J_{SiH} =$ 34.2	^{13}C IR	487

Table 7 (Continued)

Complex	Prep.[1a] (% Yd)	Color m.p.	Anal.	NMR solvent (temp.)[1b]	^{1}H[1c] M-H	^{1}H[1c] Si-H	^{29}Si[1c]	Other Data	Ref.
7-42* $[\mathrm{Cp^*Ru}]_2[\mu\text{-}\eta^2\text{-HSi}(t\text{-Bu})_2]\text{-}(\mu\text{-}\eta^2\text{-HSiHEt})(\mu\text{-H})(\mathrm{H})$	[2i] (82)	orange —	Y	T (60) T (-90)	-12.83 (br) -15.50 (br) -12.32 (s) -13.26 (s) -14.29 (s) -16.67 (s)	5.66 (br) $J_{SiH} = 160$ 5.64 (br)	—	^{13}C IR X-ray	487
7-43 $[\mathrm{Cp^*Ru}]_2[\mu\text{-}\eta^2\text{-HSi}(t\text{-Bu})_2](\mu\text{-}\eta^2\text{-HSiPhH}^1)(\mu\text{-H})(\mathrm{H})$	[2j] (68)	orange —	Y	T (20) T (-90)	-12.31 (br) -15.35 (br) -16.46 (s) -14.00 (s) $J_{SiH} = 49$ -12.84 (s) -12.31 (br) -11.64 (s) $J_{SiH} = 26$	6.29 (s) $^1J_{SiH1} = 172$ 6.37 (br)	—	^{13}C IR X-ray	487
7-44* $[\{\mathrm{Cp^*Ru}\}_2(\mu\text{-}\eta^2\text{-HSiPh}_2)\}_2\text{-}(\mu\text{-H})(\mathrm{H})]$	J (—)	—	—	T (25) T (-80)	-11.54 (s) -12.75 (s) -12.96 (s) -14.50 (s)		—	^{13}C IR	386
Cobalt Triad									
7-45 $\mathrm{CpRh(SiMe_3)_2(\eta^2\text{-}HSiEt_3)}$ [2k]	K (—)	—	N	T	-13.1 (d) $^1J_{RhH} = 35.4$	—	28.8 (d, $SiEt_3$) $^1J_{RhSi}=$ 17.9 $^2J_{SiH} =$ 24.3 17.1 (d, $SiMe_3$) $^1J_{RhSi} =$ 26.6 $^2J_{SiH} = 6.0$	^{13}C	226
7-46* $[\mathrm{(Ph_3P)_2(H^2)_2Ir(\eta^2\text{-}H^1SiEt_3)_2}]^+ \mathrm{SbF_6^-}$ [2l]	L (—)	—	N	Y (-80)	-9.85 (t, H^2)	-12.75 (m, H^1)	—	VT-NMR ^{1}H	488
7-47* $[\mathrm{(Ph_3P)_2(H^2)_2Ir\text{-}}[\eta^2\text{-}(\mathrm{H^1SiEt_2})_2]^+ \mathrm{SbF_6^-}$ [2l]	L (—)	—	N	Y (-93) [2m]	-9.84 (t, H^2)	-(12.6 to 12.9) (br, H^1)	—	VT-NMR ^{1}H	488
Cobalt Triad: M_2									
7-48* $\mathrm{(OC)_2(dppm)_2HRh_2\text{-}(\mu\text{-}HSiPh_2)}$	M (—)	yellow —	N	Y (-80)	-8.91 (br s)	-1.22 (br s)	—	VT-NMR ^{31}P IR	69
7-49* $[\mathrm{(dippe)HRh}]_2(\mu\text{-}\eta^2\text{-}\mathrm{HSiHBu})_2$ [2n]	N (—)	—	N	T	-11.85 (br s)	5.42 (br s)	—	VT-NMR ^{31}P	70
7-50 $[\mathrm{(dippe)(H)Rh}]_2[\mu\text{-}\eta^2\text{-H-SiH}(p\text{-Tol})]_2$ [2o]	N (—)	—	N	T	-5.12 (br s) -11.23 (br s) -12.45 (br s)	8.33-7.62 (br s) 5.36 (br s) 4.51 (br s)	—	VT-NMR ^{31}P	70
7-51* $[\mathrm{(dippe)Rh}]_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-H-SiMe}_2)$ [2p]	O (85)	red —	Y	S: (^{1}H) T: (^{29}Si)	-6.25 (m)	—	163 (m)	VT-NMR ^{31}P X-ray	125
7-52 $[\mathrm{(dippe)Rh}]_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-H-SiMePh})$	O (62)	red-brown —	Y	S	-6.00 (pt) $^1J_{RhH} = 15.1$	—	—	VT-NMR ^{31}P	125
7-53 $[\mathrm{(dippe)Rh}]_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-H-SiPh}_2)$ [2p]	O (77) [2q]	red —	Y	S: (^{1}H) T: (^{29}Si)	-6.17 (sept) $^1J_{RhH} = 14$	—	137-141 (br m)	VT-NMR ^{31}P X-ray	124, 125

Table 7 (Continued)

Complex	Prep.[1a] (% Yd)	Color m.p.	Anal.	NMR				Other Data	Ref.
				solvent (temp.)[1b]	^{1}H[1c] M-H	^{1}H[1c] Si-H	^{29}Si[1c]		
7-54* $[(dippe)Rh]_2(\mu\text{-SiHBu})(\mu\text{-}\eta^2\text{-HSiHBu})_2$	O (62)	yellow —	Y	S	-8.03 (m) $^1J_{RhH}$= 24 -8.48 (m) $^1J_{RhH}$= 22	6.78 (br s, HSi*H*Bu) $^1J_{SiH}$= 173 6.52 (br s, HSi*H*Bu) $^1J_{SiH}$= 173 4.59 (br s, Si*H*Bu) $^1J_{SiH}$= 165	125.5 (br t, H*Si*HBu) $^1J_{SiH}$=180 (average) 90.2 (br m, *Si*HBu)	VT-NMR ^{31}P	70
7-55 $[(dippe)Rh]_2[\mu\text{-SiH}(p\text{-Tol})][\mu\text{-}\eta^2\text{-HSiH}(p\text{-Tol})]_2$ [2p]	O (84)	orange —	Y	T: (^{1}H, ^{31}P) S: (^{29}Si)	-6.89 (m) $^1J_{RhH}$= 25	7.58-6.41 (br s)	142-100 (br)	VT-NMR ^{31}P X-ray	70
7-56 $[(dippp)Rh]_2(\mu\text{-H})(\mu\text{-}\eta^2\text{-H-SiPh}_2)$ [2p]	O (64)	red-brown —	Y	T	-8.55 (pt) $^1J_{RhH}$ = 14.6	—	—	^{31}P	125
7-57* $(OC)_2(dppm)_2(H)Ir_2(\mu\text{-}\eta^2\text{-H-SiPh}_2)$ [2r]	P (—)	—	N	Y (-20)	-11.86 (t)	- 3.84 (t)	—	VT-NMR ^{31}P	71
Ni Triad									
7-58* $[(Cy_3P)Pt(\mu\text{-HSiMe}_2)]_2$ [2s]	Q (80)	cream-white 180-184 (d)	Y	S	[2t]	—	—	^{31}P IR X-ray	489a
7-59* $[(Ph_3P)Pt(\mu\text{-}\eta^2\text{-HSiHAr}]_2$ [2u] Ar = 2-isopropyl-6-methylphenyl	R (73)	— >150 (d)	N	S		8.42 (cis) $^2J_{PtSiH}$ = 137, 78 8.92 (trans) $^2J_{PtSiH}$ = 137, 72	—	^{31}P IR X-ray (trans)	490
				U	1.49 (cis) [2v] 1.56 (trans)[2v]	7.80 (cis) 8.32 (trans)			
7-60* *trans*-$[(Et_3P)Pt(\eta^2\text{-HSi(Hex)-}\{PtH(PEt_3)_2\})]_2$ [2w]	S (20)	—		S	-2.24 (dd) $^1J_{PtH}$= 994	0.98 $^1J_{SiH}$= 31	195 (m) $^1J_{PtSi}$= 262	^{13}C, ^{31}P ^{195}Pt IR X-ray	77

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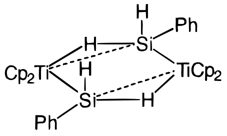
* Structural formulas for compound numbers marked with an asterisk may be found at the end of the table. † Abbreviations: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Hex, hexyl; Cy, cyclohexyl; Ph, phenyl; *p*-Tol, *p*-tolyl; Cp, η^5-C_5H_5; Cp′, MeC_5H_4; Cp*, η^5-C_5Me_5; dppe, $Ph_2PCH_2CH_2PPh_2$; dippe, $(i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2$; dippp, $(i\text{-}Pr)_2PCH_2CH_2CH_2P(i\text{-}Pr)_2$; dppm, $Ph_2PCH_2PPh_2$; depe, $Et_2PCH_2CH_2PEt_2$; d, decomposes; lt., light; dk., dark; brt., bright.

Footnotes: [1a] Reagent Key: A, Cp_2MR_2; B, $Cp_2M(PMe_3)_2$; C, $(ArH)Cr(CO)_3$; D, $(R_2PCH_2CH_2PR_2)_2MCO$; E, $M_x(CO)_y$; F, $M(CO)_4(dppe)$ or $M(CO)_4(tdppme)$; G, $Cp'Mn(CO)_3$ or $Cp'Mn(CO)_2(PR_3)$; H, $[Cp^*Ru(\mu\text{-OMe})]_2/Me_3SiOTf$; I, $[Cp^*Ru(\mu\text{-OMe})]_2$; J, $[Cp^*Ru(\mu\text{-H})_2]_2$; K, $Cp(C_2H_4)(H)Rh(SiEt_3)$ + heat; L, $[IrH_2(THF)_2(PPh_3)_2]SbF_6$; M, $Rh_2H_2(CO)_2(dppm)_2$; N, $[(dippe)Rh]_2(\mu\text{-SiHR})_2 + H_2$ (sealed), R = Bu or *p*-Tol; O, $[(L_2)Rh]_2(\mu\text{-H})_2$ (L_2 = dippe or dippp); P, $(OC)_3(dppm)_2Ir_2$; Q, $[(Cy_3P)Pt(C_2H_4)_2]$; R, $[(Ph_3P)_2Pt(C_2H_4)]$; S, $(R_3P)_3Pt$ (R = Et, Pr). [1b] Solvent key: Q, CCl_4; R, not specified; X, $CDCl_3$; S, C_6D_6; T, C_7D_8; U, THF-d_8; Y, CD_2Cl_2; Y′, CH_2Cl_2; V, $C_2D_2Cl_4$; W, $(CD_3)_2CO$; Z, CD_3CN. Data are for ambient temperature in °C unless specified otherwise. [1c] In ppm. Coupling constants in Hz. Assignments: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet. [1d] Isolated from the reaction of $(MeO)_3SiH$ with Cp_2TiMe_2. Disproportionation of $(MeO)_3SiH$ produces SiH_4 which then reacts with dimethyltitanocene. The reaction of Cp_2TiCl_2 with $KSiH_3$ also produced the Cp_2TiSiH_3 dimer. [1e] Produced from decomposition of $[Cp_2TiSiH_3]_2$ or by reaction of SiH_4 with Cp_2TiMe_2. [1f] The highest field resonance was assigned to the Ti−H−Ti bridge. [1g] Additional resonance at −20 ppm is present only at lower temperature. [1h] Data taken in THF-d_8 at −50 °C. [1i] Other derivatives of $(ArH)Cr(CO)_2(HSiR_3)$; ArH = $C_6H_5CH_2NMe_2$, $C_6H_5CO_2CH_3$, 1,4-$(CH_3COO)_2C_6H_4$. [1j] Photolysis. [1k] Analysis is outside ±0.5 of calculated percent value for carbon. [1l] Additional derivative: $Mo(CO)(dppe)_2(\eta^2\text{-HSiH}_3)$. [1m] $^1H\{^{31}P\}$ NMR. [1n] Additional derivative: $(OC)(depe)_2Mo[\eta^2\text{-HSiH}_2(Hex)]$. [1o] Additional derivative: $(OC)(dppe)_2Mo[\eta^2\text{-HSiH}_2(Hex)]$. [1p] In supplementary material of these references. [1q] Additional derivative: $(OC)_4W(Ph_2PCH_2CH_2SiHPh_2)$. [1r] Additional derivatives: SiRPhF; SiMeRPh; SiRPhCl. [1s] SiH is masked. [1t] Additional derivatives: $Cp'(OC)_2Mn(\eta^2\text{-HSiR}_3)$, R_3 = SiMePhSiHMePh, $SiMe_2SiHMe_2$. [1u] $Cp'(OC)_2HMnSiHPh_2 + [Ph_3C]^+BF_4^-$ (79%). [1v] Other derivatives of $Cp'(OC)L(H)MnSiHPh_2$: L = $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4Me\text{-}p)_3$, PBu_3, PMe_2Ph, $P(OPh)_3$, $P(OEt)_3$, PMe_3. Also $Cp'(OC)L(H)MnSiHEt_2$ (L = PPh_3, PBu_3). [1w] Additional derivative: $[Cp'(OC)_2Mn(H)SiMe_2]_2$. [1x] Generated in solution. [1y] Related derivatives prepared from $[Cp(OC)(Et_3P)Fe(HSiEt_3)]^+BAr_4^-$ and $H_2SiMePh$ or H_3SiPh. [1z] Reaction of $Cp(OC)LFeSiEt_3$ with $[H(OEt_2)_2]^+BAr_4^-$ [Ar = $(CF_3)_2C_6H_3$]; L = PEt_3, PPh_3. [2a] Other derivatives, $[Cp(OC)PPh_3Fe(\mu\text{-HSiR}_3)]^+BAr_4^-$: R_3Si = $SiEt_3$, SiHMePh. [2b] Prepared from reaction of $Cp(OC)(Et_3P)FeSiEt_3$ with $[H(OEt_2)_2]^+BAr_4^-$ followed by H_2SiPh_2. [2c] Reaction of $Cp(Me_3P)_2RuSiCl_3$ with $[H(OEt_2)_2]^+BAr_4^-$ [Ar = $(CF_3)_2C_6H_3$]. [2d] From reaction of $HSiPh_3$ with $RuH_2(H_2)_2(PCy_3)_2$. [2e] $(Me_2SiH)_2X$ (X = C_6H_4, O) or $CH_3CH{=}CHSiMe_2H + L_2(H)_2(H_2)_2Ru$ (L = PCy_3). [2f] AA′XX′. [2g] Prepared by photolysis of $[(OC)_4FeFe(CO)_3(SiHPh_2)](\mu\text{-}\eta^2\text{-}H^2Si^2Ph_2)$, **7−38**. [2h] Additional derivative from H_2SiPh_2. [2i] Reaction of $[Cp^*Ru(\mu\text{-H})]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si(t\text{-Bu})_2]$ and a large excess of H_2SiEt_2. [2j] $[(Cp^*)_2Ru_2(\mu\text{-H})]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si(t\text{-Bu})_2] + PhSiH_3$. [2k] Additional

Table 7 (Continued)

derivatives: $CpRh(SiMe_3)_3H$, $CpRh(SiEt_3)_3H$, $CpRh(SiEt_3)_2(SiMe_3)H$, $CpRh(SiMe_3)_3D$, and $CpRh(SiMe_3)_2(SiEt_3)D$. Dynamic process places silyl groups in η^2-silane position but Et_3Si group prefers this position. [2l] Observed in solution only and stable at low temperature. Preparations use $2HSiEt_3$ or $HEt_2SiSiHEt_2$ to afford complexes **7−46** and **7−47**, respectively. Deuterium analogue prepared with η^2-$DSiEt_3$. No ^{29}Si satellite peaks were observed by NMR. Complexes have cis arrangement of phosphine and η^2-silane and trans hydrides. The η^4-$Et_2HSiSiHEt_2$ derivative was also made with PCy_3 but the stereochemistry is different, phosphines are trans. [2m] Solvent mixture: $CD_2Cl_2 + CF_3Cl$. [2n] Fluxional on NMR time scale. ^1H NMR indicated two isomers in solution in approximately 3:1 ratio (data given for major isomer cis). Not isolated, observed in solution only and stable for a few hours under H_2 atmosphere. Deuterated analogue also prepared. $[(dippe)HRh]_2(\mu$-η^2-H-$SiMe_2)_2$ was previously prepared, isolated, and structurally characterized but results unpublished. [2o] Fluxional on NMR time scale. Not isolated, observed in solution only and stable for few hours under H_2 atmosphere. ^1H NMR indicated two isomers in solution (cis/trans: 3/1) and data are reported together. [2p] Complexes are fluxional on NMR time scale. ^{29}Si NMR signals are poorly resolved and broad even at low temperatures. [2q] Deuterium analogue also prepared. $[(dippe)Rh]_2(\mu$-H$)(\mu$-η^2-$SiHPh_2)$ was also prepared by reaction of Ph_2SiH_2 and $[(dippe)Rh]_2(\mu$-H$)(\mu$-η^2-$CH{=}CH_2)$ or from reaction of $[(dippe)Rh]_2(\mu$-$SiPh_2)_2$ (**3−88**) + H_2. [2r] Observed in solution at low temperature (−20 °C). [2s] Additional derivatives: $[(R_3P)_2HPt(\mu$-$SiMe_2)]_2$, $R_3P = Me(t$-$Bu)_2P$, $Ph(i$-$Pr)_2P$, Ph_3P; $[(R_3P)_2HPt(\mu$-$SiPh_2)]_2$, $R_3P = Me(t$-$Bu)_2P$, $Ph(i$-$Pr)_2P$, Ph_3P, Cy_3P. $[\{Me(t$-$Bu)_2P\}_2DPt(\mu$-$SiMe_2)]_2$ was prepared and ^2H NMR showed the Pt−D−Si resonance at δ 1.87 ppm (J_{PtD} = 93.3 and 18.5 Hz). Low yields of complex are formed by thermolysis of $[(Cy_3P)HPt(SiMe_2Ph)]_2$. $[(Cy_3P)HPt(SiMe_2)]_2$ was also made by reaction of $(Cy_3P)Pt(C_2H_4)_2$ with $HMe_2SiSiMe_3$. [2t] Pt−*H*−Si not observed. [2u] Two isomers formed, cis/trans ratio 1:3. [2v] Pt−H coupling not resolved. Assignments in THF-d_8 are from $^1H-^1H$ NOESY experiment. [2w] See **2−87** and **2−88** for related derivatives. Trace amounts of *trans*-$[(Pr_3P)Pt\{\eta^2$-$HSi(Hex)[PtH(PPr_3)_2]\}]_2$ were formed from reaction of $(Hex)SiH_3$ and $(Pr_3P)_3Pt$ (NMR characterization only).

Compound structures for Table 7:



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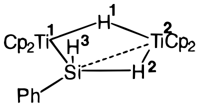

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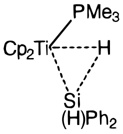

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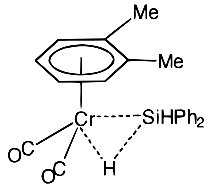

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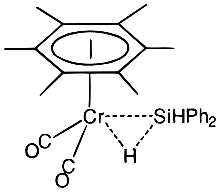

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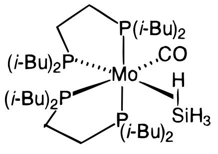

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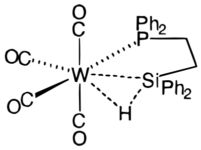

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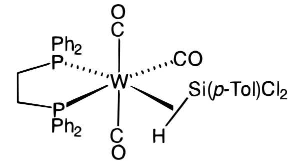

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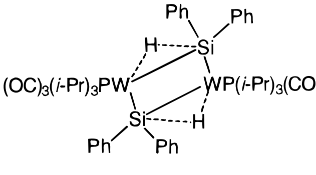

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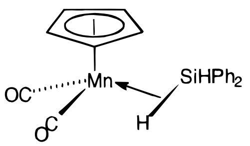

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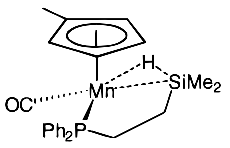

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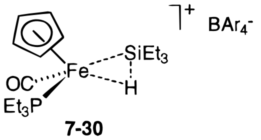

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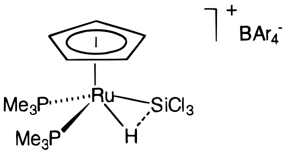

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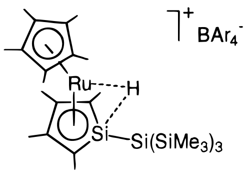

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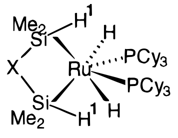
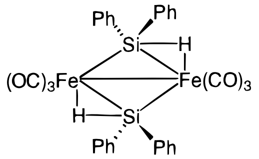


X = C_6H_4

7-35



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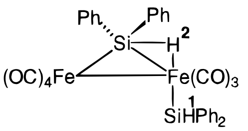

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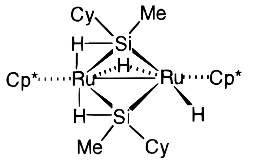

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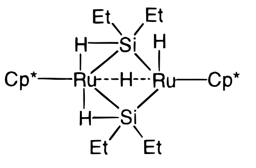

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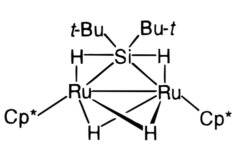

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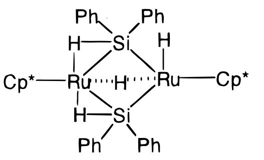

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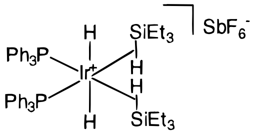

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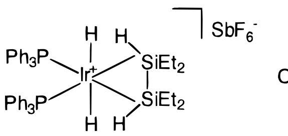

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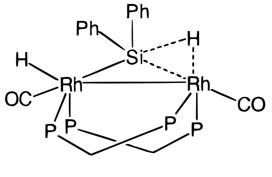
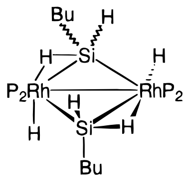


P = PPh_2

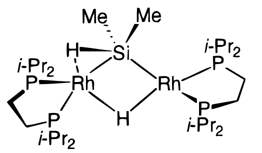
7-48



P = $P(i$-$Pr)_2$

7-49

Table 7 (Continued)



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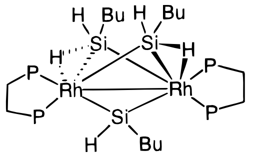
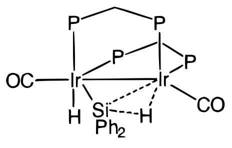


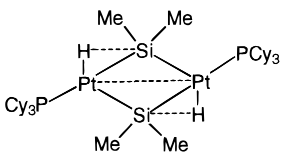
P = P(i-Pr)$_2$

7-54



P = PPh$_2$

7-57



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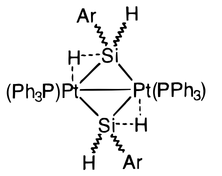
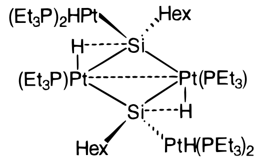


Ar = 2-isopropyl-6-methyl-phenyl

7-59



7-60

Table 8. X-ray Structures of σ-Complexes*,†

Complex	M-H	Si-H	M-Si	Ref
[Cp$_2$Ti(μ-HSiHPh)]$_2$ (**7-1b***)	Ti^1-H^4 1.76 (3) Ti^2-H^3 1.76 (3)	Si^1-H^1 1.47 (3) Si^1-H^3 1.58 (3)	Ti^1-Si^1 2.604 (2) Ti^1-Si^2 2.891 (2) Ti^2-Si^1 2.851 (2) Ti^2-Si^2 2.583 (2)	467
Cp$_2$Ti(μ-HSiHPh)(μ-H)TiCp$_2$] (**7-2b***)	Ti^1-H^1 1.97 (4) Ti^2-H^1 1.97 (4) Ti^2-H^2 1.59 (6)	Si-H^3 1.47 (3) Si-H^2 1.56 (7)	Ti^1-Si 2.61 (2) Ti^2-Si 2.78 (2)	467
Cp$_2$(Me$_3$P)Ti(η^2-HSiHPh$_2$) (**7-3***)	Ti-H^1 1.81 (5)	Si-H^1 1.69 (5) Si-H^2 1.56 (5)	2.597 (2)	468
Chromium Triad				
(η^6-C$_6$Me$_6$)(OC)$_2$Cr(η^2-HSiHPh$_2$) (**7-5***)	1.61 (4)	1.61 (4) (SiH^1) 1.39 (3) (SiH^2)	2.456 (1)	470
(OC)(depe)$_2$Mo(η^2-HSiH$_3$) (**7-8***)	[a]	[a]	2.556 (4)	22
(OC)(dppe)$_2$Mo(η^2-H^{1}SiH$^2_2$ Ph) (**7-11***)	1.70 (5)	Si-H^1 1.77 (6) Si-H^2 1.42 (6) Si-H^2 1.41 (6)	2.501 (2)	471
Chromium Triad: M$_2$				
{(OC)$_3$[(i-Pr)$_3$P]W(μ-SiHPh$_2$)}$_2$ (**7-16***)	[b]	[b]	2.523 (3) 2.708 (3)	473
Manganese Triad				
Cp'(OC)$_2$Mn(η^2-HSiHPh$_2$) (**7-18***)			2.364 (2)	[c]
Cp'(OC)$_2$Mn(η-HSiPh$_3$) (**7-21a**)	1.55 (4)	1.76 (4)	2.424 (2)	[d]
Cp'(OC)$_2$Mn(H)SiMePhNaph [e] (**8-1**)			2.461 (7)	491
Cp'(OC)$_2$Mn(η-HSiPh$_2$F) [f] (**7-22**) N.D.	1.569 (4)	1.802 (5)	2.352 (4)	458
Cp'(OC)$_2$Mn(η-HSiCl$_3$) (**7-23**)	1.47 (3)	1.79 (4)	2.254 (1)	331a
(Cp*)(OC)$_2$Mn[η-H^{1}SiH^{2}Ph$_2$)] (**7-24**)	Mn-H^1 1.52 (3)	Si-H^1 1.77 (4) Si-H^2 1.43 (3)	2.395 (1)	458
Cp'(OC)Me$_3$PMn-[η-H^{1}SiH^{2}Ph$_2$] (**7-25**)	Mn-H^1 1.49 (4)	Si-H^1 1.78 (4) Si-H^2 1.343 (4)	2.327 (1)	458

Table 8 (Continued)

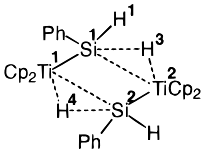
Complex	M-H	Si-H	M-Si	Ref
Cp'(OC)Mn(η^2-HSiPh$_2$CH$_2$CH$_2$-PPh$_2$) (**7-28***)	1.53 (4)	1.75 (4)	2.457 (2)	482
Fe Triad				
{Cp*Ru(H)[η-Me$_4$C$_4$Si-Si(SiMe$_3$)$_3$]}[BPh$_4$] (**7-33**)	1.48 (7)	1.70 (7)	2.441 (3)	484
[(Cy)$_3$P]$_2$(H^2)$_2$Ru[(μ-H^{1}SiMe$_2$)$_2$-C$_6$H$_4$] (**7-35***)	RuH^1 1.65 (3) 1.63 (3) RuH^2 1.67 (3) 1.60 (3)	SiH^1 1.88 (3) 1.83 (3)	2.425 (1) 2.429 (1)	486
Fe Triad: M$_2$				
[(OC)$_3$Fe]$_2$(η^2-HSiPh$_2$)$_2$ (**7-37***)	1.57[g]	2.10[g]	2.358 (6), 2.406 (6)	56
[(OC)$_4$FeFe(CO)$_3$(SiHPh$_2$)]-(μ-η^2-HSiPh$_2$) (**7-38***)	Fe^{2}H^2 1.66 [g]	Si^{2}H^1 1.43[g] Si^{1}H^2 1.66[g]	Fe^{1}Si^1 2.301 (2) Fe^{2}Si^2 2.365 (2) Fe^{2}Si^1 2.385 (2)	56
[{Cp*Ru}$_2$(μ-η^2-HSiEt$_2$)}$_2$(μ-H)-(H)] (**7-40***)	Ru^{1}H^1 1.71 (5) Ru^{1}H^2 1.63 (4) Ru^{1}H^3 1.72 (4) Ru^{2}H^1 1.69 (5) Ru^{2}H^4 1.45 (4)	Si^{1}H^2 1.75 (4) Si^{2}H^3 1.68 (4)	Ru^{1}Si^1 2.544 (2) Ru^{1}Si^2 2.551 (2) Ru^{2}Si^1 2.338 (1)	386
[Cp*Ru(CO)$_2$]$_2$(μ-η^2:η^2-H$_2$Si(t-Bu)$_2$) (**8-2**) [h]	1.43 (4) 1.44 (4)	1.75 (4) 1.77 (3)	2.447 (1) 2.457 (1)	487
[Cp*Ru]$_2$[μ-η^2-HSi(t-Bu)$_2$]-(μ-η^2-HSiHEt)(μ-H)(H) (**7-42***)	Ru^{1}H^2 1.79 Ru^{2}H^2 1.72 [i]	Si^{1}H^1 = 1.47	Ru^{1}Si^1 2.414 (4) Ru^{1}Si^2 2.680 (3) Ru^{2}Si^1 2.322 (3) Ru^{2}Si^2 2.365 (3)	487
[Cp*Ru]$_2$[μ-η^2-HSi(t-Bu)$_2$]-(μ-η^2-HSiPhH)(μ-H)(H) (**7-43***)	Ru^{2}H^1 1.76 (3) Ru^{1}H^1 1.73 (3) Ru^{2}H^3 1.64 (3) Ru^{1}H^2 1.43 (3) Ru^{2}H^4 1.64 (3)	Si^{1}H^3 1.89 (3) Si^{2}H^4 1.77 (3) Si^{1}H^5 1.50 (3)	Ru^{2}Si^1 2.438 (1) Ru^{1}Si^1 2.300 (1) Ru^{2}Si^2 2.675 (1) Ru^{1}Si^2 2.375 (1)	487
Co Triad: M$_2$				
[(dippe)Rh]$_2$(μ-H)(μ-η^2-HSiMe$_2$)$_2$ (**7-51***) [j]	Rh^1-H^1 1.65 (3) Rh^2-Si^1 1.91 (3) Rh^2-H^2 1.51 (4)	Si-H^2 1.73 (4)	Rh^1-Si^1 2.308 (1) Rh^2-Si^1 2.463 (1)	125
[(dippe)Rh]$_2$(μ -H)(μ-η^2-HSiPh$_2$) (**7-53***) [j]	Rh^1-H^1 1.71 (6) Rh^2-Si^1 1.90 (6) Rh^2-H^2 1.61 (6)	Si-H^2 1.66 (6)	Rh^1-Si 2.298 (2) Rh^2-Si 2.487 (2)	124,125
[(dippe)Rh]$_2$[μ-SiH(p-Tol)]-[μ-η^2-HSiH(p-Tol)]$_2$ (**7-55***) [k]	Rh^1-H^4 1.49 Rh^1-H^2 1.47	Si^1-H^1 1.41 Si^2-H^2 1.47 Si^2-H^3 1.31 Si^3-H^4 1.43 Si^3-H^5 1.39	Rh^1-Si^1 2.336 (2) Rh^2-Si^1 2.356 (20 Rh^1-Si^2 2.349 (2) Rh^2-Si^2 2.477 (2) Rh^1-Si^3 2.444 (2) Rh^2-Si^3 2.350 (2)	70
Ni Triad: M$_2$				
{[(Cy)$_3$P]$_2$Pt(μ-HSiMe$_2$)]$_2$ (**7-58***)	1.78	1.72	2.324 (2) 2.420 (2) [l]	489
trans-[(Ph$_3$P)Pt(μ-η^2-HSiHAr]$_2$ **(7-59*)** Ar = 2-isopropyl-6-methylphenyl	Pt$\cdots$H^1 1.821	Si$\cdots$H^1 1.674 SiH^2 1.556	2.325, 2.427 [l]	490
trans-[(Pr$_3$P)Pt(η^2-HSi(Hex)-{PtH(PPr$_3$)$_2$})]$_2$ (**7-60***)	[m]	[m]	Si^1- Pt^1 2.431 (4) [l] Si^1- Pt^2 2.353 (3) Si^2- Pt^1 2.347 (3) Si^2- Pt^2 2.441 (4) [l] (ring Si-Pt) Si^1- Pt^4 2.377 (4) Si^2- Pt^3 2.375 (4) (terminal Si-Pt)	77

Table 8 (Continued)

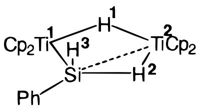
* Structural formulas for compound numbers marked with an asterisk may be found at the end of the table. † Abbreviations: N.D., neutron diffraction.

Footnotes: [a] Not located (positional disorder). [b] Indicated hydrogens were not located. [c] Footnote 22 cited in ref 458. [d] Footnote 20 cited in ref 458. [e] Prepared from Cp′Mn(CO)$_3$ and HSiPhMeNaph. [f] Prepared from reaction of Cp′(OC)$_2$Mn(η-HSiHPh$_2$) with [Ph$_3$C]$^+$BF$_4^-$.[458] [g] To compensate for underestimation of error for hydrogen atoms, parameters were truncated by one significant figure. [h] Prepared from **7−41** under CO atmosphere.[487] [i] Three of the four H-atoms bound to Ru atoms were located in the Fourier difference map. The H-atom bridging the two Ru centers and terminal Si−H were located but not refined. [j] Average lengthening of bridged Rh−Si bond relative to unbridged is 0.17 Å, and Si−H distances are roughly 0.2 Å longer than the length in a free silane. [k] Silyl hydrides were located in the difference map but were not refined. [l] Pt−Si distance containing nonclassical interaction. [m] Hydride located but not refined.

Compound structures for Table 8:



7-1b



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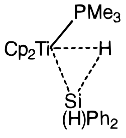

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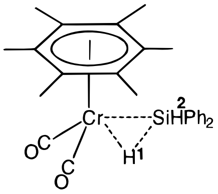

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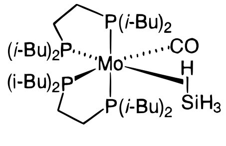

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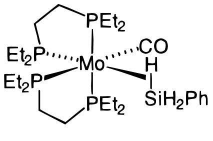

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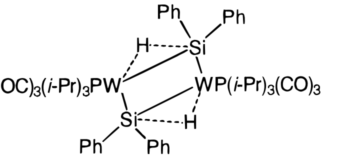

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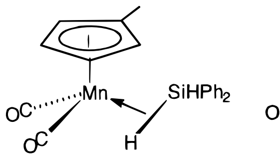

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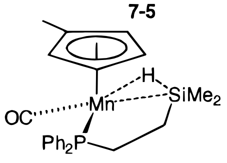

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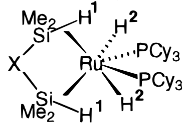
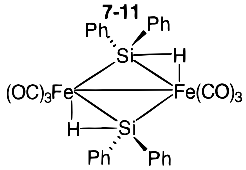


X = C$_6$H$_4$

7-35



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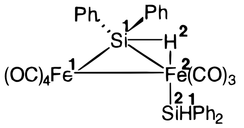

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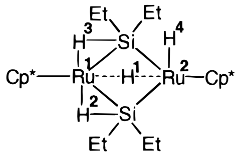

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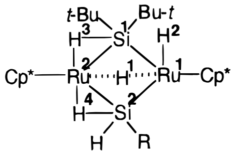
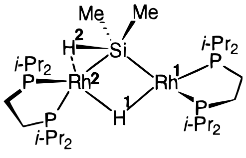


R = Et (**7-42**)
R = Ph (**7-43**)



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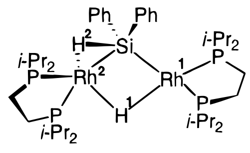

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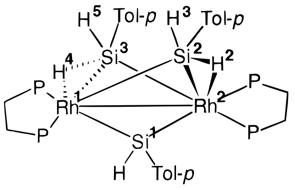
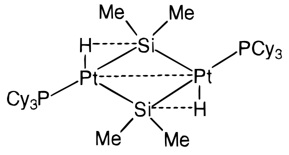


P = P(*i*-Pr)$_2$

7-55



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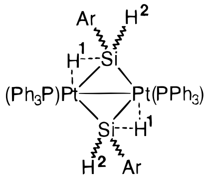
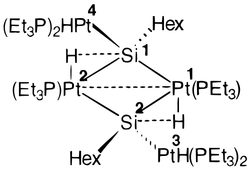


Ar = 2-isopropyl-6-methyl-phenyl

7-59



7-60

Table 9. Comparison of 2c−2e and 3c−2e Distances for M−Si[a]

metal−silicon	range (Å)	range for σ interactions
Ti	2.646−2.765(10)[b]	2.583−2.891(7)
Cr	2.343−2.431(11)	2.456(1)
Mo	2.513−2.670(13)	2.501−2.556(2)
W	2.469−2.652(21)[c]	2.523−2.708(2)
Mn	2.319−2.564(8)	2.254−2.461(8)
Fe	2.197−2.422(119)	2.358−2.406(4)
Ru	2.190−2.465(58)	2.300−2.680(15)
Rh	2.203−2.406(43)	2.298−2.487(8)
Pt	2.255−2.444(65)	2.348−2.439(3)

[a] Number in parentheses is the number of independent measurements. [b] One value outside of range: 2.159 Å.[307] [c] One value outside of range: 2.388 Å.[323]

matter to establish a "normal" TM−Si distance as has been discussed in detail for Cp′L$_2$Mn(H)SiR$_3$ (L = CO or phosphine) systems by Schubert.[5a] When the cases from Table 8 are added to Table 5, most of the values for 3c−2e interactions fall within the range defined by 2c−2e bonds as compared in Table 9. Furthermore, in some instances the σ-interactions expand the long end of the range (Ti, Cr, W, Ru, Rh) as well as the *short* end of the range (Ti, Mo, Mn). Thus, the TM−Si distance does not not appear to be a reliable indicator of either the presence or absence of a 3c−2e interaction. Since TM−H distances are not known with similar precision and accuracy, such distances also may not be a reliable guide.

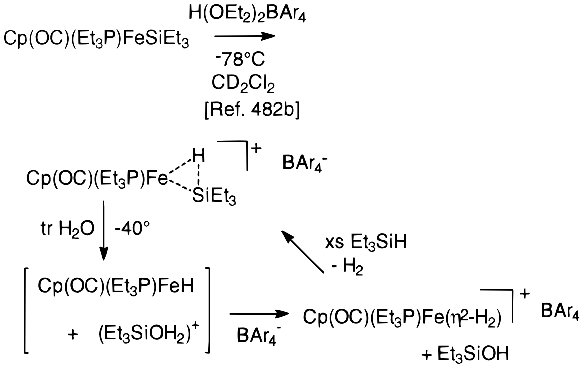
There are several examples of complexes produced from SiH$_4$, as well as primary and secondary silanes where both an η^2-HSi (3c−2e) interaction and a Si−H (2c−2e) interaction are present in the same complex. Such systems allow for a direct comparison of the two types of bonds in the same derivative. Not all of the examples shown in Table 7 are crystallographically characterized, and of those that are, the hydrogens at both silicon and the metal are not always located. Of the examples included in Table 8 where two different Si−H bonds are identified in a single silicon center (**7−1b**, **7−2b**, **7−3**, **7−5**, **7−8**, **7−11**, **7−24**, **7−25**, **7−43**, and **7−55**), the difference in the 2c−2e vs 3c−3e Si−H distances varies from about 0.10 Å (Ti) to 0.39 Å (Ru) and corresponds to a 7 to 26% increase in the Si−H bond distance. In an additional example, $[(OC)_4FeFe(CO)_3(SiHPh_2)](\mu\text{-}\eta^2\text{-}HSiPh_2)$ **7−38**, there is a $HSiPh_2$ terminal group and a bridging $-HSiPh_2$ unit with a difference in the Si−H distance of 0.23 Å. Several other systems in Table 8 exhibit ≥ 18% increase (SiH ≥ 1.75 Å) for a presumed η^2-HSi interaction and include **7−21a**, **7−22** to **7−25**, **7−19**, $Cp(OC)_2Mn(HSiCl_2Ph)$,[1d] **7−28**, **7−35**, **7−37**, **7−40**, **7−41**, and **7−43**. The longest Si−H distance in a $-HSiPh_2$ unit that bridges a TM−Si center was reported for the dinuclear iron complex $[(OC)_3Fe]_2(\eta^2\text{-}HSiPh_2)_2$ (**7−37**) with a value of 2.10 Å[56] which indicates a rather *weak* interaction. It is tempting to attribute such long Si−H distances to an oxidative addition trajectory that is close to the product of a 2c−2e M−H interaction, and in this case the FeH bond is relatively short and within 0.10 Å of the FeH bonds given in Table 5.

A second indication of a nonclassical 3c−2e interaction in an (TM)HSi sequence is revealed in NMR coupling constants. The $^1J_{SiH}$ coupling constants in free silanes are usually found between 150 and 200 Hz and the J_{SiH} values are generally found below 20 Hz in classical H−TM−Si (2c−2e) interactions. Thus, when the Si−H coupling constant falls below 10−20 Hz, a "strong" Si−H interaction is unlikely.[5] The range of J_{SiH} values for nonclassical interactions appeared to be about 40−70 Hz in the earlier systems (where structural analyses also supported the interaction[1d]) but subsequent studies suggested that the range needs to be extended on both ends. For example, in a recently reported η^2-HSi chelate complex of Ru with the ligand $HSiMe_2OSiMe_2H$ (**7−36**[486a]), the J_{SiH} was 22 Hz but the J_{SiH} value was 98 Hz in the chelate system $(OC)_4W(Ph_2PCH_2CH_2SiHPh_2)$ (**7−6**).[472] In both cases structural data support a σ, η^2-HSi interaction. A relationship between the coupling constant and the extent of oxidative addition has not yet been established.

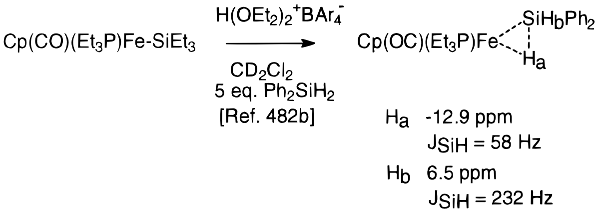
Table 7 contains complexes that have been prepared or physically characterized since 1980 (exceptions appear in Mn derivatives). Approximately half of the examples contain Cp or arene ligands and about one-third are dinuclear metal complexes.

B. Synthesis

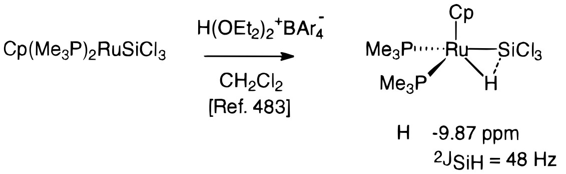
In general, the methods of synthesis of complexes with agostic interactions do not differ from those that have been described in section III for silylmetal complexes with 2c−2e bonds. The exception involves the protonation of a TM−Si bond in a preformed complex, eq 18. The success of this protonation reaction requires a nonnucleophilic anion such as $B[C_6H_3(CF_3)_2]_4^-$ as the counterion to the proton transfer reagent. Solvents must be scrupulously dry since traces of water remove the coordinated silyl group as illustrated in eq 19. For this reason, excess silane is used which then displaces the coordinated H_2 to give the product complex. Another useful tactic is to run the protonation in the presence of a second silane as shown in eq 19. The only complex that has been actually isolated by this synthetic route is shown in eq 20. The results suggest that complexes with coordinated η^2-H_2 may serve as precursors to η^2-HSi coordination. This tactic was recently employed to generate the first chelating η^2-HSi systems with $HMe_2SiXSiMe_2H$ (X = C_6H_4, O).[486a] Whether the approach can be utilized for metals other than the iron triad will require additional investigation.



(18)



(19)

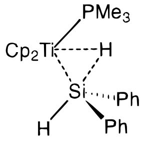


(20)

C. Titanium and Vanadium Triads

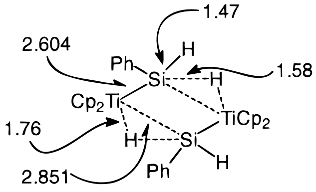
Complexes of titanium and vanadium triads that exhibit agostic interactions are primarily (but not exclusively) metallocene derivatives and then only with titanium from the titanium triad. A novel complex $Cp_2(Me_3P)Ti(\eta^2\text{-}H^1SiH^2Ph_2)$ (**7−3**) was generated when Ph_2SiH_2 reacted with $Cp_2Ti(PMe_3)_2$.[468] In this case there are clearly two different Si−H bonds associated with the Si center and the two Si−H distances differ by 0.13 Å. The Si center appears to be nearly trigonal bipyramidal with a H−Si−H ∠ of 156° (Figure 34). In contrast to **7−3**, the zirconium analogue (of the same stoichiometry), **3−5**, exists as two isomers of $Cp_2Zr(H)(SiHPh_2)\cdot PMe_3$.[82] The J_{HH} coupling constants (≤ 10 Hz) indicate no strong SiH···Zr interaction.

As discussed in section III, transition-metal complexes can promote redistribution of ligands at silicon centers. Such an approach was used by Tilley and co-workers to generate complexes with $-SiH_3$ ligands.[21a] Harrod examined the redistribution of $(MeO)_3SiH$ in the presence of Cp_2TiMe_2 and isolated the complex $[Cp_2Ti(\mu\text{-}HSiH_2)]_2$, **7−1a**, which slowly decomposed in solution to $[Cp_2Ti(\mu\text{-}HSiH_2)(\mu\text{-}H)TiCp_2]$ (analogue of **7−2b**[466]). Related compounds were obtained when excess $PhSiH_3$ was reacted with



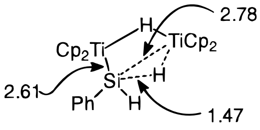
7-3

Figure 34. Titanium complex with σ Si···H···Ti interactions.[468]



(*cis*) **7-1b**

Figure 35. Titanium complex with σ Si···H···Ti interactions (bond distances in angstroms).[467]



7-2b

Figure 36. Titanium complex with σ Si···H···Ti interactions (bond distances in angstroms).[467]

Cp_2TiMe_2 to give the Ti(III) dimer, **7−1b** (Figure 35). When a stoichiometric ratio of the two reactants was used, a mixed Ti(III) dimer, **7−2b**, was formed although this dimer may also be viewed as a Ti^{IV}/Ti^{II} mixed dimer (Figure 36). The dimer **7−1b** was transformed to **7−2b** unless excess silane was present. Additional examples of the titanium dimers were prepared from the reaction of Cp_2TiMe_2 with $MeSiH_3$, $BuMeSiH_2$, Ph_2SiH_2, and $PhMeSiH_2$. Only the dimer related to **7−2b** is formed from these silanes and only the dimer from $BuMeSiH_2$ appeared to be stable.[35] Three different J_{SiH} values were observed in solutions of **7−2b**: 148, 58, and 14 Hz. The intermediate value is in the range of an agostic interaction. Although there are Zr(IV) dimers (for example, see **3−13** and **3−14**) none appear to display any evidence for an agostic interaction (^{29}Si NMR measurements were not reported).

In somewhat related chemistry, the reaction of $Cp_2Ta(L)CH_3$ ($L = CH_2{=}CH_2$) with excess $HSiR_3$ provided the symmetrical isomer of $Cp_2Ta(H)(SiR_3)_2$ [$SiR_3 = SiMeH_2$ (**2−13**), $SiMe_2H$ (**3−18**), $SiMe_3$ (**4−19**), $SiMe_2Cl$ (**4−20**), $Si(OMe)_3$ (**4−21**)] and the unsymmetrical isomer was only observed for $SiR_3 = SiMeH_2$ (**2−14**).[13a] The crystal structure of **3−18** was obtained and the hydride (Ta−H), located in the metallocene wedge in the final difference Fourier map, was closer to one of the silicon centers than to the other (1.83 Å vs 2.48 Å). Although this suggested a possible σ-interaction of one of the $-SiMe_2H$ groups, the positional parameters for the hydride could not be refined. A recent neutron diffraction study supports a symmetrical placement of TaH relative to the two silicon centers,[13b] consistent with the observed ^{1}H NMR data which showed that the two $SiMe_2H$ groups were equivalent. Although an associated niobium complex $Cp_2Nb(H)(SiMe_2Cl)_2$ (**4−9**) was originally reported with a σ NbHSi interaction, refinement of the structure in the correct space group showed a symmetrical placement of the Nb−H between the two Si centers.[136] The ^{1}H and ^{29}Si spectral data for $Cp'_2Nb(H)_2(SiPh_2H)$ (**3−16**, $Cp' = C_5H_4SiMe_3$), also were consistent with a "classical" interaction.[39]

Table 10. Comparison of Structural Data in Isoelectronic Complexes

parameter	$C_6Me_6Cr(CO)_2$-(H)$SiHPh_2$ **7−5**[470]	$C_5Me_5Mn(CO)_3$-(H)$SiHPh_2$ **7−19**[458]
M−Si	2.456(1)	2.395(1)
M−H	1.61(4)	1.52(3)
$Si-H_{(br)}$	1.61(4)	1.77(3)
$Si-H_{(term)}$	1.39(3)	1.43(3)

The first proposed agostic V···HSi interaction involved a study of systems that were closely related to Cr and Mo complexes described in the next section. The study involved the photolysis of $CpV(CO)_4$ in liquid Xenon (−80 °C) in the presence of $HSiEt_{3-x}Cl_x$ ($x = 0, 2, 3$). The identification relies on IR measurements since the products were too thermally labile for isolation. The two silanes, $HSiEt_3$ and $HSiCl_3$, seemed to give different products.[494] With $HSiCl_3$, the ν(C−O) in the product $[CpV(CO)_3(H)(SiCl_3)]$ was shifted to a wavenumber higher than in the starting $CpV(CO)_4$ and was similar to that exhibited by the known classical dihydride, $CpV(CO)_3(H)_2$. No ν(V−H) was detected for the product but an oxidative addition product was assumed. In the case of $HSiEt_3$, the ν(C−O) bands were lower than the starting material which suggested a σ-donating ligand. The relative intensities of the ν(C−O) bands were similar to those exhibited by $CpV(CO)_3(\eta^2\text{-}H_2)$. Although these results are somewhat tenuous in terms of the usual standards for sigma interactions, they do suggest that suitable adjustment of substituents at both V and/or Si is needed. Appropriate substituents may result in the isolation or observation of a σ-interaction by NMR methods.

D. Chromium and Manganese Triads

The majority of the Cr and Mn nonclassical complexes involve an aromatic unit such as $(ArH)Cr(CO)_2(HSiR_3)$ (ArH = benzene derivative) or $CpMn(CO)_2(HSiR_3)$. The Mn complexes are the most extensively studied of all systems that exhibit a σ-interaction. In general, the complexes are prepared by photolysis or thermolysis of the carbonyl precursor, (ArH or Cp)$M(CO)_3$. Several variations of substituents at silicon have been studied, particularly when TM = Mn and for many, solid-state structural data are also available.

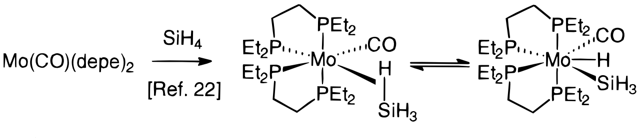
One of the few agostic chromium derivatives that has been structurally characterized is $(C_6Me_6)Cr(CO)_2(\eta^2\text{-}HSiHPh_2)$ (**7−5**[470]), which is isoelectronic to $Cp^*Mn(CO)_2(\eta^2\text{-}HSiHPh_2)$ (**7−19**[458]). In this case, the pertinent hydrogen positions were refined. A comparison of selected parameters for these related compounds is given in Table 10. The SiH_{term} is shorter in **7−5** (Cr) compared to **7−19** (Mn). The authors rationalized the difference between the two systems by assuming an earlier stage in the oxidative addition of the silane to Cr than in the case of Mn. Consistent with this proposal is the fact that the M−H distance is longer in **7−5** than in **7−19**. The Cr−Si distance which is 0.06 Å longer than the Mn−Si distance is also as long as the covalent radius of Cr(0) and was anticipated to be 0.01 to 0.02 Å greater than the isoelectronic Mn(I). The J_{SiH} coupling constant is also about 8% higher than that reported for **7−19**. Several additional $(ArH)Cr(CO)_2(H_a)SiH_bPh_2$ complexes have been prepared (none with X-ray data) where the $J(SiH_a)$ coupling constants range from 79 to 82.5 ± 2 Hz and the $^1J(SiH_b)$ values range from 201 to 221.5 Hz.[469] Also, examples of $(ArH)Cr(CO)_2(H)(SiCl_3)$, ($ArH = C_6H_{6-n}Me_n$, $n = 0$, 1 (**4−27**), 3 (**4−29**);[137] ArH = FC_6H_5 (**4−28**), $F_2C_6H_4$, $C_6H_5CF_3$, $(CF_3)_2C_6H_4$[139]) have been prepared but all were depicted as the full oxidative addition product (2c−2e bonds). The dihydride, $[C_6H_3(CH_3)_3]Cr(CO)(H)_2(SiCl_3)_2$, **4−31**, has also been reported and although the authors favored a Cr(IV) species (2c−2e Cr−H bonds) the system is fluxional.[138] Part of the argument hinged on the inability to measure a J_{SiH} coupling constant and the expectation that the resonance associated with CrHSi should be closer to the region of H−Si in $HSiCl_3$ (∼ +5 ppm). Since the line width was about 160 Hz at room temperature, this may have precluded observation of any J_{SiH} coupling constants which are <100 Hz. There is also no requirement that the TMHSi (3c−2e) resonance be closer to the normal Si−H region and indeed, is usually found in the TMH region (as was the case for **4−31**). The enthalpy of metal−silane (silane = Et_3SiH) binding has been measured by photoacoustic calorimetry (PAC) and was 28 kcal/mol for $(C_6H_6)Cr(CO)_3$ and 24.4 kcal for $CpMn(CO)_3$ (after photolyis).[495] Incomplete oxidative addition to the metal was also concluded in this study.

The $Cp'Mn(CO)_2(\eta^2\text{-}HSiR_3)$ system has been extensively studied and details of the work done in the 1980s have been summarized well by Schubert.[5] The nonclassical Si−H distance tends to be found between 1.75 and 1.80 Å for a number of $(C_5R_5')(OC)LMn(\eta^2\text{-}HSiR_3)$ complexes[5] and although X-ray data for TM−H(Si) are not always reliable, a neutron diffraction study of $Cp'(OC)_2Mn(\eta^2\text{-}HSiFPh_2)$ (**7−22**) gave a Si−H distance of 1.802 Å.[458] The J_{SiH} values for 17 derivatives range from a low of 20 Hz in $Cp'(OC)(Me_3P)Mn(H)SiCl_3$ to a high of 69 Hz in $Cp'(OC)_2Mn(\eta^2\text{-}HSiHPhNp)$.[458] The Re complex, $Cp(OC)_2Re(H)SiPh_3$ exhibited a Si···H distance of 2.19 Å (position of the hydrogen was determined by minimization of intramolecular contacts[496]) which is greater than the 2.00 Å suggested by Schubert for a Si···H interaction. In the $Cp'M(CO)_2(HSiR_3)$ system, the factors which *promote* the formation of an agostic interaction include (a) lighter metal of the triad; (b) small, electron-withdrawing ligands; and (c) electron-donating substituents at silicon. However, this may not be uniformly observed for other metal triads.

Stable, mononuclear complexes derived from $M(CO)_6$ (M = Cr, Mo, W) or $Mn_2(CO)_{10}$ (M = Mn, Re) have not yet been isolated. The photochemical reaction of $M(CO)_6$ with $HSiEt_3$ has been monitored by IR and UV−vis spectroscopy. The formation of $M(CO)_5(HSiEt_3)$ was proposed and the enthalpy of substitution of CO by Et_3SiH was 16 (M = Cr), 19 (M = Mo), and 18 (M = W) kcal/mol as determined by PAC.[495] A comparison of the results for $Cr(CO)_6$ and $(C_6H_6)Cr(CO)_3$ illustrated the stabilizing affect of the aromatic ring on the formation of the silane adduct.

Flash photolysis studies of $Cr(CO)_6$ in the presence of $HSiR_3$ also showed the formation of $Cr(CO)_5(HSiR_3)$.[497] When the reaction was conducted with $HSiClR_2$, two adducts appeared to form and were assigned to $Cr(CO)_5(HSiClR_2)$ and $Cr(CO)_5(ClSiHR_2)$. A series of 14 silanes were ultimately studied and the rate of silane dissociation from $Cr(CO)_5(HSiR_2R')$ was determined. The rates (k_d) varied from 2.6 s^{-1} (for the $HSiEt_3$ adduct) to ≫12 000 s^{-1} (for the $HSi(C_6F_5)_3$ adduct). The dissociation rates are highest for silanes with electron-withdrawing groups as well as larger, more sterically demanding substituents. The weakening of the SiH···TM interaction with more electron-withdrawing substituents is opposite to that observed in the related Mn case. It was suggested that σ-donation was more important for an electrophilic Cr center and back-bonding into the σ*-orbital of the silane is less significant in the Cr case.

Since silane adducts of the Cr triad are not particularly stable when all other ligands are carbonyls, what substituents will stabilize the adduct sufficiently to result in isolation? Clearly, aromatic ligands provide such stability but what other groups or strategies might be effective? An interesting approach has been developed by Kubas and co-workers with the 16-electron complex $Mo(CO)(R_2PCH_2CH_2PR_2)_2$ (R = Ph, Et, *i*-Pr) which binds small molecules such as SiH_4 or primary silanes. An X-ray study of **7−11** (adduct of $PhSiH_3$) in which the three hydrogen atoms were located and refined, indicated two short H−Si distances (1.42 and 1.41 Å) and one long Si−H distance (1.77 Å) consistent with the assignment of a σ-complex. NMR data were reported for seven complexes involving both primary and secondary silanes and all exhibited a J_{SiH} coupling constant between 39 and 61 Hz, indicative of the η^2-HSi interaction.[471] The most novel of the complexes reported by Kubas and co-workers was that formed from SiH_4.[122] For the three complexes, $(OC)(R_2PCH_2CH_2PR_2)_2Mo(\eta^2\text{-}HSiH_3)$ (R = *i*-Bu, **7−6**; Ph, **7−7**; Et, **7−8**), the $^1J_{SiH}$ coupling constants are in the range expected for an η^2-silane. Although an X-ray study was reported for **7−6**, a positional disorder between the η^2-SiH_4 and CO ligands precluded the location of the four hydrogen atoms on silicon. The derivative **7−8** is unique in exhibiting an equilibrium between the six-coordinate agostic complex and the seven-coordinate oxidative addition product (**1−4**) as shown in eq 21. The equilibrium between **1−4** and **7−8** was the first tautomeric equilibrium reported for a mono-

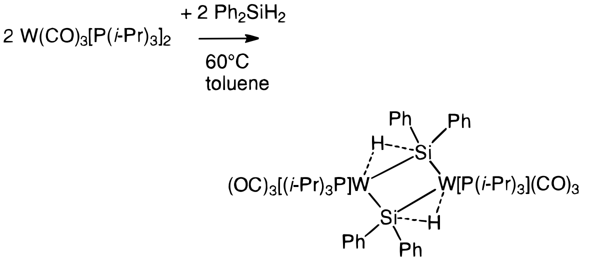


depe = $Et_2PCH_2CH_2PEt_2$ **7-8** **1-4**

(21)

nuclear complex. The thermodynamic parameters for conversion of the η^2-silane and the hydridosilyl were $\Delta H = -0.61$ kcal/mol and $\Delta S = -2.1$ eu and illustrate how close the balance between the nonclassical and classical Si−H interactions may be. A similar combination of Mo(η^2-HSi)/HMoSi was proposed to explain the solution data in **2−19b** where only the oxidative addition product was crystallographically characterized.[42]

A second strategy for stabilizing an agostic interaction has been promoted by Schubert and involves a "chelate" effect with phosphines such as $Ph_2PCH_2CH_2SiR_2H$. Formation of an agostic interaction in similar Mn complexes, $Cp'(OC)Mn(Ph_2PCH_2CH_2SiHR_2)$ (R = Me [**7−28**], Ph [**7−29a**])[482a] was previously reported. In reaction of the chelate with $W(CO)_6$, two products were obtained which enabled a clear identification of the complex with an agostic interaction. With short reaction times the product isolated was $(OC)_5W(Ph_2PCH_2CH_2SiR_2H)$ (R = Me, Ph) where the $^1J_{SiH}$ value corresponded to a 2c−2e bond, i.e., an uncoordinated Si−H. On prolonged photolysis, $(OC)_4W(Ph_2PCH_2CH_2SiPh_2H)$ (**7−14**) was formed as evidenced by a J_{SiH} coupling constant of 98 Hz.[472] An example that has only briefly been described is $(OC)_3(dppe)(H)W[SiCl_2(p\text{-Tol})]$ (**7−15**) which exhibited a J_{SiH} value of 34.8 Hz, although in $(OC)_3(dppe)(H)WSiCl_3$ it appeared that full oxidative addition occurred since J_{SiH} was 19.9 Hz.[1d,472] The reaction of $W(CO)_3(PR_3)_2$ [a fragment related to $(OC)_3(dppe)W$] with $PhSiH_3$ provided a fluxional, seven-coordinate oxidative addition product. However, with Ph_2SiH_2, a bridging silyl complex, as shown in eq 22 (bridging hydrogens were not found in the solid-state structure and are in assumed positions) was obtained.[473]



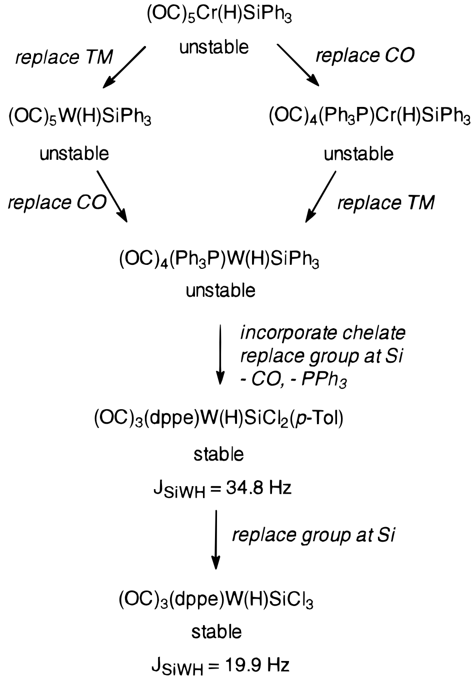
(22)

7-16

Schubert has shown how stable agostic interactions can be tuned in Cr triad complexes through the use of appropriate substituents or metal centers as outlined in Scheme 22 (adapted from ref 1d).

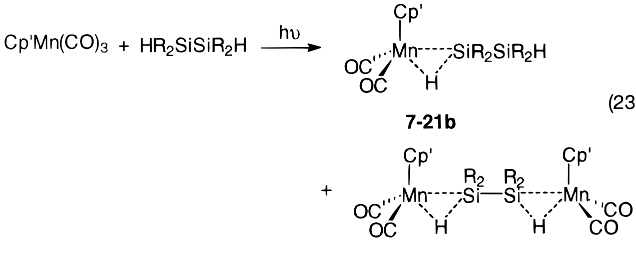
Photoelectron spectroscopy (PES) has also been utilized as a probe for Mn−Si−H interactions.[474,476,480,498] Data for the manganese complexes **7−17**, **7−18**, **7−21a**, **7−22**, **7−24** to **7−26** as well as $Cp'Mn(CO)_2(\eta^2\text{-}HSiCl_3)$ indicated a d^6-electron count for the metal, thus Mn(I). The Si−H interaction with manganese is in the initial stages of oxidative addition to the metal. The interaction was described as involving the filled Si−H σ-bonding orbital with empty metal orbitals. In contrast, $Cp(OC)_2MnHSiCl_3$ appears to be consistent with a d^4 metal or Mn(III) center with MnH and MnSi 2c−2e bonds, and thus complete oxidative addition. An interesting dilemma was posed by the observation that the J_{SiH} for $Cp(OC)_2MnHSiCl_3$ was 54.8 Hz [compared to 64 Hz for $(MeC_5H_4)(OC)_2MnHSiCl_3$ (**7−23**)] within the range usually expected for a nonclassical interaction; and the Si···H distance was 1.8 Å which is also about that demonstrated in other Mn derivatives where agostic interactions have been proposed. The authors rationalized the observed J_{SiH} as due to nonbonded coupling resulting from the narrow angle between d_{z^2} and d_{yz} orbitals which hold the Si and H atoms in close proximity.[498] If this is actually the case, some caution interpreting NMR data as a criterion for agostic interactions may be necessary.

Scheme 22



The reaction of the preformed manganese dimer, $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}dppm)]$ with Ph_2SiH_2 gave $[Mn_2(\mu\text{-}H_2SiPh_2)(CO)_6(\mu\text{-}dppm)]$ (**3−38**). The structure of the manganese dimer was proposed on the basis of a pseudotriplet observed in the ^1H NMR spectrum at −13.09 ppm but no coupling constants were reported nor were structural parameters determined.[499]

A double oxidative addition of a 1,2-dihydrodisilane to a metal center may provide a possible route to metal disilene complexes. A variation of this approach was attempted by Karch and Schubert who added $HSiR_2SiR_2H$ (SiR_2 = $SiPh_2$, SiPhMe, $SiMe_2$) to $Cp'Mn(CO)_3$ (photolysis). Two types of products were obtained as shown in eq 23 and involve successive reaction of the Si−H bonds of the disilanes with one and then two manganese centers. An example



7-21b

(23)

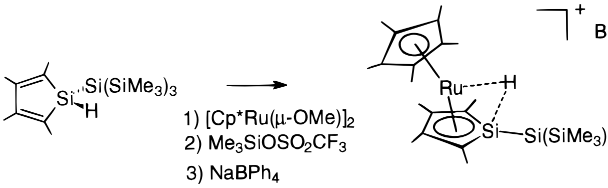
of the former is Cp′(OC)$_2$Mn(η^2-HSiPh$_2$SiHPh$_2$) (**7−21b**) and of the latter, [Cp′(OC)$_2$Mn(H)SiMePh]$_2$ (**7−29b**). The two different SiHs in **7−21b** were clearly distinguished in the ^{1}H NMR spectrum with two different coupling constants: one typical of a terminal Si−H and the other typical of a HSi σ-interaction with a metal. There was no evidence for the elimination of H$_2$ from Cp′(OC)$_2$Mn(η^2-H−SiR$_2$SiR$_2$H) to give the disilene complex.[147]

As a last commentary for this section, the reaction of CpMn(CO)$_3$ with HSiEt$_3$ has been reinvestigated and the results were suggestive of two pathways. In one, a direct reaction of photochemically generated CpMn(CO)$_2$ forms CpMn(CO)$_2$(η^2-HSiEt$_3$), **A**. In a second pathway, CpMn(CO)$_2$(Et$_3$SiH), **B** (undefined interaction with the ethyl group), forms before conversion to **A**. The authors suggested that the CpMn(CO)$_2$ unit "walks" along an alkyl chain to form **A**.[500]

E. Iron Triad

Although there are few *isolated* examples of mononuclear iron triad complexes with proposed agostic interactions, there are several dinuclear complexes that have been reported. There are no reports of agostic interactions involving osmium centers.

One of the most novel mononuclear systems with an agostic interaction involves a silacyclopentadienyl ligand to Ru (**7−33**) and the generation of the complex is shown in eq 24. The pertinent bridging H-atom was located and refined in the crystal structure [Ru−H = 1.48(7) Å and Si−H = 1.70(7) Å]. The J_{SiH} coupling constant is 41 Hz (J_{SiH} in the starting silole was 181 Hz). An isolated, cationic complex, [Cp(Me$_3$P)$_2$Ru(η^2-HSiCl$_3$)]$^+$ BAr$_4^-$ [Ar = 3,5-(F$_3$C)$_2$C$_6$H$_3$, **7−32**], was obtained from reaction of Cp(Me$_3$P)$_2$RuH with HSiCl$_3$ (described earlier in section VI).[483] The J_{SiH} coupling constant was 48 Hz but no crystal structure was reported. The isolation of **7−32** contrasts to the Mn case where HSiCl$_3$ appears to oxidatively add to the metal center, although less back-bonding might be expected from a cationic metal and thus a more stable agostic interaction such as that in **7−32** could result. Although the complex was not well characterized, Cp*(Me$_3$P)Ru(H)(SiR$_3$)$_2$ (SiR$_3$ = SiMe$_2$OEt), may also contain an agostic interaction.[180]



(24)

The displacement of coordinated η^2-H$_2$ has been utilized successfully in the formation of a complex that contains 2 η^2-HSi interactions at the same metal center (eq 25).[486a] The chelating silane *o*-(HMe$_2$Si)$_2$C$_6$H$_4$ (disil) has been employed in formation of other complexes such as (Ph$_3$P)$_2$(H)$_3$Ir(disil) (**4−294**) although these do not contain an agostic interaction. The X-ray structure of **7−35** was reported and the Si−H distances were 1.88(3) and 1.83(3) Å. The RuSi distances were at the longer end of the values reported for Ru−Si bonds. A single η^2-H$_2$ in L$_2$(H$_2$)$_2$RuH$_2$ (L = PCy$_3$) has also been replaced by the tertiary silane, HSiPh$_3$, to give L$_2$H$_2$(H$_2$)Ru(η^2-HSiPh$_3$) (**7−34**).[486a] A novel chelating system was formed when the vinylsilane, Me$_2$(CH$_3$CH=CH)SiH was reacted with L$_2$(H$_2$)$_2$RuH$_2$ and the proposed structure is shown in Figure 37. The ^{1}H NMR spectrum exhibited an TM−H resonance at −7.74 ppm (in C$_7$D$_8$) and a doublet in the ^{29}Si NMR spectrum at −11.3 ppm with J_{SiH} = 105 Hz. The Si−H coupling constant supported the Ru−H−Si interaction shown in Figure 37.[486b]

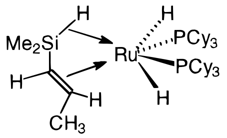
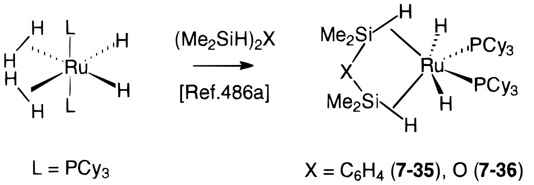


Figure 37. Vinylsilane with a chelating η^2-HSi interaction to Ru.

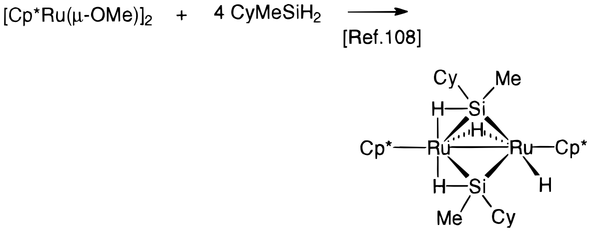


(25)

Mononuclear complexes with metals of the iron triad have been isolated in which the variable-temperature NMR experiments supported an agostic interaction. Such cases have been described in an earlier section (V.B.b) and included L$_3$FeH$_3$SiR$_3$ (L = PPh$_2$(n-Bu), SiR$_3$ = SiMePh$_2$)[462] and (dppe)(OC)$_2$Fe(H)SiR$_3$ (SiR$_3$ = Si(OMe)$_3$, Si(OEt)$_3$, SiMe$_3$, SiMe$_2$Ph, SiPh$_3$).[49,172] In these cases, the low-temperature NMR data supported an exchange mechanism with η^2-HSiR$_3$ ligands. The fluxional behavior observed in RuH(SiHPh$_2$)(CO)L$_2$ [L = PMe(t-Bu)$_2$] was explained through the agostic interaction shown in Figure 26 (section V.B).

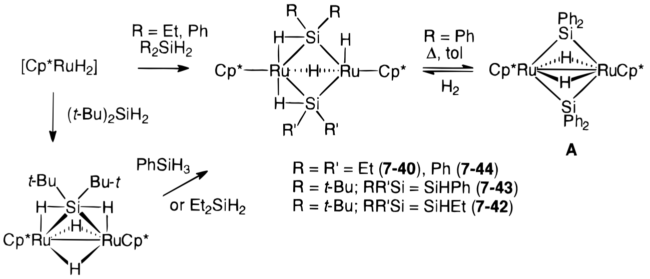
Except for PES studies, the investigations that have been outlined thus far involve solid and solution phases but there has been a gas-phase study reported using Fourier transform mass spectroscopy (FTMS) where the binding energies of silanes to Fe$^+$ have been measured. The order of binding energies was found to be Me$_2$SiH$_2$ > Me$_3$SiH > MeSiH$_3$ > Me$_4$Si > SiH$_4$.[501a] The interaction between the Fe$^+$ ion and the hydrosilane was viewed as an agostic interaction by the authors of the study. The binding energies ranged from 31.3 ± 1.8 kcal/mol (SiH$_4$) to 39.9 ± 1.4 kcal/mol (Me$_2$SiH$_2$).

Both [Cp*Ru(μ-OMe)]$_2$ and [Cp*RuH$_2$]$_2$ reacted with silanes to provide Ru−H−Si-bridged dimers[108,487] and examples are shown in eqs 26 and 27. With Ph$_2$SiH$_2$, [Cp*Ru(μ-OMe)$_2$]$_2$ gave {[Cp*Ru]$_2$(μ-SiPhOMe)(μ-OMe)(μ-H)} (**3−58c** and **3−59**) with no Ru−H−Si bridges. Complex **A** (shown in eq 27; isolation described in ref 487a) reacts with acetylene followed by H$_2$ to provide more complex dimers that still contain agostic interactions.[487] A tautomeric equilibrium has been demonstrated in the products produced from reaction of **7−41** with CO (eq 28).



7-39

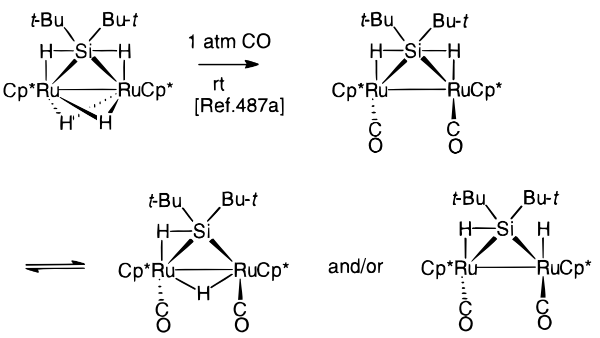
(26)



A

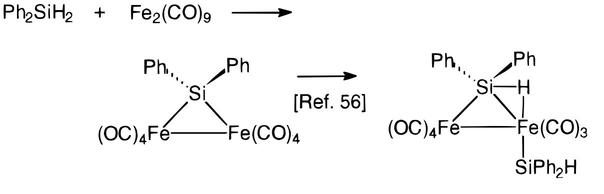
7-41

(27)



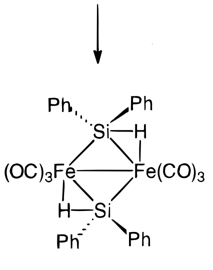
(28)

Although reactions of iron carbonyl compounds with silane have been previously studied, new variations continue to emerge as illustrated in eq 29.



(29)

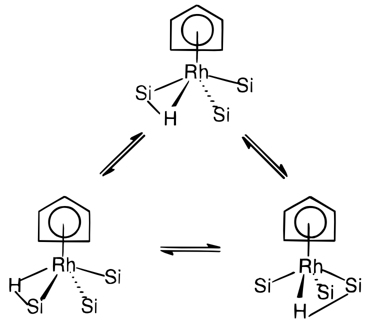
7-38



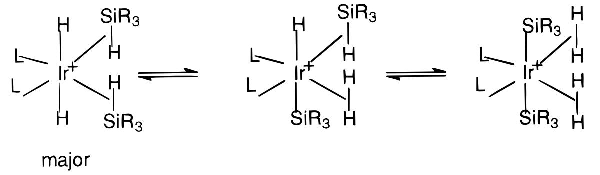
7-37

Earlier studies may not have recognized the agostic interactions demonstrated in the solid-state structures of **7−37** and **7−38**. The observed J_{SiH} coupling constants were also consistent with the formulations shown for **7−37** and **7−38**.

Scheme 23



Scheme 24



F. Cobalt and Nickel Triads

Complexes containing agostic or nonclassical Si−H interactions are relatively rare for the Co and Ni triads. Only a few examples have been reported for these metals (Rh, Ir, and Pt only) and only a few have been fully characterized. The reports for the Co triad are dominated by dinuclear complexes.

The Rh complex, $CpRh(SiMe_3)_2(\eta^2\text{-}HSiEt_3)$ (**7−45**), and several derivatives [including $CpRh(SiMe_3)_3H$, $CpRh(SiEt_3)_3H$, $CpRh(SiEt_3)_2(SiMe_3)H$, $CpRh(SiMe_3)_3D$, and $CpRh(SiMe_3)_2(SiEt_3)D$] were prepared and exhibited a dynamic exchange process as evidenced by NMR spectroscopy.[226] It was suggested that the exchange process involved an η^2-silane moiety. In the mixed silyl systems such as **7−45**, the $SiEt_3$ group preferrentially resided in an η^2-silane site. Observation of different coupling constants confirmed this preference. For example, in complex **7−45** the J_{SiH} coupling constant for the $SiEt_3$ moiety was 23.4 Hz, whereas for the $SiMe_3$ group it was 6.0 Hz. The J_{RhSi} coupling constant also supported the agostic interaction: $J_{RhSi} = 17.9$ Hz for $SiEt_3$ and 126.6 Hz for $SiMe_3$. A dynamic exchange process places different silyl groups in the η^2-silane position (Scheme 23).

The mononuclear Ir complexes $[(Ph_3P)_2H_2Ir(\eta^2\text{-}HSiEt_3)_2]^+SbF_6^-$ (**7−46**) and $[(Ph_3P)_2H_2Ir[\eta^2\text{-}(HSiEt_2)_2]^+SbF_6^-$ (**7−47**) were observed by low-temperature NMR spectroscopy in the reaction of $[IrH_2(THF)_2(PPh_3)_2]SbF_6$ with $2Et_3SiH$ or $HEt_2Si{-}SiEt_2H$, respectively.[458] The complexes were stable at low temperature only (decomposition occurred above 280 K) and were very sensitive to reaction with nucleophiles. A fast dynamic exchange process was suggested from the NMR data. A mechanism involving an η^2-silane and silyl dihydrogen species (Scheme 24) was proposed but only the bis(η^2-silane) complex was detected. No satellites could be seen in the ^{29}Si spectrum probably due to the multiplicity and line width of the resonance as well as to lack of solubility at low temperature. The Ir(III) center in this system is electrophilic and thus the metal center would disfavor the oxidative addition of the silane.

Several nonclassical dinuclear rhodium and iridium complexes have been reported (**7−48** through **7−57**) all of which contain chelating phosphine

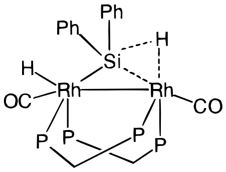


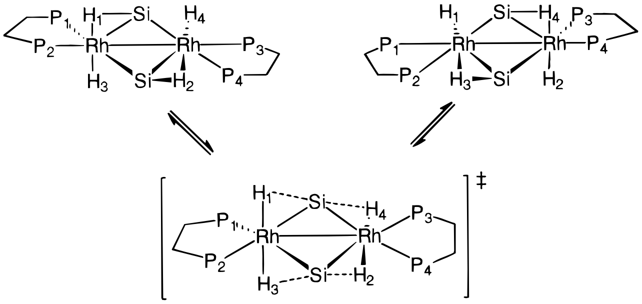
Figure 38. Proposed structure of **7−48** at low temperature (P = PPh$_2$).

ligands and bridging silicon species. Fluxional behavior was observed for all of these derivatives and are described below.

Reaction of primary or secondary silanes with Rh$_2$H$_2$(CO)$_2$(dppm)$_2$ at low temperature generally afforded complexes of the type Rh$_2$(μ-SiRR′)H$_2$(CO)$_2$(dppm)$_2$ (see for example complexes **2−71** and **3−86**) which were fluxional on the NMR time scale. However, when Ph$_2$SiH$_2$ was reacted with this Rh precursor, (OC)$_2$(dppm)$_2$HRh$_2$(μ-HSiPh$_2$) (**7−48**) was generated. Low-temperature NMR reveals two hydride resonances at −1.22 and −8.91 ppm which have been assigned to the agostic Si−H and Rh−H species, respectively (Figure 38). The fluxionality of these species involved the exchange of the hydrogen atoms bound to Rh and Si via rapid reductive elimination and oxidative addition of Si−H bonds. With the sterically demanding chelating phosphine dippe [dippe = 1,2-bis(diisopropylphosphino)ethane] additional agostic Rh−H−Si complexes formed including **7−49** to **7−55**. Three of these complexes [(dippe)Rh]$_2$(μ-H)(μ-η^2-HSiR$_2$)$_2$ [R = Me (**7−51**), Ph (**7−53**)] and [(dippe)Rh]$_2$[μ-SiH(p-Tol)][μ-η^2-HSiH(p-Tol)]$_2$ (**7−55**) have been structurally characterized by X-ray crystallography.

Butyl- and p-tolylsilane (2 equiv) react with [(dippe)Rh]$_2$(μ-H)$_2$ to give complexes [(dippe)HRh]$_2$(μ-η^2-HSiHR)$_2$ [R = Bu (**7−49**), p-Tol (**7−50**)].[70] These complexes were observed only in solution. If excess H$_2$ is removed from the reaction mixture then gradually bis(μ-silylene) complexes (see for example **2−74**) are formed. Complexes **7−49** and **7−50** were regenerated from the bis(μ-silylene) complexes by reaction with H$_2$. A mixture of two isomers was observed for **7−49** and **7−50** by NMR in about a 3:1 ratio (major isomer was cis) and both isomers exhibit fluxional behavior which involved exchange of the two hydride resonances. A similar derivative [(dippe)Rh(H)]$_2$(μ-η^2-HSiMe$_2$)$_2$ was isolated and crystallographically characterized but the results were not published.[70] It is not clear if the agostic Si−H interactions persist in solution or if oxidative addition of the Si−H bonds to the Rh center occurred. Both possibilities would give two different hydride signals that are trans to each other at each rhodium. A value for $\Delta G^\ddagger = 11.4 \pm 0.2$ kcal/mol was calculated for the exchange of the two hydrides in the major isomer of **7−49**. No activation parameters could be calculated for the minor isomer since signals for the hydrides indicated that the low-temperature limit was not reached. A probable mechanism (Scheme 25) for the fluxionality involves a twisting of the two rhodium centers where the H−Rh−H moiety rotates through 90°, concomitantly with breaking of one of the agostic Si−H bonds and formation of another agostic Si−H interaction, allowing for exchange between the terminal hydrides (at rhodium) and the agostic hydrides (at silicon). The phosphine ligands simultaneously twist by 90°, resulting in exchange of the two phosphorus atoms on each dippe ligand (see Scheme 25). An alternative mechansism was also proposed involving a “flapping” process but the former mechanism best explains the variable-temperature NMR data.

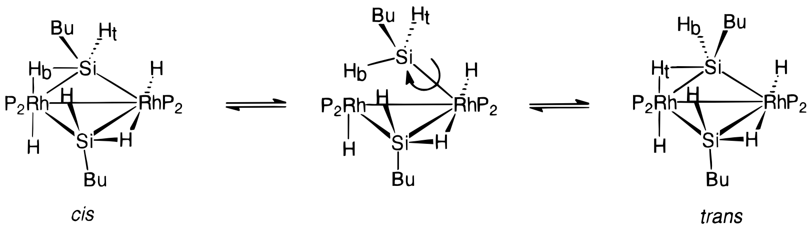
Scheme 25



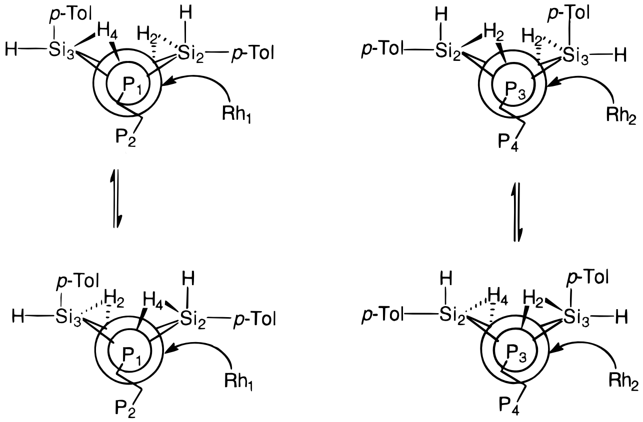
The deuterium analogue of **7−49**, [(dippe)Rh(D)]$_2$(μ-η^2-DSiDBu)$_2$ (generated from reaction of [(dippe)Rh]$_2$(μ-SiHBu)$_2$ with D$_2$), was also prepared. Variable-temperature ^{1}H NMR data showed signals for both silyl hydrides and rhodium (agostic) hydrides, indicating that these sites undergo slow exchange. A possible mechanism for the exchange involves breaking of the Si−H agostic interaction followed by rotation around the Rh−Si bond and re-formation of a new agostic Si−H interaction. This allows for exchange of the terminal and bridging Si−H sites and interchange of the cis and trans isomers (see Scheme 26).[70] A temperature invariance was observed for the K_{eq} between the two isomers suggesting that $\Delta H° \approx 0$ for conversion of the two isomers. The variable-temperature NMR data for **7−50** were similar to those for complex **7−49** but were more complex.

When four or five equiv of butylsilane or p-tolylsilane were reacted with [(dippe)Rh]$_2$(μ-H)$_2$ two new complexes were generated, [(dippe)Rh]$_2$(μ-SiHBu)(μ-η^2-HSiHBu)$_2$ (**7−54**) and [(dippe)Rh]$_2$[μ-SiH(p-Tol)][μ-η^2-HSiH(p-Tol)]$_2$ (**7−55**).[70] These complexes were isolated as air-stable crystalline solids and both show fluxional behavior in solution by NMR spectroscopy. An X-ray crystal structure was reported for **7−55** and displayed a [P$_2$Rh]$_2$ unit which possessed three silicon ligands bridging the dirhodium unit. Two of the silicon ligands contained agostic Si−H moieties, and the third ligand was a bridging silylene group. Examination of the crystallographic data showed that the oxidative addition of the Si−H bond of one of the silyl ligands appeared to be arrested at an intermediate stage, whereas addition of the other ligand had reached a later stage [Rh−Si = 2.477(2) vs 2.444(2) Å]. Steric crowding and electronic factors could also influence the bond lengths. The 3c−2e interactions allowed the coordination number of the Rh centers to increase without an increase in the formal oxidation state. The [(dippe)Rh]$_2$ unit appeared to provide the proper environment for the formation of η^2-HSiR$_3$ complexes possibly due to the presence of chelating phosphines. The electronic environment about the metal and silicon centers clearly influences the extent and stability of the oxidative addition of Si−H bonds as well as the coordination of a dihydrogen ligand to metal centers.[501b]

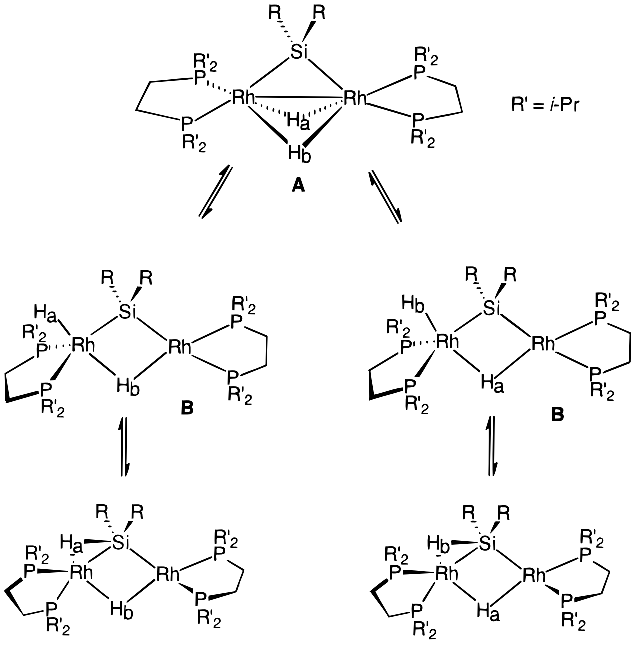
Scheme 26



Scheme 27



Scheme 28

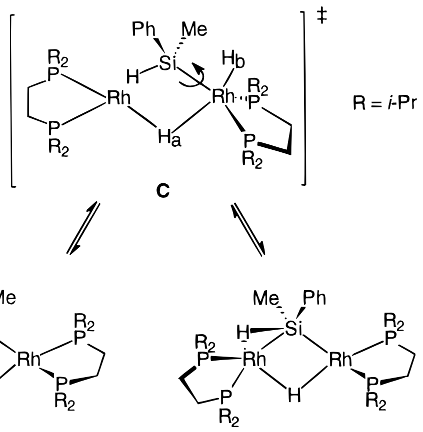


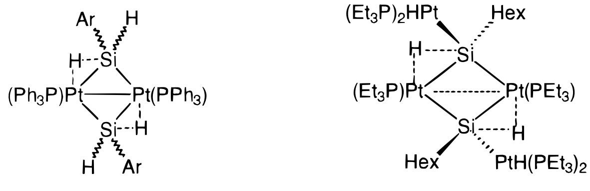
Both complexes **7−54** and **7−55** were examined by variable-temperature NMR spectroscopy.[70] The ^{1}H NMR spectrum for complex **7−54** was temperature invariant down to −85 °C and the resonances observed were consistent with a solid-state structure similar to that of **7−55**. The ^{1}H NMR spectrum for **7−54** revealed five resonances assignable to the hydrides at rhodium and silicon, consistent with a structure having three SiH(*n*-Bu) moieties and two hydrides bound to rhodium. Three of the resonances appeared at low field (6.78, 6.52, and 4.59 ppm) implying that two of the hydrides were in similar environments. The remaining two signals were found in the high field region at − 8.03 and − 8.48 ppm, typical of Rh−H resonances. The NMR spectra for **7−55** were slightly more complicated and the intricacies exhibited in the spectra are probably due to loss of symmetry in solution due to the steric interactions involving the *p*-tolyl groups on silicon. Complex **7−55** showed changes in the ^{1}H and ^{31}P NMR spectra as the temperature was lowered and it appeared that the two hydrides (Si−H and agostic Rh−H) were exchanging as were the two phosphines. Slight changes seen in the variable low temperature ^{31}P spectra and at the lower limit suggests that two different conformers may be present. It is likely that the exchange of the phosphorus nuclei is due to the fluxionality of the rhodium hydrides. There are two types of phosphorus environments in complex **7−55**: those cis to the bridging silylene (Si$_1$) group (P$_2$ and P$_4$) and those that are trans (P$_1$ and P$_3$). Scheme 27 gives a view along the two P$_{\text{trans}}$−Rh−Si$_{\text{silylene}}$ axes to emphasize the agostic interactions (see **7−55**, Table 7). If the agostic hydrides shift between the silyl ligands then P$_1$ and P$_3$ would exchange as would P$_2$ and P$_4$, but there was lack of supporting evidence for this motion in the ^{1}H NMR spectrum.[70] Hydride exchange around the entire molecule is also possible to explain the low-temperature ^{31}P NMR data but this is not consistent with the ^{1}H data. An additional possibility is that the molecule locks into two different conformations at low temperature.

One equivalent of secondary silane (such as Me$_2$SiH$_2$, Ph$_2$SiH$_2$, and MePhSiH$_2$) also reacted with [(dippe)Rh]$_2$(μ-H)$_2$ to give [(dippe)Rh]$_2$(μ-H)(μ-η^2-HSiRR′)$_2$ [RR′ = Me (**7−51**), Ph (**7−53**), R = Me, R′ = Ph (**7−52**)] in good yields.[124,125] Complexes **7−51** and **7−53** have been structurally characterized by X-ray crystallography. A related derivative with dippp, (i-Pr)$_2$PCH$_2$CH$_2$CH$_2$P(i-Pr)$_2$, also contains a single RhHSi bridge, [(dippe)Rh]$_2$(μ-H)(μ-η^2-HSiPh$_2$), **7−56**.[125] Complexes **7−51** through **7−53** were thermally stable up to 80 °C but were air and moisture sensitive. Examination of the solid-state structures of **7−51** and **7−53** showed that the binuclear core is asymmetric and contained a bridging μ-η^2-HSiR$_2$ silyl group and a bridging hydride ligand. The two Rh−Si distances in **7−53** differ in length with the μ-η^2-HSiR$_2$ silicon distance longer by nearly 0.19 Å (2.487(2) vs 2.298(2) Å). A similar trend was also seen in the solid-state structure of **7−51**.

Labeling experiments with [(dippe)Rh]$_2$(μ-D)$_2$ and Ph$_2$SiH$_2$ resulted in complete scrambling of H/D, indicating a fluxional intermediate. At room temperature, complexes **7−51** through **7−53** appeared to be symmetrical (structure **A** in Scheme 28) in solution by NMR spectroscopy but as the temperature was lowered fluxional behavior was observed.[124,125] The

Scheme 29





7-59

Ar = 2-isopropyl-6-methyl-phenyl

7-60

Figure 39. Structure of two complexes containing Si···H···Pt σ-interactions.

room-temperature ^{31}P spectrum for **7−53** showed a slightly broadened doublet, but at lower temperatures a complex spectrum was observed, suggesting two dynamic processes (one with coalescence at ∼ −40 °C and the other at ∼ −80 °C). The ^{31}P NMR spectrum of **7−53** at −95 °C showed the presence of four inequivalent phosphorus nuclei consistent with the solid-state structure (agostic structures **B** in Scheme 28). Within the intermediate temperature range a structure of type **B** was suggested. The fluxionality was attributed to exchange of the bridging and agostic hydrides which would also result in equivalency of the Rh and P environments. The room-temperature ^{1}H spectrum showed a single hydride resonance but at −96 °C two signals were seen indicating two different TMH environments. The ^{29}Si satellites were not observed probably due to the extensive coupling to Rh and P. Complexes **7−51** and **7−52** with the less sterically demanding substituents at silicon, have lower activation barriers than **7−53** ($\Delta G^{\ddagger} = 8.6 \pm 0.2$ kcal/mol at 193 K for conversion of structure **A** to **B** in Scheme 28). The differences in coalescence temperature for these complexes result from differing activation barriers for hydride exchange (lower with subsequent replacement of Ph with Me groups).

Notably, complex **7−52** showed four inequivalent ^{31}P resonances at room temperature and a rapid exchange of the groups attached to silicon was suggested as illustrated in Scheme 29.[125] This exchange should also occur in complexes **7−51** and **7−53**. Reaction of a second equivalent of silane with complexes **7−51** through **7−53** resulted in the formation of the symmetrical bridging bis(silylene) species (see **3−88**) through loss of H_2. The agostic complexes can be regenerated from **3−88** by reaction with H_2.

The formation of agostic Si−H complexes of the Ni triad are currently limited to Pt. The possibility of an η^2-HSiR$_3$ interaction in *cis*-(Cy$_3$P)$_2$Pt(H)SiR$_3$ was briefly mentioned in relation to a study of platinum hydrides but no details were provided.[489b] An early report in 1980 showed elongated Pt−H and Si−H distances in the solid-state structure of [(Cy$_3$P)Pt(μ-η^2-HSiMe$_2$)]$_2$ (**7−58**) supporting a nonclassical interaction (Table 8).[489a] The hydride was not located by ^{1}H NMR spectroscopy but a related derivative {[Me(*t*-Bu)$_2$P]Pt(μ-η^2-DSiMe$_2$)}$_2$ revealed a Pt−D resonance in the ^{2}H NMR spectrum at +1.9 ppm with a coupling of J_{PtD} = 93.3 Hz. More recently the Pt dimer species **7−59** (Figure 39a) and **7−60** (Figure 39b) were prepared and characterized by X-ray crystallography. Complex **7−59** was obtained in high yield as a mixture of cis and trans isomers (1:3)[490] and the "normal" Si−H resonance was observed at an unusually low field in the ^{1}H NMR spectrum (8.4 ppm for the cis and 8.9 ppm for the trans isomer). The "agostic" hydride appeared at about 2 ppm as an unresolved multiplet and was located and refined in the solid-state structure of the trans isomer. Complex **7−60** was formed by reaction of Pt(PEt$_3$)$_3$ with (Hex)SiH$_3$ at room temperature. The coupling constants of J_{SiH} = 31 and J_{PtSi} = 262 for **7−60** supported the agostic interaction and an unusually large downfield shift was observed in the ^{29}Si NMR spectrum (+195 ppm).[77] If the reaction is run for a short time (∼20 min) then mixtures of [(Et$_3$P)$_2$Pt]$_2$(μ-SiHR)$_2$ (R = Hex; **2−87**) and **7−60** are formed in a 3:4 ratio.

The possibility of an η^2-silane interaction in a palladium complex was recently suggested. The reaction of [(phen)Pd(CH$_3$)(OEt$_2$)]$^+$ with 2 equiv of HSiR$_3$ (R = Et, Ph) at low temperatures results in loss of CH$_4$ and formation of the cationic complex, [(phen)Pd(SiR$_3$)$_2$(H)]$^+$. At −95 °C, the two silyl groups are equivalent by ^{1}H and ^{13}C NMR spectroscopy and no ^{29}Si satellites were observed. The broadness of the peaks precluded the measurement of any ^{29}SiH coupling less than 40 Hz. The cationic complex may be either a Pd(IV) hydride or a fluxional Pd(II) species (with an η^1-SiR$_3$ and an η^2-HSiR$_3$).[287]

G. β-HSi Agostic Interactions

Although the complexes discussed in this section do not contain a silicon bound directly to the metal center there is evidence that a Si−H in a β-position can interact with the metal in an agostic fashion. Table 11[502−509] summarizes the examples that have been reported, most of which have also been characterized crystallographically (Table 12). The majority of the cases reported contain an −SiHMe$_2$ group [two examples have −SiH(Mes)$_2$ (**11−9**) or −SiH(Mes) (**11−7**)] and a metal from groups 4−6. Another commonality is that the α-atom (X in M−X−SiH) is either N (5 cases) or an sp^2- or sp-C (4 cases).

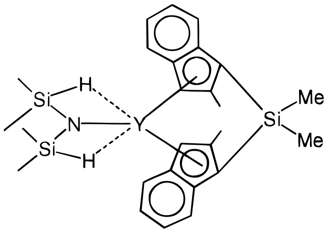
The β-agostic complexes were made by a variety of routes since the atom that bears the silyl substituent can, in principle, be quite varied. The data that distinguish the complexes in Tables 11 and 12 from those in Tables 7 and 8 involve the Si−H distances

Table 11. Systems with β-SiHM Interactions*,†

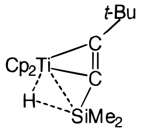
Complex	Prep.[a] (%Yd)	Color m.p.	Anal.	NMR solvent (temp.)[b]	^{1}H[c] M-H	^{1}H[c] Si-H	^{29}Si[c]	Other	Ref.
11-1* *rac*-{$Me_2Si^1[C_9H_5]_2$ $YN(Si^2Me_2H)_2$	A(95)[d]	yellow	Y[e]	S(25)		2.97[f,g]	4.32[f,g] (Si^2) -22.4[h] (Si^1) $^1J_{SiH}$ = 142[i]	^{13}C IR, MS X-ray	502
11-2* $Cp_2Ti[(t\text{-}Bu)C{\equiv}C\text{-}SiMe_2H]$ [j]	B(46)	—	—	T(30) T(-80)		-3.74 -7.32	-0.5 $^1J_{SiH}$ = 123 17.6 $^1J_{SiH}$ = 93	^{13}C IR X-ray	503
11-3 $Cp_2Ti(HMe_2SiC{\equiv}C\text{-}SiMe_2H)$	B(—)	—	—	S(30 ? (-108)		-0.96 (br) 4.58 -8.04	0.46 $^1J_{SiH}$ = 147 -22.7 $^1J_{SiH}$ = 176 34.3 $^1J_{SiH}$ = 92	^{13}C IR	503
11-4* $Cp_2Zr(H)[N(t\text{-}Bu)\text{-}(SiMe_2H)]$ [k]	C(86)	off-white	Y	S	5.53(d) J = 3.1	1.21	-73.4 (d of sept) $^1J_{SiH}$ = 113.2 $^2J_{SiH}$ = 6.4	^{13}C IR X-ray	504
11-5 $Cp_2Zr(Cl)N(t\text{-}Bu)\text{-}(SiMe_2H)$ [k]	D(83)	yellow	Y	S		2.58(sept) J = 2.7	-52.3(d of sept) $^1J_{SiH}$ = 126.5 $^2J_{SiH}$ = 6.8	^{13}C IR X-ray	504
11-6* $\{[(HMe_2Si)_2N]_2\text{-}Cl_2Zr\}_2$	E(25)	colorless	Y	T(20)		5.06(sept)	9.51	^{13}C IR, MS X-ray	505
11-7* $[MesHSiPCy]_3Cr\text{-}(CO)_3$ [l]	F(39)	ocher 209-212 (d)	—	S(25)	-7.69(d)	5.64(d) 6.50(m)	-45.2(dm) $^1J_{SiH}$ = 135.7 -20.5(brd) $^1J_{SiH}$ = 228.6 -16.9(dd) $^1J_{SiH}$ = 210.9	^{31}P IR, MS X-ray	506
11-8* $(OC)_4W{=}C(NMe_2)\text{-}SiMes_2H$	G(67)	red-orange 134 (d)	Y	S		-2.40(s) J_{SiH} = 106 J_{WH} = 34	-89.3(d) J_{SiH} = 106	^{13}C X-ray	507
11-9* $Cp^*(Cy_3P)RuC\text{-}(SiMe_2H){=}CPh_2$ [m]	H(42)	—	Y	S	-11.6(d)		-81.30(d of m) $^2J_{SiH}$ = 66	^{13}C, ^{31}P MS(FAB) X-ray	508
11-10* $\{(t\text{-}Bu)[(H)Me_2Si]]N\}_3Er$	I(42)	pink 48	N	S			429	^{13}C MS, IR X-ray	509

* Structural formulas for compound numbers marked with asterisks may be found at the end of the table. † Abbreviations: Me, methyl; Bu, butyl; Cy, cyclohexyl; Mes, 2,4,6-trimethylphenyl; Cp, C_5H_5; Cp*, C_5Me_5.

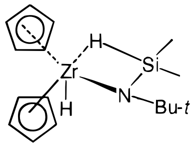
Footnotes: [a] Reaction key: A, $Y[N(SiHMe_2)_3]{\cdot}THF + (C_9H_6\text{-}2\text{-}Me)_2SiMe_2$; B, $Cp_2TiCl_2 + Mg + RC{\equiv}CSiMe_2H$; C, $[Cp_2ZrHCl]_2 + LiN^tBu(SiMe_2H){\cdot}THF$; D, **9−2** + CH_3Cl; E, $ZrCl_4 + Li[N(SiHMe_2)_2]$; F, $(MesHSiPCy)_3 + [Cr(CO)_3(MeCN)_3]$; G, photolysis of $(OC)_5(W{=}C(NMe_2)[Si(H)Mes_2]$; H, $Ph_2C{=}C(Li)SiMe_2H + Cp^*LRuCl$; I, $ErCl_3 + Li(N(t\text{-}Bu[Si(H)Me_2])$. [b] Solvent key: S, C_6D_6; T, $C_6D_5CD_3$. [c] In ppm. Coupling constants are in Hz. [d] *Rac/meso* = 3:1. *Rac* form from recrystallization from toluene. [e] Analysis is outside ±0.5 of calculated percent value for carbon. [f] *Rac* form. [g] Apparent nonet derived from a doublet of septets. Doublet splitting = 4.6 Hz and $^3J_{H,H}$ = 2.44 Hz; assigned to H···Y···H coupling. [h] Doublet of septets for $N(SiMe_2H)_2$ in ^{29}Si spectrum. [i] $^1J_{SiH}$ in $Y[N(SiHMe_2)]_3(THF)_3$ is 164 Hz. [j] Other derivatives: $Cp_2Ti(PhC{\equiv}CSiMe_2H)$ and $Cp_2Ti(HMe_2SiC{\equiv}CSiMe_2H)$. [k] Other derivatives: $Cp_2ZrX[N^tBu(SiMe_2H)]$, X = I, Br, F. [l] Additional derivatives: $[(Ar)HSiPCy]_3Cr(CO)_3$, Ar = Ph, *o*-Tol, *o*-$CF_3C_6H_4$, *o*-*i*-PrC_6H_4; and $[(Ar)HSiPCy]_3Mo(CO)_3$, Ar = Ph, Mes, none of which exhibited a β-agostic interaction.[506] [m] Isolated as a solvate with 0.5 equiv of C_7H_8. Additional derivative prepared by ligand exchange of **9−9** with $PPhMe_2$. $^1J_{SiH}$ = 57 Hz for $Cp^*(Me_2PhP)RuC(SiMe_2H){=}CPh_2$. Compound structures for Table 11:



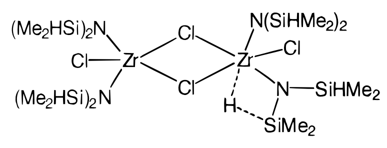
11-1



11-2

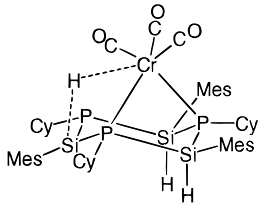


11-4



11-6

Table 11 (Continued)



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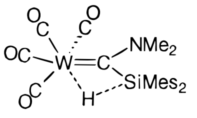
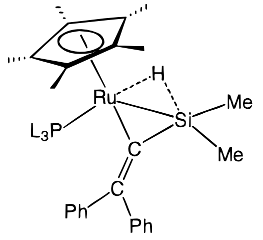
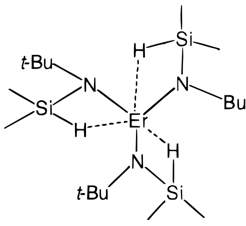


11-8



11-9



11-10

Table 12. X-ray Structures of β-Agostic Complexes

complex	M···H	Si−H	M···Si	ref
rac-[(η^5-C_9H_5-2-Me)$_2$SiMe$_2$]Y[N(SiHMe$_2$)$_2$] (**11−1**)	2.54(2)	1.45(2)	3.082(1)	502
Cp_2Ti(t-BuC≡CSiMe$_2$H) (**11−2**)	1.82(5)	1.42(6)	2.655(2)	503
Cp_2(H)Zr[N(t-Bu)SiMe$_2$H] (**11−4**)	*a*	*a*	2.857(2) 2.853(2)	504
Cp_2Zr(Cl)[N(t-Bu)(SiMe$_2$H)] (**11−5**)	2.266(30)	1.416(31)	2.931(1)	504
[(HSiMe$_2$)$_2$N]$_2$(Cl)Zr(η^2-Cl)$_2$[N(SiHMe$_2$)$_2$]$_2$ (**11−6**)	2.40(3)	1.45(2)	2.943(1)	505
[MesHSiPCy]$_3$Cr(CO)$_3$ (**11−7**)	1.75(5)^b	1.34(5) 1.52(4)^b 1.38(4)	2.616(1)^b	506
(OC)$_4$W[C(NMe$_2$)SiMes$_2$H] (**11−8**)	2.10(10)	1.50(10)	2.776(3)	507
Cp*(Cy$_3$P)RuC(SiMe$_2$H)=CPh$_2$ (**11−9**)	1.58(5)	1.70(3)	2.507(2)	508
{t-Bu[(H)Me$_2$Si]N}$_3$Er (**11−10**)	2.32(3) 2.41(3) 2.37(3)	1.411(3) 1.461(3) 1.481(3)	*c*	509

[a] Indicated hydrogens were not located. Disordered structure. [b] Distances that involve the agostic interaction. [c] Data not provided.

(when refined) and the $^1J_{SiH}$ coupling constants. The TM−Si distances in the β-agostic complexes are only slightly longer than the TM−Si distances summarized in Table 6 and the value of TM···Si in Cp_2-Ti[(t-Bu)C≡CSiMe$_2$H] (**11−2**) is actually within the range exhibited by 2c−2e TM−Si bonds. In almost all cases in Table 12, the Si−H bond distance is "normal" or a little shorter than 1.48 Å [the exception is Cp*(Cy$_3$P)RuC(SiMe$_2$H)=CPh$_2$ (**11−9**) where the Si−H distance has elongated to 1.70 Å]. A third feature involves the value of the $^1J_{SiH}$ coupling constant which is >90 Hz except for **11−9**, which is also the example where the Si−H bond distance was in the range normally observed in σ-Si−H complexes. The change in the $^1J_{SiH}$ to a smaller value in the complex relative to a model (usually the free ligand, or noncoordinated Si−H in the same molecule) ranges from a low of 50.6 Hz observed for **11−1** to 109 Hz for **11−9** (data at room temperature). The low temperature study of Cp_2Ti[(t-Bu)C≡CSiMe$_2$H] (**11−2**) and Cp_2Ti(HMe$_2$SiC≡CSiMe$_2$H) (**11−3**) showed that the $^1J_{SiH}$ coupling constant was smaller at lower temperatures. In **11−2**, the J_{SiH} decreases from 123 Hz at 30 °C to 93 Hz at −80 °C. At the lower temperature the J_{SiH} in **11−2** is 106 Hz less than in the alkyne precursor. For **11−3**, J_{SiH} decreases from 147 Hz at 30 °C to 92 Hz at −108 °C. In at least two cases the presence of additional noncoordinated Si−H units in the same complex provided support for the weak β-interaction. In the complex **11−3** which contains the ligand HMe$_2$SiC≡CSiMe$_2$H, the uncoordinated Si−H exhibited a resonance at 4.58 ppm ($^1J_{SiH}$ = 176 Hz) and the coordinated Si−H at −8.04 ppm had J_{SiH} = 92 Hz (measured at −108 °C), illustrating the different roles that a Si−H group can play in the complex. In **11−7**, there are three Si−H units and the difference in $^1J_{SiH}$ of the noncoordinated Si−H relative to coordinated Si−H is 92.9 and 75.2 Hz.

Additional support for the presence of an interaction between Si−H and the metal center is suggested by IR data. Coordination of the Si−H would be expected to weaken the Si−H bond and result in a shift of the characteristic Si−H stretching frequency (usually observed between 2100 and 2200 cm^{-1} in a silane) to a lower wavenumber. Since most IR data are taken on mulls, the observed numbers reflect interactions in the solid. The value of the shift to lower wavenumbers reported for the complexes (relative to the free ligand or the starting complex) in Table 10 were 268 (rac-**11−1**), 195 (**11−4**), 126 (**11−5**), 159 (**11−6**), 148 (**11−7**), and 253 (**11−10**) cm^{-1}. Such data suggests a weakening of the Si−H bond in the complex and is consistent with the proposed β-agostic interaction. To promote the H−Si interaction with the metal center it is expected that the M−X−Si angle should deform to bring the silicon center closer to the metal, that is, it should become more acute than 109°. Unfortunately, such data are not always provided, but the angles that have been reported are often <100°: 103.4° (rac-**11−1**), 95.1° (**11−4**), 99.1° (**11−5**), 102.8° and 117.2°(**11−6**), and 87.8° (**11−7**) and 79.1° (**11−9**).

Support for an unusual interaction between Si−H and Y in rac-{Me$_2$Si^1[C$_9$H$_5$]$_2$YN(Si^{2}Me$_2$H)$_2$ (**11−1**) is indicated by the large Si−N−Si angle of 153.3° found in the coordinated (HMe$_2$Si)$_2$N− ligand. The solid-state data (bond distances and angles and IR data) supported the presence of some interaction between H−Si and the metal center. That the interaction

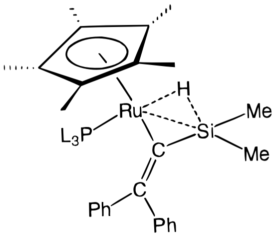


Figure 40. β-Agostic interaction in complex **11−9**.

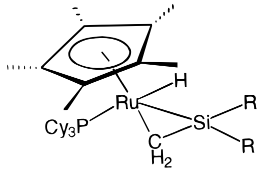


Figure 41. Cp*(Cy$_3$P)(H)Ru(η^2-CH$_2$=SiPh$_2$).

persists in solution was indicated by the J_{SiH} coupling constants which were lower than observed in the "free" ligand but larger than the range observed for the Si−H interactions described in VI.A−F. The values of the coupling constants suggest that the β-SiH interactions are weak. However, in *rac*-**11−1** the methyl groups of N(SiHMe$_2$)$_2$ appeared as two doublets throughout the temperature range −80 to +130 °C, which is consistent with retention of the Si−H interaction with the metal center. The observation was unique to the *rac* isomer and *meso*-**11−1** appeared to have a more flexible geometry. At room temperature, the two SiHMe$_2$ units in **11−3** exhibited fluxional behavior and a "flip-flop" type of coordination was proposed between the H−Si and the Ti center. The spectral data at room temperature were an average of the two different types of Si−H interactions that were observed at low temperature (see Table 11).

The presence of the agostic interaction can have a stabilizing effect on the formation of a complex. For example, the −N(SiMe$_3$)$_2$ analogue of **11−1** could not be isolated. Complex **11−9** (Figure 40) is stable at 45° for 1 day[502] but the closely related derivative, Cp*(Cy$_3$P)(H)Ru(η^2-CH$_2$=SiPh$_2$) (see Figure 41) undergoes 60% decomposition at room temperature in 19 h.[336,510]

The examples outlined in Tables 11 and 12 appear to represent an "arrested" oxidative addition of Si−H to the metal center. The Si−H bonds are not "stretched" but the TM···Si "nonbonded" distances are only slightly longer than the range exhibited by the respective 2c−2e TM−Si bonds. The cases may also be viewed as an initial stage of a β-hydride migration. Such a β-H transfer was observed as the major reaction pathway in the low-temperature photolysis of Cp*Fe(CO)$_2$CH$_2$SiHMe$_2$[511] and of CpW(CO)$_3$-CH$_2$SiHMe$_2$.[512] The product, Cp*Fe(CO)(CH$_2$SiMe$_2$)H, which is most appropriately represented as a metallasilacyclopropane, decomposed above about −50 °C.[511a] The tungsten derivative was stable to 200 K and was characterized by NMR spectroscopy.[512] A more stable η^2-silene was generated from the Ru system shown in eq 30. A similar β-hydride elimination occurred to form a disilene complex whose intermediacy was suggested from trapping experiments as shown in eq 31.[511b]

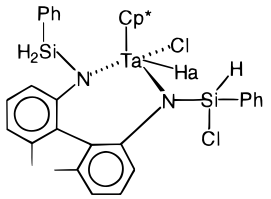


Figure 42. Tantalum complex with proposed TaH···Si interaction to give a pentacoordinate Si center.

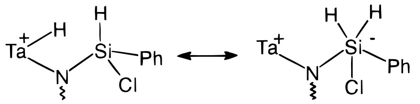
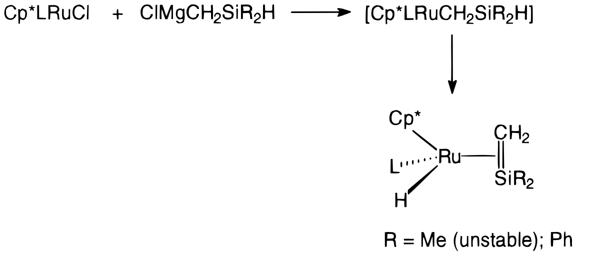
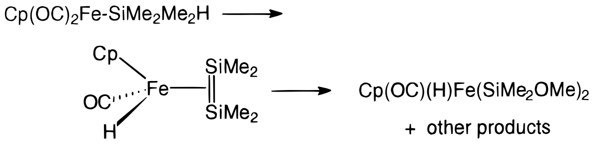


Figure 43. Resonance forms for Ta system in Figure 42.



(30)



(31)

That variations of nonclassical interactions of H−Si with metal centers continue to evolve is illustrated in the recently characterized tantalum system shown in Figure 42.[513] The Si center of the SiHPhCl group is distorted toward trigonal-bipyramidal geometry. The hydride ligand at Ta was located and refined to a distance of 1.83 Å (Ta−H in a related compound was 1.67 Å).[513] The H$_a$···Si distance was 1.86 Å, within a range that may be considered bonding. The authors favored a bonding mode involving the resonance forms shown in Figure 43 which involves a five-coordinate center at Si. This interpretation contrasts to the β-SiH agostic complexes described in the earlier part of this section where a Si−H σ-bond coordinates to the metal but is similar to the description of the silicon center given for the σ-complex, Cp$_2$-Ti(PMe$_3$)(η^2-HSiHPh$_2$) (**7−3**).[468]

VII. Calculations: Nature of Bonding and Relative Bond Energies

Various calculations and measurements such as photoelectron spectroscopy have been reported for silyl−transition-metal complexes which attempt to address the nature of the TM−Si bond or the TM···HSi interaction. The calculations vary in sophistication and are usually performed on "model" compounds. The purpose of this section is to summarize the findings or observations and not to critique the different calculation methods. As described in earlier sections, TM−Si bonds tend to be shorter than expected and this is often attributed to π-back-bonding from the metal into a suitable acceptor orbital on silicon. As illustrated in Figure 10, the mean TM−Si bond distances steadily decrease from the Sc through the Ni triads. The differences between a simple calculated distance and the observed mean is greater for groups 8−10. Attempts to verify a "multiple" bonding component have led to somewhat ambiguous results. Since the range of compounds discussed contains both electron-poor and electron-rich transition metals plus variations of substituents at both the metal center and at the silicon center, it is unlikely that all TM−Si bonds will exhibit the same bonding situation. Another major question centers around the nature of the TM···HSi interaction: is it best represented with 2c−2e bonds or with 3c−2e bonds? Still another question involves the relative bond strengths for TM−Si compared to TM−C as well as TM−Si compared to TM−H. Such questions arise in studies attempting to use Si−H addition to a TM as a model for CH addition to the same metals.[514] There is no universal answer concerning bond strengths and comparative studies of related TM−Si and TM−C derivatives are rare. The following discussion is loosely divided into a section concerning bond energies, a section concerning the nature of the TM−Si bond and finally, calculations that address various aspects of structure.

A. Bond Energies

The mean TM−Si distance decreases by about 0.6 Å from Sc to Ni and the bond energies may increase from electron-poor to electron-rich metals. Although limited in scope, various calculation studies demonstrate this trend. The calculated values (LCAO−HFS) for D_e(Ti−H) and D_e(Ti−SiH_3) in $Cp_2Ti(H)SiH_3$ were 58.7 and 29.9 kcal/mol, respectively[515] [the derived (calculated) value for the first Ti−Me in Cp_2TiMe_2 is estimated to be 69 kcal/mol[516]]. The calculated difference [at the MP2/III//MP2/III (RHF/III//MP2/III) level] in the Zr−C vs Zr−Si bond developed from the hypothetical reaction of $Cl_2Zr(CH_3)H$ with SiH_4 to give $Cl_2Zr(SiH_3)H$ and CH_4, was determined to be 14.3 kcal/mol with the Zr−Si bond the weaker of the two.[517] Ziegler calculated the M−El bond energies in Cl_3MEl (M = Ti, Zr, Hf) and Cl_2ScEl (El = C and Si) by a nonlocal density functional method.[518] The D(TM−C) and D(Sc−C) bond strengths were calculated to be greater than D(TM−Si) by about 12 kcal. In the series Cl_xTM−Si, the bond energies increase in the sequence TM = Ti (50) < Sc (52) < Zr (57) < Hf (65 kcal/mol). In the same study,[518a] the bond strengths in $(OC)_4CoEl$ were also computed and were found to be reversed in value compared to the Ti triad: 51 for El = SiH_3 and 38 kcal/mol for El = CH_3.

A gas-phase study of the reaction of the metal cations, Ti^+, V^+, and Cr^+ with SiH_4 provided experimental bond energies at 0 K for a variety of TM^+-SiH_x (x = 0, 1, 2, 3) species. In all cases the TM−Si bond energies were significantly weaker than the analogous TM−CH_x^+ species[519] (the value of [{TM^+−CH_3} − {TM^+−SiH_3}] decreases through the sequence TM = Ti^+ (∼12 kcal/mol) > V^+ > Cr^+ (∼8.4 kcal/mol);[519] and in the sequence TM = Fe (∼11 kJ/mol) > Co^+ > Ni^+ (<1 kcal).[520] Additional guided ion beam studies of Cu^+ and Zn^+ indicated that the TM^+−SiH_3 and TM^+−CH_3 bond energies are probably similar.[521] In all of these cases, of course, there are no supporting ligands on the TM that might stabilize a silyl-metal complex (and subsequently lead to isolation), but the trend seems to be a decreasing difference in bond energy values between TM−CH_3 and TM−SiH_3 proceeding across the transition-metal series.

Table 13. Bond Dissociation Energies (kcal/mol) Calculated from Oxidative Addition Reactions[a]

metal	reaction[b]	M−Si	M−H	M−C	ref
Rh	a,b	78[c]	65[d]	55[c,e]	517
Rh	c	48−51[f,g] 43−48[g,h]	48−49[f,g] 48−50[f,h]	*i*	522
Ir	c	53−56[f,g] 51−54[g,h]	57−59[f,g] 58−61[g,h]	*i*	522
Pd	d	51[f] 49[h]	49[f] 52[h]	29[f] 27[h]	9bc
Pt	d	64(60)[f,j,k] 61(58)[h,j]	52(58)[f,j] 54(59)[h,j]	42[f] 40[h]	9a, 523

[a] Numbers have been truncated to two significant figures. [b] Reactions: (a) $RhCl(PH_3)_2$ + SiH_4.[517] (b) $RhCl(PH_3)_2$ + E_2H_6.[517] (c) $MCl(CO)(PH_3)_2$ (M = Rh, Ir) + SiH_4.[522] (d) $M'(PH_3)_2$ (M′ = Pd, Pt) + SiH_4 (H_2, CH_4).[9] [c] MP2/III//MP2/III(RHF/III//MP2/III). [d] MP2/III. [e] Carbon analogue of reaction b. [f] MP2. [g] Range from different ligands trans to the M−X bond (X = H or SiH_3). [h] MP4SDQ. [i] Not calculated from carbon analogue of reaction a. [j] Value in parentheses is taken from ref 523. [k] In a later report, the Pt−SiH_3 energy was revised downward to 58 kcal/mol (MP2) and 56 (MPSDQ).[524]

When the TM is an electron-rich metal in model complexes, the calculated TM−Si bond appears to be stronger than the corresponding TM−C. The energetics of a series of oxidative addition reactions of SiH_4 (and Si_2H_6), CH_4 (and C_2H_6), and H_2 to heavier metal complexes was investigated by Sakaki and coworkers at various theoretical levels. A selection of the values reported for TM−Si, TM−H and TM−C bonds where TM = Rh, Ir, Pd, and Pt are summarized in Table 13[522−524] and also includes parameters calculated by Morokuma for Rh.[517]

In the model system, $RhCl(PH_3)_2(SiH_3)_2$, the Rh−Si bond energy was calculated to be 78 kcal/mol and at the MP2/III level to be about 20 kcal/mol stronger than Rh−C. There is a 2.4 kcal/mol drop in bond energy in each step of the sequence, Rh−Si > Rh−H > Rh−C.[517] However, in a related study involving the addition of SiH_4 to $TMCl(CO)(PH_3)_2$ (TM = Rh, Ir; Vaska complexes), the Rh−Si bond energy was significantly lower and demonstrates the effect that substituents and metal geometry may have on the nature of the TM−Si bond. The Pt−SiH_3 bond was also calculated to be about 20 kcal/mol stronger than Pt−CH_3 in the addition of H−EH_3 to $Pt(PH_3)_2$ [MP2, MP3, MP4/DQ, and MP4/SDQ[9,523]]. The bond energies for Ir−H and Ir−SiH_3 are calculated to be similar to Pt−H and Pt−SiH_3 and likewise the Rh−H and Rh−SiH_3 bond energies are nearly the same as Pd−H and Pd−SiH_3 energies (for analogous systems). In both the Co and Ni triads, the heaviest metal formed the stronger bond to silicon (and also to carbon compared to hydrogen in the Ni triad). The origin of the similarities in the Ir and Pt bonds is discussed in some detail by Sakaki.[522] The lower reactivity of $[RhCl(CO)(PH_3)_2]$ compared to $[RhCl(PH_3)_2]$ is attributed, in part, to the larger steric repulsion in the octahedral geometry produced from the former complex. A conclusion of the calculation study of the Vaska-type complexes was that CO coordination to the metal disfavors oxidative additions, although the many isolated complexes in Tables 2-4 would argue otherwise. The importance of a constant set of substituents in comparing different TM−Si systems is illustrated in the DFT calculation of the Co−Si bond energy in the complex, $(OC)_4CoSiCl_3$. The Co−Si bond dissociation energy of 75.9 kcal/mol was approximately 5.5 kcal/mol higher than the carbon analogue[164] (similar to the results obtained by Morokuma cited in Table 13). Since $TM-SiCl_3$ bonds are shorter than comparable $TM-SiH_3$ (or SiR_3) bonds (see discussion in section IV) it is likely that the D_e in $(OC)_4CoSiH_3$ would be less than that calculated for $(OC)_4CoSiCl_3$. Whether the TM−Si bond energy increases across a transition-metal series probably cannot be generalized as the same sets of substituents at both metal and silicon cannot be held constant across the series. For instance, in the UPS study of the $(OC)_4CoSiCl_3$, $(OC)_5MnSiCl_3$ and *cis*-$(OC)_4Fe(SiCl_3)_2$ the orbital ionization energies seem to indicate that bonding interactions are weaker in the Co−Si complex than in the Fe−Si and Mn−Si complexes.[164]

Actual experimental measurements of bond energies are few and far between. The Ta−Si BDE's in $Cp_2Ta(PMe_3)(SiR_3)$ are about 5−8 kcal/mol weaker than the TaPh bond in $Cp_2Ta(PMe_3)Ph$.[88] Since TM−Ph bonds are significantly stronger than TM−alkyl bonds, it is likely that $Ta-SiR_3$ bonds are at least as strong or perhaps stronger than Ta−alkyl bonds. From DSC mesurements it was possible to obtain $D(Pt-SiMe_3)$ for the complex $[PtIMe_2(Me_3Si)(bipy)]$. The value of 55.7 ± 3.3 kcal/mol for Pt−Si in this Pt(IV) derivative is about 24 kcal/mol larger than that of a $Pt^{IV}-CH_3$ bond.[11,525]

B. The Nature of the TM···HSi Interaction

When a hydrosilane reacts with a TML_n fragment, variations of products are produced that contain a range of H−Si interactions. At one extreme, the H−Si bond is cleaved to give a full oxidative addition product [H−TM−Si] and the coordination number of the metal center in the product is defined by $nL + 2$. At the other extreme, the H−Si bond is barely stretched and the H−Si σ-bond donates electron density to the metal center. Since the σ interaction occupies one coordination site the coordination number of the metal center in the product is now defined by $nL + 1$. The nature of bonding in X−H σ-donation to metal centers has been reviewed in some detail.[514,7b]

The TM−Si bond distances tend to be short especially in complexes that contain electron-rich metals and this observation has been discussed in previous reviews.[1a,b] There is no general agreement as to the origin of this bond shortening. Another unknown factor is the extent to which the hydrogen which was originally bound to the silicon center is still interacting with the silicon center in the product complexes. In this section, the contributions that have been made by various calculation methods to rationalize these observation will be described.

Hückel calculations in the mid-1980s identified two types of interactions between a Si−H σ-bond and a d^n TML_x fragment. In the first type, the H−Si σ-bond is complexed to the metal atom as a 2-electron ligand (a 3c−2e interaction). In the second type, oxidative addition to the metal center occurs and the H−Si bond in the silane is broken forming TM−H and TM−Si, both of which are 2c−2e bonds. It was argued that for $CpMnL_2(HSiR_3)$, there was no case where the separation of H and SiR_3 was complete and that the metal in the product had the same formal oxidation state as in the reactant. It was proposed that even in the extreme case, that the bonding in this manganese system was better described as a hydride (H^-) coordinated to the metal and the metal coordinated to a SiR_3^+ fragment. Thus the oxidation state of the metal was retained.[527]

The 3c−2e interactions are illustrated in Figures 1 and 2 for Si−H and are similar to those proposed for other σ-donors such as C−H and H−H bonds. The Si−H bond exhibits a greater basicity than either a H−H or a C−H bond and thus contributes to better σ-donor interaction by Si−H.[7a] On the other hand, the Si−H bond is also weaker than H−H and probably the C−H bond as well, thus the Si−H bond would also be a better π-acceptor than either H−H or C−H. Substituents at both the metal center and the silicon center can obviously alter the outcome in oxidative addition of $HSiR_3$ to L_nM. Different metal centers vary in degree of both acceptor and donor properties and the donor/acceptor nature of the HSi bond can be tuned by the remaining substituents at the silicon center. The earliest system studied was based on $CpMn(CO)_2(HSiR_3)$.[5] Electron-withdrawing substituents in $HSiR_3$ provide increased binding energy to the Mn and ultimately lead to Si−H cleavage. Electron-donating groups on silicon decrease the binding interaction of HSi with the Mn center and give products with a 3c−2e bond. In the manganese system, data from the solid state (Table 5) and UV photoelectron spectra[476,480,498] both support a silane−metal interaction that approaches complete oxidative addition with electron-withdrawing chlorine substituents on the silicon. Earlier calculations supported π-back-bonding from the Mn unit to the Si−H σ^*-orbital (although the authors preferred a description that did not involve the term oxidative addition). A strong interaction between the metal and the σ^*-orbital of the silane would be expected to lead to a full oxidative addition product.[7a] If a metal is not a strong donor, the interaction between metal and silane would require the metal to be a good σ-acceptor, and in this case the interaction would be reinforced by electron-withdrawing substituents at silicon. In the σ-acid fragment, $Cr(CO)_5$, the binding energy of the silane with the Cr center does increase with more electron-donating groups on silicon[497] (see section VI).

Support for π-back-bonding into a silyl group is by no means universal, and the number of measurements or calculations on a range of systems is minimal. Several papers have dealt with complexes from the iron triad and photoelectron spectra have been obtained for $CpFe(CO)_2L$ ($L = SiCl_3$, $SiMe_3$)[456a] and *cis*-$(OC)_4Fe(SiCl_3)_2$.[164] In the study of $CpFe(CO)_2(SiR_3)$ ($R = Cl$, Me) it was determined that the $SiCl_3$ group is a better π-acceptor than CN and about half as effective as CO. It was suggested that the origin of the π-acceptor ability of $SiCl_3$ could involve the Si−Cl σ^*-orbitals. The group electronegativity of $SiCl_3$ is larger than $SiMe_3$ making the former a poorer σ-donor than the latter. The sum of single bond covalent radii for silicon and iron is 0.22 Å longer than that actually observed for $CpFe(CO)_2SiCl_3$. Lichtenberger argues that even if the sum of the covalent radii is corrected for electronegativity differences, the ionic contribution to bond shortening would only account for about one-half of the shortening. The remainder must be due to π-back-bonding of the metal to the $SiCl_3$ group. With a trialkylsilyl group, neglible π-back-bonding occurs and with a lower group electronegativity there should be little ionic contribution to the Fe−Si bond. Therefore, bond shortening should not be observed for a $-SiMe_3$ substituent. Unfortunately, the structural parameters for $CpFe(CO)_2SiMe_3$ have not been determined but in the closest analogue, *cis*-$(OC)_4Fe(SiMe_3)_2$, the Fe−Si bond distance is in close agreement with the sum of the single bond covalent radii suggested by Lichtenberger.[456]

In contrast to the results just described for $CpFe(CO)_2(SiR_3)$ ($R = Cl$, Me), the authors concluded from UPS studies that π-back-donation was not significant in the complex, *cis*-$(OC)_4Fe(SiCl_3)_2$.[164] The DFT calculated Fe−Si distance was 2.45 Å which is less than the VDW (van der Waals radii) sum of 2.56 Å used by these authors. Bond shortening was attributed to polarization effects. Curiously, the DFT calculated Fe−Si distance for *cis*-$(OC)_4Fe(SiCl_3)_2$ is the same as that observed in the solid state for *cis*-$(OC)_4Fe(SiMe_3)_2$.[456] The extent of shortening is actually consistent with arguments used by Lichtenberger based on electronegativity. It is probable that the differences in these two iron complexes are due to the presence of only CO ligands in the second case.

The electronic properties of the 16e complex $RuXH(CO)(PH_3)_2$ ($X = H$, SiH_3) have been analyzed by core potential ab initio methods at the MP2 level.[189] The calculated structure is that of a square pyramid with the strongest σ-donating group in the apical position. The SiH_3 and H groups appear to have comparable properties as ligands in this system and as σ-donors can compensate for electron deficiency at the metal. No distortion of the SiH_3 group producing an agostic interaction was observed in the calculated structure.

A rare isostructural set of osmium complexes, $OsCl(CO)(PPh_3)_2(SiR_3)$ ($R = F$, Cl, OH, Me) has been characterized in the solid, and calculations were performed on the model complexes $OsCl(CO)(PH_3)_2(SiR_3)$ ($R =$ same series).[197] The Os−Si bond distances in the four derivatives were found to increase in the sequence: 2.25 (SiF_3) < 2.27 ($SiCl_3$) < 2.32 [$Si(OH)_3$] < 2.37 ($SiMe_3$) Å. Since the ΔEN in group electronegativity of $SiMe_3$ vs SiF_3 is 1.17, a decrease in bond distance of about 0.11 Å from the $SiMe_3$ complex to the SiF_3 complex would be predicted by the Stevenson−Schomaker equation. An ionic contribution could then account for the observed bond shortening in the sequence. Ab initio calculations and NBO analyses indicate a π-bonding contribution which increases in the sequence Me < OH < Cl < F. The SiF_3 group was estimated to have almost half the π-acceptor capability of a CO similar to $SiCl_3$ in the previously described study of $CpFe(CO)_2SiCl_3$.[456] Two other features were revealed in the calculations. The d-orbitals on silicon which were involved in the polarization of the Si−R σ^*-orbitals were important in the quantitative description of the Os−Si bond. The second feature was a three-center bond among Os, Si, and the C of the CO group which decreased in the sequence F > Cl > OH > Me.

An ab initio MO calculation (MP2 and MP4 levels) of the complex $[OsCl(CO)(PH_3)_2$“H_2SiH_3”$]$ has been performed.[526] Two isomeric σ-complexes, Os−SiR_3(η^2-H_2) and Os−H(η^2-$HSiR_3$), which are close in energy, were found. The η^2-binding of H−SiR_3 is stronger although this is almost balanced by the stronger H−H bond strength. Thus, observation of the two forms was predicted. In the actual case of the complex, $[OsCl(CO)(P(i\text{-}Pr)_3$“$H_2SiPh_3$”$]$, it is the η^2-$HSiPh_3$ form that is observed.[528]

The simplified system, *cis*-$Mo(CO)(PH_3)_4H(SiH_3)$, was used as a model for the complex *cis*-$Mo(CO)(depe)_2(H\cdots SiHPh_2)$ which contains a σ-H−Si interaction.[529] A H−Mo−Si angle of about 45° was calculated for the model with a H···Si distance of 1.813 Å which is close to that observed in the actual complex. The silicon center exhibited a distorted trigonal-bipyramidal geometry with the Si−H axial and coordinated to Mo. Analysis of the density Laplacian around the H−Mo−Si triangle was consistent with a dative $H^-\rightarrow Mo$ interaction and the Mo−Si interaction was primarily covalent. Thus, the description of the complex lies closer to the classical extreme of oxidative addition. In an η^2-H_2 complex, the H−H remains almost unperturbed by the $M\rightarrow H_2$ σ^* back-bonding thus the description of such complexes is closer to the nonclassical dihydrogen extreme. A seven-coordinate isomer, *cis*-$Mo(CO)(PH_3)_4H(SiH_3)$, of energy similar to the pseudooctahedral η^2-H−Si form was not observed. The cis orientation of the CO and (η^2-$HSiH_3$) contrasts with the isomer observed for the $Mo(CO)(dppe)_2(\eta^2\text{-}H_2)$ complex where the CO and H_2 ligands occupy trans positions. The cis preference in the hydrosilane complex may be rationalized through strong σ^*-accepting ability of the H−Si bond.

A σ-interaction between a metal center and a H−Si bond is not restricted to silicon in an α-position as has been discussed in section VI. Calculations have been performed on the model system, $Cl_2Ti[C(SiH_2CH_3){=}CH_2]^+$ (Cl is often used in calculations as a surrogate for Cp^-).[530] The eclipsed optimized structure exhibits a small Ti−C−Si angle (93°) and an interacting Si−H bond of 1.589 Å that is longer than the “normal” Si−H bond. The Ti···H distance of 2.06 Å, supports an interaction between the β-SiH and the

Ti center. The β-SiC in the model complex also exhibits an agostic interaction with the metal center. These calculations predate the actual observation of β-SiX interactions. More recently, ab initio calculations (DFT and MP2 level) have been performed for the complex, $Cp_2Ti[\eta^2\text{-}trans\text{-}(t\text{-}Bu)C{\equiv}CSiHMe_2]$ (**11−2**[503]) which provide good agreement with the experimental parameters.[531] In this interesting system the complex appears to be best formulated as a d^2 Ti center which back-bonds both to the acetylene and H−Si units, illustrating the strong σ^*-accepting ability of the H−Si bond.

C. Calculations Concerning Structure

Molecular mechanics calculations have been performed on Ti complexes such as $Cp_2Ti(SiHRR')PMe_3$ (R, R′ = H, Me, Ph) to shed some light on the steric requirements in dehydrocoupling reactions.[34] It was found that the barriers to rotation of the silyl ligands in these formally four-coordinate Ti(III) complexes are quite small, but the difference between the $PhSiH_2-$ and $PhMeSiH/Ph_2SiH$ ligands of 3.0−3.5 kcal/mol may be sufficient to account for the large rate difference in dehydrocoupling of primary silanes compared to secondary silanes. Steric effects in the addition of silanes (primarily tertiary silanes) to $CpMn(CO)_2(heptane)$ has been probed by photoacoustic calorimetry and variable-temperature kinetic studies.[532] Steric effects in this oxidative addition reaction do not appear to be exerted until the cone angle of the silane exceeds ~135°. This angle corresponds to tertiary silanes, R_3SiH, where R is an ethyl group or larger alkyl group.

Steric effects in the nine-coordinate complex $[ReH_5(PR_3)_2(SiR_3)_2]$ have been evaluated at the IMOMM(MP2:MM3) (IMOMM, integrated molecular orbital molecular mechanics) computational level.[533] The geometry optimization of $[ReH_5(PCyp_3)_2(SiH_2Ph)_2]$ (**2−29**; Cyp = cyclopentyl) and $[ReH_5\{PPh_2(i\text{-}Pr)\}(SiHPh_2)_2]$, (**3−37**; neutron diffraction) gave results that better match the solid-state data than did those of MP2 optimization of the model system, $[ReH_5(PH_3)_2(SiH_3)_2]$. The steric effects are larger in **3−37** than in **2−29**. The total MM energy could be divided into a sum of terms of which van der Waals and "bending" interactions proved to dominate. Of these two, the more important contributions involve P and Si ligand pairs.

Since hydride ligands are difficult to identify in X-ray data (see Tables 5, 8, and 11 for examples), calculation methods could be used to suggest or support the locations of "missing" atoms. Ab initio MO calculations with analytical gradients were used to locate the positions of the H atoms in $[ReH_2(SiPh_3)(CO)(PMe_2Ph)_3]$ (**4−61**) and $[ReH_6(SiR_3)(PPh_3)_2]$ (**4−63**).[534] For both of these compounds, structural data for the heavy elements are available. For the calculations all alkyl and aryl groups were replaced by H atoms. The optimized model for **4−61** indicated that the complex could be described either as a distorted pentagonal-bipyramidal structure or a distorted bicapped trigonal-bipyramidal structure (seven-coordinate). The Si···H distances are relatively short (2.1−2.3 Å) and are significant. The model complex **4−63** is consistent with a nine-coordinate tricapped trigonal-prismatic structure (Si and P ligands in equatorial sites). Although weaker, there may be Si···H interactions. The transfer of electron density from silicon to rhenium appears to be the origin of the attractive interaction between silicon and the hydride ligands.

The reaction of SiH_4 with gaseous W^+ was followed by FT-ICR (Fourier transform ion cyclotron resonance). The initial reaction of SiH_4 and W^+ proceeds with little barrier to give the insertion complex $[(H)WSiH_3]^+$ followed by H_2 elimination to give $[WSiH_2]^+$. Additional species were formed from successive addition of SiH_4 and dehydrogenation through two reaction channels to end with the silicon cage, $[WSi_{10}H_n]^+$ ($n = 6, 4$). Ab initio calculations (CASSCF level) were utilized to obtain structures for $[WSiH_2]^+$ and $[WSi_2H_2]^+$ (and $[WSi_2H_4]^+$). The ground state for $[WSiH_2]^+$ appears to be a high-spin silylene complex with a dative bond between SiH_2 and W. The two lowest energy forms for $[WSi_2H_4]^+$ (not observed by FT-ICR) are the disilene complex and the silylsilylene complex. A form of 1,2-dihydrogen elimination from these two complexes would generate the two lowest energy forms of $[WSi_2H_2]^+$. Successive species with increasing numbers of silicon centers were assumed to have cyclic structures.[535a] In an earlier ion beam study, Ni^+, Co^+, and Ti^+ reacted exothermically with SiH_4 to give a single dehydrogenation product $[TMSiH_2]^+$. The estimated metal ion−silylene bond energy for Co and Ni was 67 ± 6 kcal/mol.[535b]

VIII. Miscellaneous Oxidative Addition Reactions

A. Lanthanides

The first lanthanide−silicon bond was reported in 1985 and was generated in the anion formed according to the reaction shown in eq 32.[536] The Sm analogue was crystallographically characterized and the Sm−Si bond distance of 2.880 (2) Å suggested partial covalent bonding between the two elements. Several related derivatives of Lu, Dy, Ho, Er, Tm, and Lu were later reported by the same route.[537] The first neutral lanthanide silyl complexes were prepared by the σ-bond metathesis of a lanthanum alkyl complex (eq 33[85,538]) and are summarized in Table 14.[85,538,539] Both $Cp^*_2SmSiH(SiMe_3)_2$ (**14−1**) and $Cp^*_2NdSiH(SiMe_3)_2$ (**14−6**) form dimers in the solid state but are monomeric in solution. The Cp* resonances of **14−6** decoalesce below room temperature and the activation barrier for rotation about the Nd−Si bond

$$Cp_2LnCl{\cdot}NaCl{\cdot}2DME + LiSiMe_3 \xrightarrow{\text{pentane}} [Li(DME)_3][Cp_2Ln(SiMe_3)_2] + NaCl + LiCl \quad (32)$$

Ln = Sm, Lu

$$Cp^*_2LnCH(SiMe_3)_2 + H_2Si(SiMe_3)_2 \longrightarrow Cp^*_2LnSiH(SiMe_3)_2 + CH_2(SiMe_3)_2 \quad (33)$$

Ln = Sm (**14-1**), Nd (**14-6**)

Table 14. Lanthanide Complexes Prepared from Hydrosilanes

Complex	Prep.[a] (%Yd)	Color m.p.	Anal.	NMR			Other	Ref.
				solvent (temp)[1b]	^{1}H[1c] Si-H	^{29}Si[1c]		
14-1 $Cp^*_2SmSiH(SiMe_3)_2$	A(48)	red 173-175	Y	S(22)	10.10(s)	-23.51	^{13}C IR X-ray[d]	85, 538
14-2 $(C_5Me_4Et)_2SmSiH(SiMe_3)_2$	A(35)	dk red 88-89	Y[e]	S(20)	10.49(s)[f]		^{13}C IR	85
14-3 $Cp^*_6Sm_3(\mu\text{-}SiH_3)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}SiH_2SiH_2)$	B	—	—	—	—	—	X-ray[g]	539
14-4 $[Cp^*_2SmSiH_3]_3$	B	—	—	—	—	—	X-ray[h]	539
14-5 $Cp^*_6Sm_3(\mu\text{-}SiH_3)(\mu_3\text{-}\eta^1,\eta^1,\eta^3\text{-}SiH_2SiH_2SiH_2)$	B	—	—	—	—	—	X-ray[i]	539
14-6 $Cp^*_2NdSiH(SiMe_3)_2$	A(49)	blue-grn 179-180 MW =534[j]	Y[e]	S(22) T(-100)	-24.46(s) [k]	—	IR	85, 538
14-7 $(C_5Me_4Et)_2NdSiH(SiMe_3)_2$	A(20)	blue-grn oil	N	S(80)	[k]	—	IR	85

[a] Reactants: A, $(C_5Me_4R)_2SmCH(SiMe_3)_2 + H_2Si(SiMe_3)_2$; B, $Cp^*_2SmCH(SiMe_3)_2 + PhSiH_3$ or Ph_2SiH_2. [b] Solvent key: S, C_6D_6; T, C_7D_8; X, $CDCl_3$. Data are for ambient temperature in °C unless specified otherwise. [c] In ppm. Coupling constants are in Hz; s = singlet. Heteroatom spectra are normally proton decoupled. Coupling constants are reported with respect to the nucleus measured. [d] Sm−Si distance is 3.052(8) Å. [e] Analysis is outside ±0.5% of calculated percentage value for carbon. [f] Line width = 18 Hz. [g] Sm−Si distances: 3.174(4), 3.093(4), 2.954(2) Å. Hydrogen atoms at silicon were not located. [h] Disordered structure. Sm−Si distances: 3.138(6) Å, 3.155(3) Å. [i] Disordered structure. [j] MW determined by cryoscopy. [k] Not assigned.

was found to be 13.3 kcal/mol.[538] Tertiary silanes such as Ph_3SiH or Ph_2MeSiH or the secondary silane $(i\text{-}Pr)_2SiH_2$ do not react with $Cp^*_2LnCH(SiMe_3)_2$. When the primary silane $MesSiH_3$ reacted with $Cp^*_2LnCH(SiMe_3)_2$, the metal product was $[Cp^*_2LnH]_2$ and the silicon product was $H_2MesSiSiMesH_2$ which resulted from dehydrocoupling of the silane reactant.[85,540]

The reaction shown in eq 33 (Ln = Sm) was found to fit a rate law that was first order in the starting metal complex and first order in the silane but with carefully purified starting complex variable induction periods were observed. The induction period is eliminated in the presence of H_2 which reacts with $Cp^*_2SmCH(SiMe_3)_2$ to give Cp^*_2SmH which in turn can catalyze the reaction shown in eq 33. Dehydrocoupling of Cp^*_2SmH and $H_2Si(SiMe_3)_2$ proceeds quantitatively to give **14−1**. Thus, it was proposed that the reaction of the alkyllanthanum complex with hydrosilanes proceeds through a second-order autocatalyic process requiring hydrogen.

The complex, $Cp^*_2SmCH(SiMe_3)_2$, was also found to cause redistribution of phenyl groups in $PhSiH_3$ and Ph_2SiH_2. The initial product is probably $Cp^*_2SmSiH_3$ (from absence of phenyl resonances in the ^{1}H NMR spectrum) but the product is unstable and converts to a second complex which contains two Cp* resonances. The second complex gives a mixture of SiH_4 and Si_2H_6 on reaction with acid. With longer reaction periods a solid mixture is obtained which contains the three trisamarium clusters $Cp^*_6Sm_3(\mu\text{-}SiH_3)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}SiH_2SiH_2)$ (**14−3**), $[Cp^*_2SmSiH_3]_3$ (**14−4**), and $Cp^*_6Sm_3(\mu\text{-}SiH_3)(\mu_3\text{-}\eta^1,\eta^1,\eta^3\text{-}SiH_2SiH_2SiH_2)$ (**14−5**). These clusters contain bridging units with one, two, and three silicon centers and no phenyl substituents on silicon.[539] The redistribution of phenyl groups was not observed in reactions of either Cp^*_2Yb or $[Cp^*_2YbMe]_2$ with $PhSiH_3$.[539] Since a barrier to rotation about the Nd−Si bond suggests that steric effects at the Ln center could be anticipated it is not surprising that the chemistry of the lanthanide metallocene can be moderated by changing the nature of the Cp ring. Redistribution was reported in the reaction of $[Cp'_2Ln(\mu\text{-}Me)]_2$ ($Cp' = t\text{-}BuC_5H_4$, Ln = Y, Tb, Yb, Lu; $Me_3SiC_5H_4$, Ln = Lu) with $PhMeSiH_2$.[541] In this case the products were $[Cp'_2Ln(\mu\text{-}H)]_2$ and $PhMe_2SiH$.

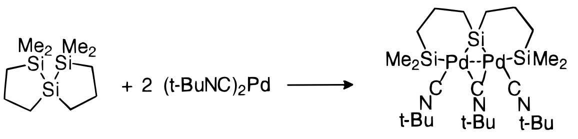
The solid structure of **14−1** showed dimers that contain Sm···CH_3Si interactions.[538] The Sm···Si distance was 3.052(8) Å, a distance that was longer than the Lu−Si distance of 2.880 Å observed in the anion, $[Cp_2Lu(SiMe_3)_2]^-$.[536]

An interesting agostic interaction between a β-SiH and a lanthanide metal center has been reported for the system $[Ln\{N(t\text{-}Bu)SiMe_2H\}_3]$ (Ln = Er, Nd) and is similar to that described in section VII for Y. The complexes are prepared by a salt elimination reaction between MCl_3 and $LiN(t\text{-}Bu)SiMe_2H$.[509] The solid-state structure of the Er derivative was determined and although the Si−H bonds appear in the normal range (1.411, 1.461, and 1.481 Å) the Er···H(Si) distances are quite short at 2.32, 2.41, and 2.37 Å. The Er−N−Si angles are all just less than 100°, following the pattern discussed in section VII for other β-MXSiH interactions. The $\delta(^{29}Si)$ resonance was observed at 429 ppm but it was not possible to obtain the J_{SiH} coupling constant. It appears that the Si−H to Er(III) interaction persists in solution as indicated by the IR spectrum (in C_6D_6). The Si−H in the free amine ligand is found at 2111 cm^{-1}, whereas in the complex, the Si–H is shifted to 1858 cm^{-1} as would be expected for a M–H–Si interaction.

B. Oxidative Addition Reactions Involving Other Si–X Bonds

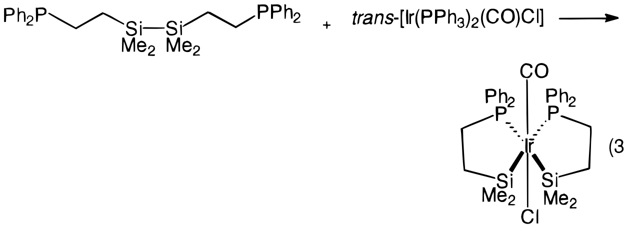
In the last two decades, there have been several reports on the oxidative addition of other X–Si bonds (for example, X = C, Si, halogen) to transition-metal centers and some recent reviews have appeared.[1d,12b] The activation of X–Si bonds to TM complexes is a useful synthetic route for the preparation of silicon-containing compounds. For example, addition of a Si–Si bond to a C–C multiple bond can be catalyzed by a transition metal to give two new Si–C bonds stereoselectively.[542] A majority of the examples involve later transition metals such as Rh, Pd, and Pt. This section is intended to provide a brief overview of other types of X–Si additions to transition-metal centers by citing a few *representative* examples and is not meant to cover all the available literature. Although addition of X-Si bonds to a TM center are relatively rare, a number of reports have appeared in the past decade. Theoretical calculations have shown that the oxidative addition of a Si–Si bond to $Pt(PH_3)_2$ or $RhCl(PH_3)_2$ is more exothermic than the addition of a H–Si bond but the activation barrier is higher for the Si–Si addition.[9,517] The Si–Si σ-bond possesses some unusual physical and chemical properties due to a high-lying HOMO and low-lying LUMO and this HOMO–LUMO difference may facilitate the interaction of a Si–Si bond with a TM center relative to a C–C bond. Activation of a Si–C bond to $Pt(PH_3)_2$ is also exothermic but has a higher activation energy than the addition of a Si–Si or a Si–H bond.[9] The addition of a Si–F bond is endothermic due to the large Si–F bond strength.[9]

Several reports have illustrated the oxidative addition of Si–Si bonds to transition-metal centers. A number of cyclic bis(silyl)palladium complexes have been prepared by Ito et al.[422,425] and just recently a novel dimeric palladium complex was isolated by activation of two Si–Si bonds in a spiro trisilane by $Pd[CN(t\text{-}Bu)]_2$ (eq 34). The spirosilane also reacted with $(\eta^5\text{-}C_5R_5)(\pi\text{-allyl})Pd$ to give a cyclic Pd(IV) complex containing two Pd–Si bonds. The latter complex was found to catalyze the ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane to give high molecular weight polymers.[543] Their earlier studies found that strained cyclic disilanes or electronegative groups on silicon promoted the oxidative addition to the Pd(0) center.[422,425] A number of the bis(silyl)palladium complexes were reacted with alkenes and alkynes to provide the corresponding 1,2-adducts.



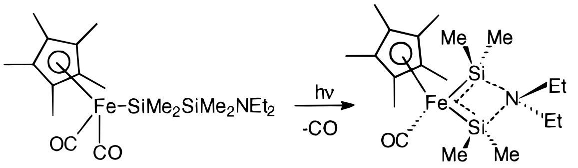
(34)

Recently, Ito and co-workers reported the first example of direct observation of Si–Si addition to Ir(I). The disilane, $Ph_2P(CH_2)_2Si(Me)_2Si(Me)_2(CH_2)_2PPh_2$ reacted with *trans*-$Ir(PPh_3)_2(CO)Cl$ to afford the six-coordinate Ir(III) complex as shown in eq 35.[415]



(35)

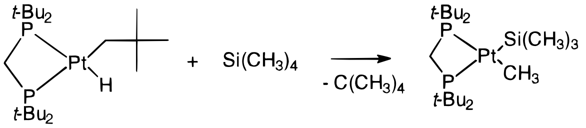
Several examples of intramolecular activation of a Si–Si bond have been reported. Ogino et al. have prepared a number of donor-stabilized bis(silylene) metal complexes from photolysis of disilylmetal systems (metal = Fe or Mn).[341] Irradiation of the aminodisilanyl(iron) complex shown in eq 36 causes initial loss of CO followed by migration of silicon to the metal center to give the bis(silylene) complex.



(36)

Pannell and co-workers have prepared and studied the reactivity of a number of oligosilyl iron complexes such as $Cp(CO)_2Fe{-}SiMe_2SiMe_2Ph$. These complexes are photochemically labile and upon irradiation exhibit two types of transformations that involve silylene ($:SiR_2$) extrusion and/or isomerization.[12a]

There are few reports of the oxidative addition of Si–C bonds to transition-metal centers. Hofmann and co-workers reported Si–C activation of $Si(CH_3)_4$ with $(dtbpm)Pt(H)[CH_2C(CH_3)_3]$ as shown in eq 37.[544]

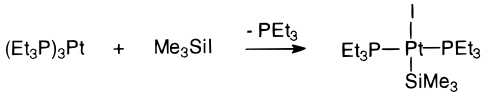


(37)

Addition of a C–Si bond was also observed with $(Me_3Si)_2O$ and $(Me_3Si)_2$ and no Si–Si cleavage of the latter was observed! The reaction is believed to occur with prior activation of a sp^3 C–H bond. Metathesis of a Si–C bond is probably involved in the reaction of $PhSiH_3$ with $Cp_2{}^*SmCH(SiMe_3)_2$.[539]

Activation of Si–C(sp) bonds is also known to occur. For example, reaction of $Me_3Si{-}C{\equiv}C{-}SiMe_3$ with $Ru(H)_2(CO)[PMe(t\text{-}Bu)_2]_2$ afforded $Ru(SiMe_3)(C{\equiv}C{-}SiMe_3)(CO)[PMe(t\text{-}Bu)_2]_2$ in high yield.[376]

The activation of a C–X bond by transition-metal centers is well-documented and is used in applications of organic synthesis.[8] Examples of Si–X (X = halogen) oxidative addition are known. Tanaka et al. have examined the reactivity of a number of halosilanes with Pt(0) complexes.[545] For example, reaction of $Pt(PEt_3)_3$ with Me_3SiI afforded the *trans*-platinum–silyl complex, $Me_3SiPtI(PEt_3)_2$ as shown in eq 38. The reactivity of the Si–X bond was estimated to increase in the order Cl (no reaction) ≪ Br < I and for $Me_{4-n}SiCl_n$ the order was $n = 1$ (no reaction) ≪ 2 <



$$(Et_3P)_3Pt + Me_3SiI \xrightarrow{-PEt_3} Et_3P{-}\overset{I}{\underset{SiMe_3}{Pt}}{-}PEt_3 \qquad (38)$$

3. The nature of the phosphine ligands bound to Pt had a significant effect on the reactivity order. The reactivities of the PtL_n complexes (L_n = phosphine) were found to increase in the order L = PPh_3, dppe (no reaction) $\ll$ $PPhMe_2$ < PMe_3 < PEt_3. Thus, electron-donating groups bound to the phosphine enhanced the sensitivity toward oxidative addition of the silicon−halogen bond.

Puddephatt and co-workers recently reported the reactivity of some halosilanes, germanes, and stannanes with $PtMe_2$(diimine) complexes to give products from trans oxidative addition of the E−X bond.[430,435] The additions occurred more readily for X = I > Br > Cl and E = Sn > Ge > Si. Chlorosilanes were found to be unreactive.

IX. Conclusion

The reaction of hydrosilanes with transition-metal complexes is a versatile method for the formation of compounds that contain a TM−Si bond (Tables 1−4, 7, and 11). All types of silanes from SiH_4 to R_3SiH have been found to react with suitable metal precursors from scandium through copper triads. The most commonly studied silicon reactant is a tertiary silane, and the most common substituents on silicon are R = Me, Et, and Ph groups. This is no doubt due to the commercial availability of either R_3SiH or R_3SiCl which is the precursor to the hydrosilane. Much less explored are reactions of silicon−silicon-bonded hydrosilanes (i.e., disilanes, oligomers, and cyclic polysilanes) with metal complexes although in these cases reactivity of both Si−H and Si−Si bonds could be observed. The majority of the reported silyl−metal complexes are found with metals from groups 8−10. Only a few metals have a limited number of silyl complexes and these are found in the Sc, Cu, and Zn triads which are at the extreme ends of the transition metal series.

The mechanism by which the silyl group becomes incorporated into a metal complex is unlikely to be the same for all metals. Tilley and co-workers were able to establish σ-bond metathesis pathways in the reaction of hydrosilanes with zirconocene and hafnocene derivatives.[21] This pathway is generally assumed for d^0-complexes and for early transition metals. An oxidative addition pathway is generally assumed for 16-electron metal centers and for 18-electron complexes that lose a ligand or ligands.[8] As an example of the latter, labeling studies demonstrated that the photochemical reaction of Cp_2MoH_2 with $DSiMe_3$ provided only $Cp_2Mo(SiMe_3)D$ and H_2 (no HD was observed).[90] Thus, a mechanism involving reductive elimination of H_2 from Cp_2MoH_2 to give a "Cp_2Mo" fragment followed by oxidative addition of the silane to the metal center is consistent.

The nature of the transition-metal coreactant changes across the series from electron-poor metals which are dominated by Cp-type ligands to electron-rich metals which are dominated by carbonyl and phosphine ligands. The metal reactant must be characterized by an open coordination site or if the metal center is an 18-electron complex, thermal or photochemical loss of a ligand must occur prior to reaction with the silane. The most likely reaction pathway, at least for groups 6−10, is an oxidative addition of the hydrosilane to the metal center. The influence that substituents at the metal might exert on the stability of a silyl complex has not been systematically studied. The factors influencing isolation of the silylmetal complex are illustrated in a study of the photolysis of the related series, (η^n-C_nR_n)$M(CO)_3$, where M = Cr (n = 6; R = H), Mn (n = 5; R = H, Me), Re (n = 5; R = H), and Fe (n = 4; R = H).[546] Photolysis of these 18-electron complexes provide coordinatively unsaturated 16-electron species, (η^n-C_nR_n)$M(CO)_2$, which subsequently reacted with neat Et_3SiH or R_3SiH in hydrocarbon glass to give (η^n-C_nR_n)$M(CO)_2(H)(SiR_3)$. The products were characterized primarily by IR and ^1H NMR spectroscopy studies. The reactivity of (η^n-C_nR_n)$M(CO)_2$ with neat Et_3SiH at 100 K followed the order: Cr > Mn > Fe > Re and for Mn, C_5Me_5 > C_5H_5. Attempted isolation of the Et_3SiH adducts showed that the Fe product decomposed above 220 K, the Cr analogue decomposed near room temperature and although the Mn derivative was stable at room temperature, attempts to isolate the product near 300 K led to decomposition.[546] However, adjustment of substituents at either Si or the metal has led to isolation by other investigators of related complexes of Cr, Mn and Re (see Tables 1−4). There are presently no known, isolated complexes of (η^4-C_4R_4)$Fe(CO)_2(H)(SiR_3)$.

The factors that promote the formation of a stable (isolable) silicon−metal complex from the viewpoint of substituents on the silicon precursor also have not been systematically evaluated although electron-withdrawing groups seem to favor an oxidative addition reaction with metal complexes from groups 7−10. Thus, $HSiCl_3$ reappears as a reactant through this range of metals (for examples, see Table 4). The advantage of products of the type, H−[TM]−$SiCl_3$, is the ability to convert the SiCl bond in the complex to other substituents by standard substitution reactions at silicon without cleavage of the TM−Si bond (for one example, see Scheme 5).

Several variations of interactions seem to occur between silanes and metals, from full oxidative addition where the Si−H bond is cleaved (see section III) to that of "arrested" addition with an interaction between a metal orbital and a Si−H sigma bond (see section VII). In reactions of silane and primary or secondary silanes the resultant complexes can contain both a normal 2c−2e Si−H bond and a 3c−2e TM(H)Si interaction and the difference between the two bonds is reflected in the respective chemical shift values (~5 ppm in the former and generally <0 ppm for the latter; see Table 7) as well as in the values of the coupling constants. Coupling constants for Si−H bonds in free silanes are usually about 200 Hz, whereas in σ-complexes, the values are less than about 100 Hz (Table 7; see also refs 1d and 5). A value lower than 20 Hz for an Si−H coupling constant probably indicates a full oxidative addition to the metal center. A relationship between coupling constants and the extent of oxidation addition has not been established as of yet. Another indication of a σ-interaction may be the relative M−HSi and MH−Si distances but often the pertinent hydrogens are either not located or not refined (see Table 8). If such distances are reported, they are known with less accuracy. Neutron diffraction studies are rare and additional data would be useful in clarifying the parameters that would be associated with "arrested" oxidative addition reactions. The range of Si−H sigma interactions is probably not yet established as illustrated in the recent publication of a new variation for a derivative of tantalum.[513] That a Si−H unit not directly bound to a metal center will also form an agostic interaction has been demonstrated in several cases where the silicon center is in a position β to the metal (see Tables 11 and 12). Such complexes are also characterized by coupling constants around 100 Hz, significantly lower than the Si−H in the free silane precursor. No reports of an agostic interaction between Si−H in a γ-position and a metal center were found.[547] Although most examples of σ-Si−H interactions involve a monosilane, there are also chelating systems, HSi···SiH, that will form two such bonds to a metal.[486] The range of stable σ- or β-Si−H interactions is quite broad. The greatest number of examples is found in the manganese through cobalt triads and seem to appear frequently in dimetallic and trimetallic complexes of the respective triads. The energy difference between the σ complex and the oxidative−addition product can be small and in some cases, both forms have been observed for the same complex.[22]

There are several interesting questions that remain relative to "arrested" oxidative addition and these include (a) how do substituents at either the silicon or the metal mediate such interactions; (b) what spectroscopic or structural parameters define an "arrested" interaction; and (c) how do Si−H interactions compete with or relate to other bonds that form either σ or agostic interactions (such as H_2 or CH).

The Si−TM bond distances have been determined for a large number of complexes with different substituents at both metal and silicon centers (Tables 5 and 8) and each metal shows a range of individual TM−Si distances where the shortest to longest bond varies from about 0.1 to 0.2 Å. Basically, the distances are shorter than expected for a single bond, especially when electron-rich metals are involved, and thus the nature of the TM−Si bond is still a matter of discussion and debate (section VII.B). Insufficient data are available to determine how substituents effect the value of the distance and this adds additional uncertainty to discussions of the nature of the bond. In addition, the TM−Si distances in 2c−2e and 3c−2e interactions also appear to overlap (Table 9). Related bond dissociation energies are essentially unknown although several values have been calculated (section VII.A).

NMR data have been reported for almost all complexes that have been prepared during the period covered by the current review. The chemical shift values for Si−H and M−H tend to occur in unique ranges but there is no apparent correlation between the ^{1}H chemical shift (for the M−H proton) and the extent of oxidative addition of Si−H to the metal center. Some correlation may be developed for ^{29}Si data although the chemical shift seems to be influenced more by substituents at silicon and not effected by changes in substituents at the metal site. In general, the ^{29}Si resonance shifts downfield in the silylmetal complex relative to the free silane precursor and also shifts downfield in $TM{-}SiR_{3-x}H_x$ as x changes from 3 to 0 in monometallic complexes (section V.A). Bridging and terminal SiR_2 groups (silylene complexes) are found even further downfield. Many complexes containing the unit $H{-}[TM]{-}SiR_3$ (R = any type of substituent) are fluxional and exhibit exchange between silyl and hydride sites. A variety of fluxional processes have been proposed including $H{-}TM{-}SiR_3 \leftrightarrow TM(\eta^2\text{-}HSi)$ intermediates (section V.B; for example, see Scheme 28 and Figure 26).

The current review has focused on examples of reactions of hydrosilanes with metal complexes that gave isolated, stable silyl-metal derivatives although some cases where characterization was performed only in solution were also included. In contrast to reactions of hydrocarbons with metals, hydrosilanes provide a broad range of products with continually evolving types of bonding interactions. There is no apparent limit in the location of the triad from which the transition metal reactant is derived although there are certainly some metals that are less studied than others. Many reactions of hydrosilanes with organic (inorganic) substrates such as hydrosilylation of multiple bonds and dehydrocoupling require a transition metal to promote the desired chemistry. It is likely that variations of both $H{-}[TM]{-}SiR_3$ and $[TM]{-}(\eta^2\text{-}HSiR_3)$ are involved in the steps that lead to the products.

As with any evolving area of study, there remain many interesting and challenging questions for silylmetal complexes and those concerning structure and modes of bonding have been mentioned earlier. The development of the reactivity of silylmetal complexes remains for the future. For example, is it possible to "dehydrogenate" $H{-}TM{-}SiHR_2$ to form silylene complexes, $TM{=}SiR_2$, or to react the Si−H unit in $H{-}TM{-}SiHR_2$ to give bimetallic complexes $H{-}TM{-}SiR_2{-}TM'{-}H$ (TM and TM′ are different transition metals such as in **4−343**) and from there to polymers with controlled structure? What other bonds to silicon may be induced to "oxidatively add" to a metal center. Such studies are currently rare (section VIII) but results do indicate that Si−Si bonds will also "add" to metal centers. One interesting aspect to explore is the formation of "nonclassical" interactions between Si−Si, Si−C, or Si−halogen bonds and transition metal centers. To date, only complexes containing a coordinated σ-EH bonds have been characterized as pointed out by Crabtree.[7b] Proper choice of σ-coordinating moiety, ligands, and metal center may provide complexes of this type in future studies. It is our hope that this summary will provide impetus for future investigations that will address some of the unanswered questions in silicon−transition-metal chemistry.

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