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Coordination Chemistry Reviews
178–180 (1998) 903–965

COORDINATION
CHEMISTRY
REVIEWS

Bimetallic silicon chemistry
New opportunities in coordination and organometallic chemistry

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PII S0010-8545(98)00164-7

Abstract

Bimetallic complexes containing silyl or siloxy ligands may display unique structures and reactivity patterns that are directly related to a subtle interplay between the metals and the ligands. Access to this class of compounds will be discussed. The recently discovered hemilabile behaviour of the bridging $-Si(OR)_3$ ligand in heterobimetallic complexes has led to a number of developments in our group and others that are reviewed here. This will include the chemistry of $Ph_2PCH_2PPh_2$ (dppm)-stabilized Fe–Pd and Fe–Pt alkyl complexes which allow, under mild conditions, controlled insertion reactions of isonitriles, alkynes or CO/olefins into the metal–carbon bond. In some cases, silicon migration reactions leading to new μ-siloxycarbene complexes have been observed. Other reactions that will be presented are the alkyne insertion into metal–hydride bonds, fluorination of the $Si(OR)_3$ ligand and the catalytic dehydrogenative coupling of stannanes $HSnR_3$. By altering the nature of the assembling ligand (μ-PR_2 vs. μ-dppm) but keeping the metals and the silyl ligand unchanged, the first examples of intramolecular silyl migration from one metal to another were discovered. Finally, the use of aminosilyl in place of alkoxysilyl ligands led to the formation of new silylene complexes, to unprecedented examples of metal-mediated substituent exchange reactions between phosphorus and silicon, and to the characterization of the first complexes containing a bridging aminosilyl ligand. Many of these reactions involve steps that are directly relevant to the mechanisms of currently investigated catalytic systems.

Keywords: Alkoxysilanes; Aminosilanes; Catalytic dehydrogenative coupling of stannanes; CO-olefin stepwise insertion; Hemilabile behaviour; Heterobimetallic; Isonitrile insertion reactions; Redistribution reactions; Silicon migration reactions; Siloxanes; μ-Siloxycarbene complexes; Silylene; Stannylene complexes

1. Introduction

Bimetallic molecular chemistry continues to attract considerable interest owing to the possibility of creating new chemical bonds between dissimilar chemical elements, the diversity of metals that can be linked directly through metal–metal bonding and the often unique reactivity of such molecules [1–7]. The simultaneous or consecutive activation and transformation of substrate molecules interacting with more than one, preferably adjacent metal centres, might be easier to achieve than on a single metal site. Furthermore, the high mobility of ligands in dinuclear complexes and clusters can promote reactions between different partners and it may be anticipated that multisite interactions involving the ligand(s) to be activated will convey information regarding the different nature of the metal atoms involved. Metal-specific electronic and steric interactions are expected to lead to increased selectivity in the overall chemical transformation. Thus, new stoichiometric and catalytic reactions or synergistic changes in activity and/or selectivity for known reactions may be attributed to the proximity of the metals, to the inherent polarity of heterometallic bonds in mixed-metal systems, and to the stereochemical properties of each metal centre [8]. A better understanding of the factors which influence elementary chemical transformations and the energetics of consecutive reactions is not only important for understanding the molecular chemistry occurring in solution, but also provide conceptual tools for suggesting new pathways in surface chemistry and surface reaction mechanisms. Furthermore, low oxidation-state heterometallic clusters are gaining increasing attention as precursors of new heterogeneous catalysts [9].

On the other hand, the mononuclear chemistry of *silicon-based ligands* has been very successfully developed over the last 40 years, since the first report by Wilkinson and coworkers of the transition metal–silyl complex [$Cp(OC)_2Fe–SiMe_3$] [10]. Owing to their synthetic applications and physico-chemical properties [11–20], organosilicon compounds continue to attract considerable academic and industrial interest and, in order to develop new metal catalysts for their synthesis or transformations, a good understanding of the reactivity of the metal–silicon bond is required [18–28]. The nature of the metal–silicon bond is still the subject of thermodynamic, spectroscopic and theoretical studies [29–36]. The activation of chemical bonds induced by coordination to a metal centre remains one of the central topics in modern coordination and organometallic chemistry, playing a major role in homogeneous and heterogeneous catalysis. Consequently, it is not surprising that the synthesis, structure and reactivity of complexes containing a metal–silicon bond have been investigated for many years. Numerous motivations exist to develop this chemistry, such as:

(i) to allow comparisons with related systems containing a M–C bond;

(ii) to provide a better insight into the elementary steps involved in very important metal-catalyzed reactions, such as the hydrosilylation of olefins and alkynes [18–20,26,37–58], the dehydrogenative coupling of primary or secondary silanes [18–20,59–73], the dehydrogenative coupling reactions of silanes with ammonia and amines to yield silazane oligomers [74], the silylformylation of aldehydes, epoxides, cyclic ethers, olefins or alkynes using CO and R_3SiH [75–84], the double silylation by addition of Si–Si bonds to unsaturated organic substrates [26] or the dehydrogenative silylation of olefins [85];

(iii) to examine and develop the scope of metal–silyl-mediated organic reactions [86–93];

(iv) to prepare new molecules to be used as original heterogeneous catalyst precursors or as single-source substrates for OMCVD [94–96].

With the desire of combining these two facets of transition metal/main group chemistry, we entered the field of heterobimetallic silicon chemistry, an area that has been scarcely examined in the past. Heterobimetallic silicon complexes containing at least one metal–silicon bond could combine features associated with both metal–metal and metal–silicon bonds, therefore allowing us to:

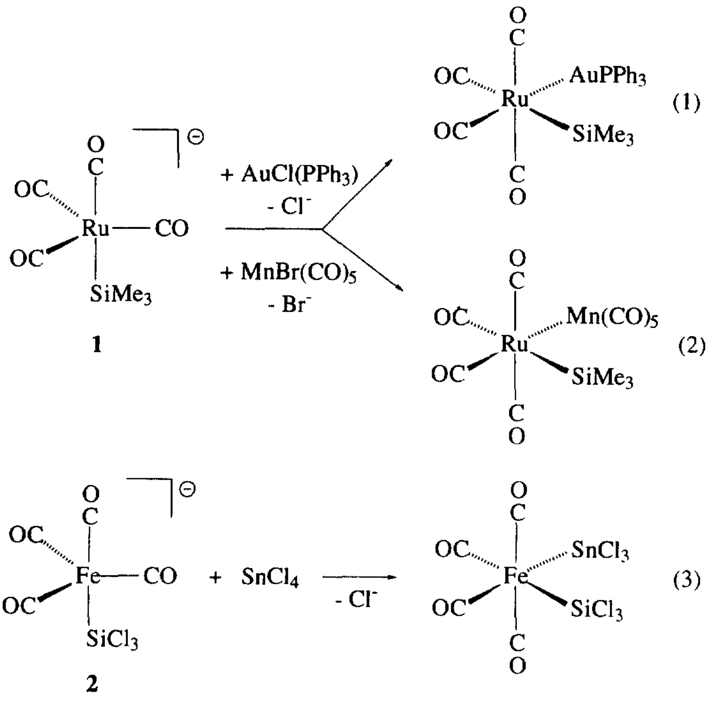
(i) take advantage of synergistic effects which could result from the presence of a heterometallic bond;

(ii) explore the reactivity of the metal–silicon bond in a bimetallic environment.

We have focused our interest on alkoxysilyl [$–Si(OR)_3$] and siloxy [$–Si(OSiR_3)_3$] complexes, which have been very little studied so far in this context, and furthermore should behave as new molecular precursors of interesting materials obtained, e.g. by sol–gel condensation routes [97–102]. We shall review here some recent results describing reactions in which an alkoxysilyl, an aminosilyl, a siloxy or a silylene ligand plays a central role in the reactivity of the molecule to which it is bonded.

2. Synthesis of heterobimetallic silyl complexes

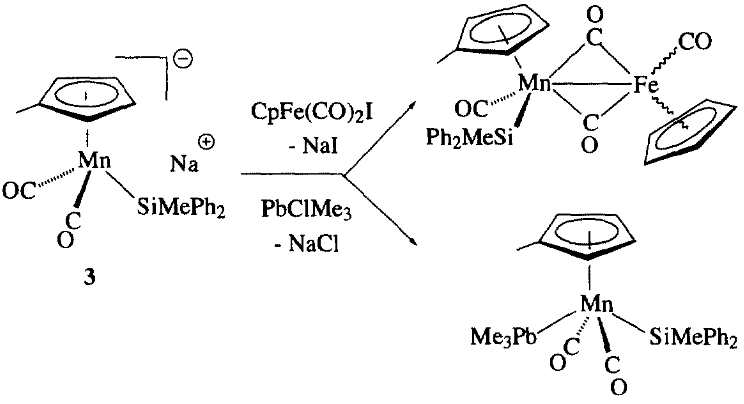
Heterobimetallic silyl-substituted complexes were synthesized for the first time by Knox and Stone in 1969 by reaction of the metalate $[(OC)_4Ru(SiMe_3)]^-$ **1** with various transition metal halides [reactions (1) and (2)] [103]. The reactivity of the related silyl-substituted iron metalate **2** has been described by Jetz and Graham [reaction (3)] [104].



The salt-elimination route using the silyl-substituted manganate reagent **3** has also been applied to the synthesis of a series of metal–metal bonded heterodinuclear compounds containing a silyl–manganese moiety [reactions (4) and (5)] [105].

The Os–Ru–$SiCl_3$ complex **4** with a dative metal–metal bond was obtained upon reaction of $[Os(CO)_5]$ with $[(OC)_4RuBr(SiCl_3)]$. On further standing in solution, isomerization to the Br-Os-Ru–$SiCl_3$ complex **5** occurred [106].

Addition of the Si–H function of the iron silyl complex $[Cp(OC)_2Fe(SiCl_2H)]$ to $[Co_2(CO)_8]$ yielded the silandiyl-bridged dinuclear compound **6** [reaction (6)] [107]. Similarly, oxidative addition of the Si–H bond of the manganese silyl derivative



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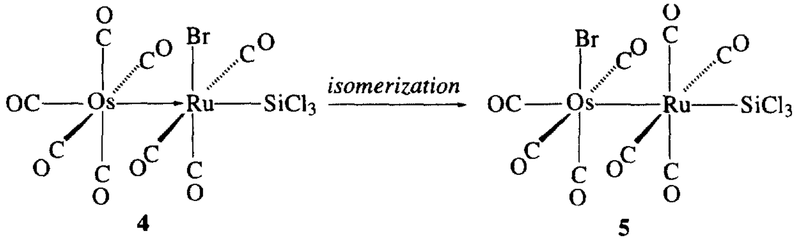

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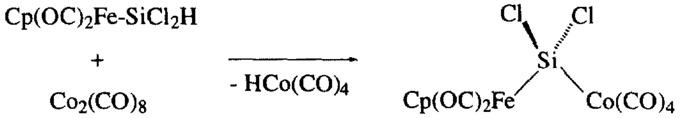
$[(OC)_5Mn(SiMe_2H)]$ across a low valent platinum centre afforded the hydride-bridged dinuclear complex **7** [reaction (7)] [108].



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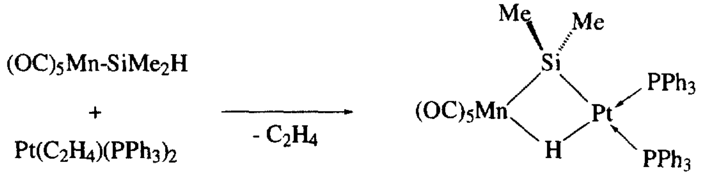

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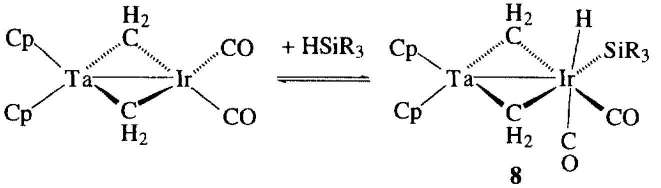
The heterodinuclear hydrido-silyl complex **8** resulted from the oxidative addition of various silanes R_3SiH to the iridium centre of the early–late complex $[Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2]$ [reaction (8)]. Noteworthy is the high catalytic activity of this system for hydrosilation and alkene isomerization reactions [109].

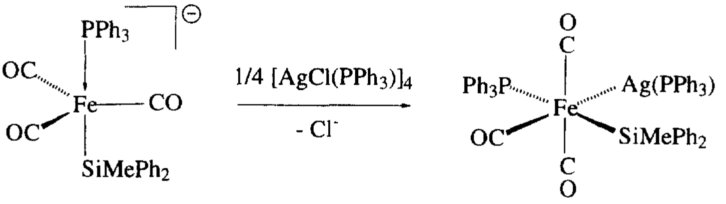
Bimetallic silyl complexes of the type $[(OC)_n(R_3Si)_2Rh\text{–}Co(CO)_4]$ ($n=2$, 3) resulted from the reaction of the tetrahedral cluster $[Co_2Rh_2(CO)_{12}]$ with various silanes $HSiR_3$. Depending on the electronic nature of the silyl group, catalytic



(8)

reactivity for silylformylation and/or hydrosilation reactions has been observed in the presence of 1-hexyne and CO [80,81].

During the last few years, silicon-containing heterobimetallic complexes of the type $[(R'_3P)(OC)_3(R_3Si)Fe{-}ML_n]$, $[(dppe)(OC)_2(R_3Si)Fe{-}ML_n]$ or $[\{(PhO)_3P\}_2(OC)_2(R_3Si)Fe{-}ML_n]$ (M = main group element or transition metal, R = alkyl, aryl, alkoxy or Cl; R′ = alkyl, aryl or alkoxy) with unsupported metal–metal bonds have been prepared by reaction of the corresponding silylated metalates, *trans*-$[Fe(SiR_3)(CO)_3(PR'_3)]^-$, $[Fe(SiR_3)(CO)_2(dppe)]^-$ or $[Fe(SiR_3)(CO)_2\{P(OPh)_3\}_2]^-$, respectively [reactions (9) and (10)] [110–116].



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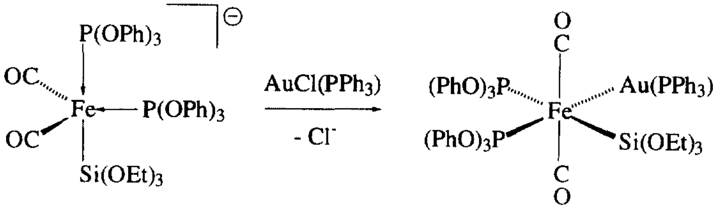
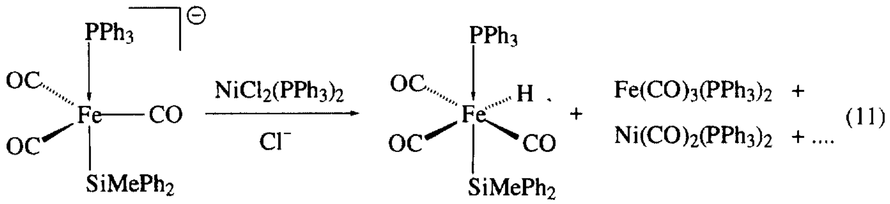


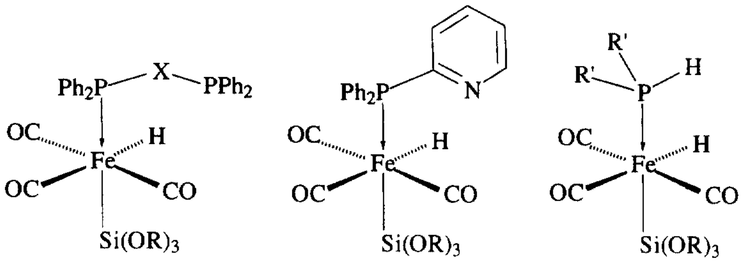
(10)

A limitation in the use of these more nucleophilic phosphine-substituted metalates is the occurrence of redox reactions, that in some cases hamper the isolation of the desired heterobimetallic silyls and lead to ligand redistribution reactions [reaction (11)] [110].

In order to direct the synthesis of heterobimetallic complexes and stabilize them to prevent fragmentation into mononuclear species, we developed the bridge-assisted synthesis of heterobimetallic silyl complexes and prepared a range of functionalized iron hydridotris(alkoxysilyl) complexes bearing an assembling or potentially assembling ligand such as $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PNHPPh_2$ (dppa), $Ph_2PC_5H_4N$, $Ph_2PCH_2C({=}O)Ph$ or PR_2H [117].

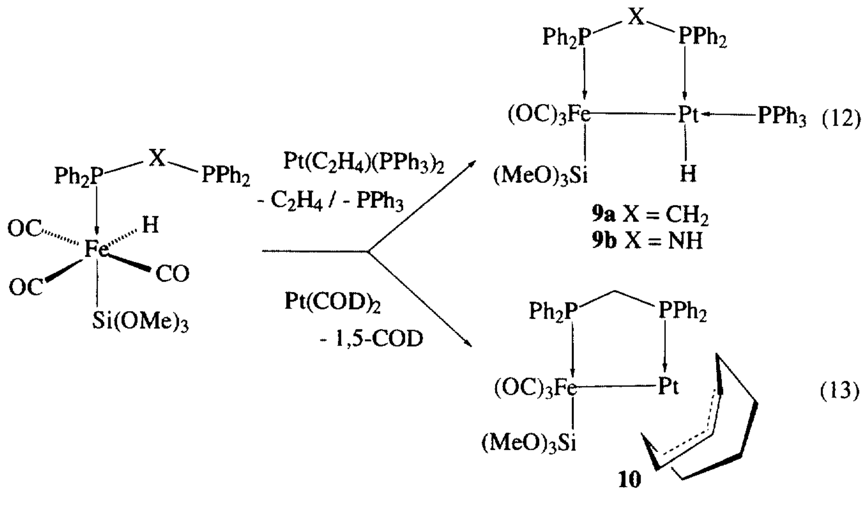
Oxidative addition of the Fe–H bond of the hydrido-silyl complexes



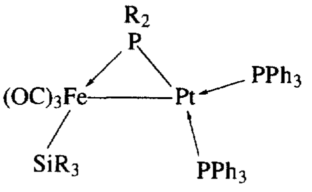


X = CH$_2$ (dppm), NH (dppa)

mer-[HFe{Si(OMe)$_3$}(CO)$_3$(η^1-Ph$_2$PXPPh$_2$)] to a low-valent metal centre afforded stable heterobimetallic complexes, in which the two adjacent metal centres are additionally connected by a bridging diphosphine backbone. Whereas the reaction mechanism for the formation of the resulting Fe–Pt hydride complexes **9** is easily rationalized [reaction (12)], a more complex sequence involving insertion of a coordinated 1,5-COD ligand, successive β-elimination and renewed insertion led to the structurally characterized π-allylic-type cyclooctenyl complex **10** [reaction (13)] [118–120].



Related phosphido-bridged silyl-substituted Fe–Pt complexes **11** and **12** were obtained by addition of $[HFe(SiR_3)(CO)_3(PR_2H)]$ to $[Pt(C_2H_4)(PPh_3)_2]$ or $[Pt(COD)_2]$, respectively and elimination of H_2 [121,122].



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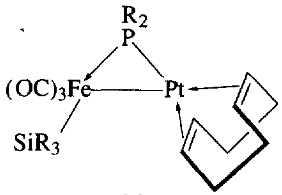

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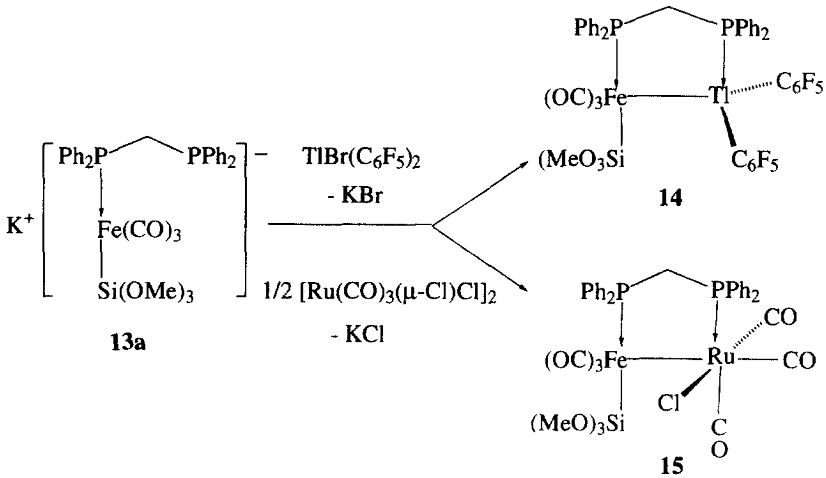
An alternative synthetic route consisting of the reaction of silyl-substituted functionalized metalates (obtained by deprotonation of the parent hydrido-silyl complexes) with various main group or transition metal halides was also developed, as exemplified in reactions (14) and (15) in the case of Fe–Tl and Fe–Ru complexes **14** and **15**, respectively [123,124].

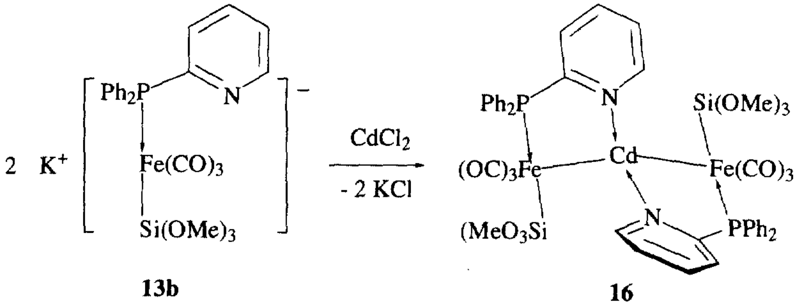


(14)

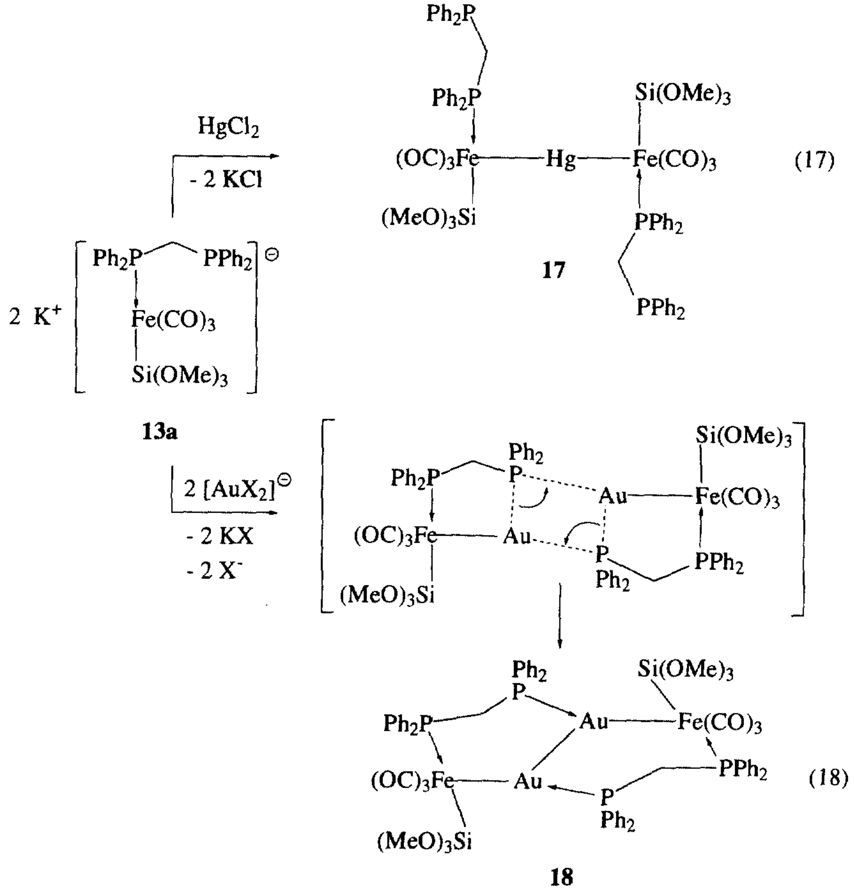
(15)

The trinuclear Fe–Cd–Fe chain complex **16**, in which two 2-(diphenylphosphino) pyridine ligands bridge the metal centres, has been obtained by reaction of the functionalized metalate **13b** with $CdCl_2$ [reaction (16)]. The flattened tetrahedral geometry around the Cd centre has been established by an X-ray diffraction study [125].

Whereas reaction of the metalate **13a** with $HgCl_2$ yielded the linear Fe–Hg–Fe chain complex **17** [reaction (17)], the tetranuclear complex **18** with an Fe–Au–Au–Fe array surprisingly resulted from the reaction of the metalate **13a** with $[Bu_4N][AuX_2]$ [reaction (18)]. The formation of this complex with its unusual structure was explained by a concerted intermolecular migration of a PPh_2 group from one gold atom to another and is driven by the well known aurophilic attraction due to relativistic effects between gold atoms with a $5d^{10}$ closed shell electronic configuration [126].

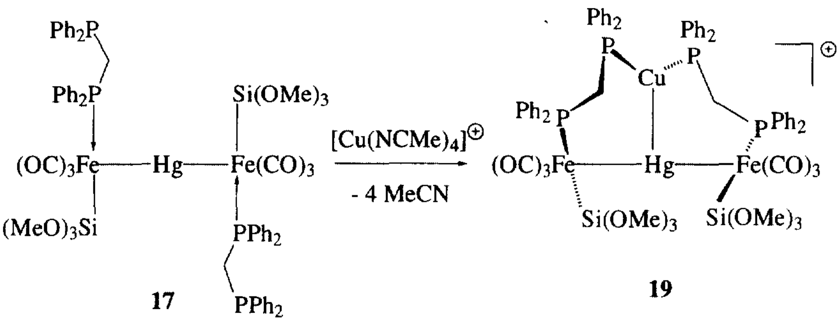


13b **16** (16)



(17) **17** **13a** (18) **18**

The pendant PPh_2 groups of the trimetallaphosphine complex **17** were used to form trimetallic inorganic mesocycles such as **19** [reaction (19)]. The new Hg–Cu interaction [2.689(2) Å] present in this complex is reminiscent of transannular interactions in organic mesocycles [127].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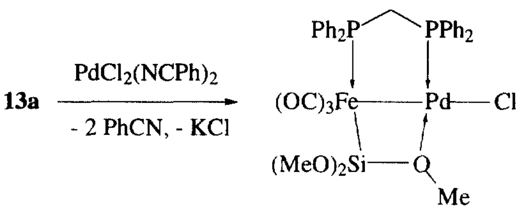
(19)

An unprecedented feature was observed in several cases where the second metal centre M adjacent to iron is Ag, Zn, In, Pd, Pt or Rh: a μ_2-η^2-Si–O bridge was established as a result of the interaction of an alkoxy group of the Si(OR)$_3$ ligand with the second metal centre [118–120,128–133]. This was first encountered and structurally characterized in the case of the dppm-bridged Fe–Pd complex **20** [reaction (20)]. The salient structural features of this complex include a relatively short distance between the oxygen and the palladium atom [2.100(4) Å], the slight lengthening of the corresponding Si–O bond [1.694(5) Å] and an Fe–Si–O angle of 100.8(2)° [118].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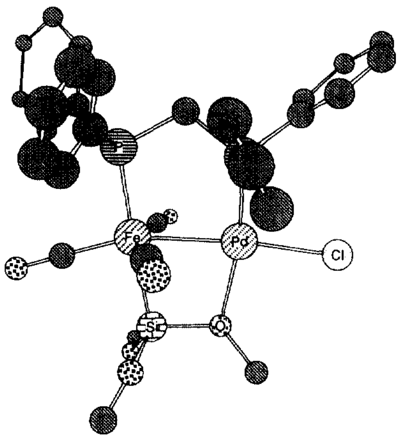

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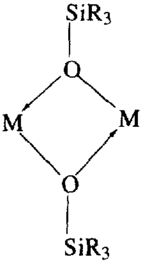
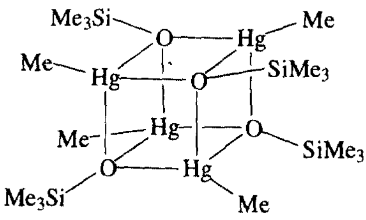
Since this dative O→M interaction will play a crucial role for the understanding of the reactivity of this type of complexes, the most salient features of this novel bonding mode will now be presented in more detail.

3. Occurrence and properties of μ_2-η^2-Si–O bridges between different metals

It has been known for many years that the oxygen atom of a siloxy group can bridge two metal centres to give dimers of type **A**. Larger aggregates can also be formed due to the propensity of the oxygen atom of siloxy groups to act as a μ_3-bridging ligand. Early examples are found in the solid-state structures of tetrameric Me–M–OSiMe$_3$ (M = Zn, Cd, Hg) cubes of type **B** [134–139].

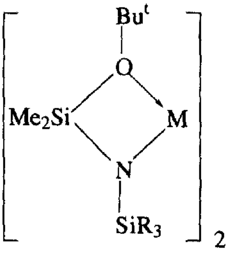


(**A**)



(**B**)

In a similar manner, the oxygen atom of an alkoxysilyl group can coordinate to metal ions. Again, dimeric (**21**) [140–142] or larger polymetallic assemblies (**22**) [143] may result from the possibility that alkoxysilyl and tris(alkoxysiloxy) ligands –OSi(OR)$_3$ may behave in a multidentate fashion.



M = Li, Na, K, Rb

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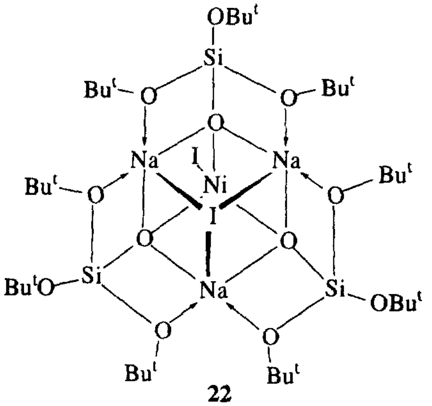

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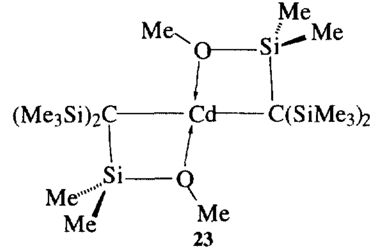
Related dative Si–O→M interactions have also been reported for some structurally characterized molecular compounds such as **23** [144,145] or **24** [142] depicted below. As expected, they are most often observed with hard metal centres, although the example of the mercury compound **25** demonstrates that even softer metal centres may interact with the oxygen atom of an alkoxysilyl group. However, the Hg–O distance of 2.878 Å is rather long and may reflect the existence of only a weak interaction [146]. Even the oxygen atom of a siloxane unit is capable of coordinating intramolecularly to a transition metal, as demonstrated recently for the zirconium complex **26**. An X-ray diffraction study of this compound revealed a quite long Zr–O separation of 2.427(3) Å, which may be correlated with a weak dative bond to the zirconium centre [147]. Although there is no metal→O interaction in complexes of type **27** and **28**, they represent very interesting examples of silylene metal complexes, which are intramolecularly stabilized by a methoxy group (see Section 9.1) [148,149].



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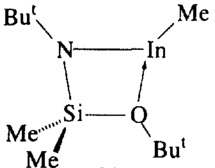

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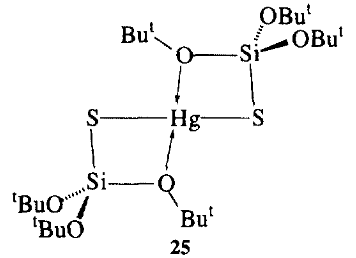

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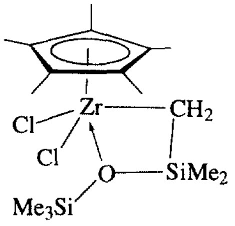

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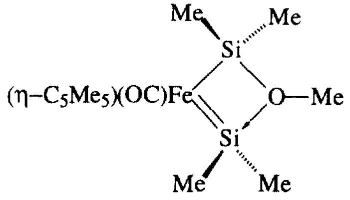

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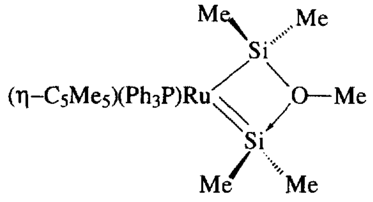

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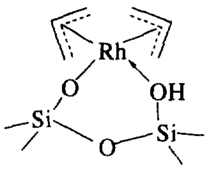
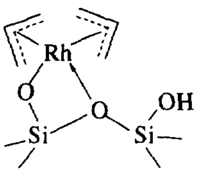
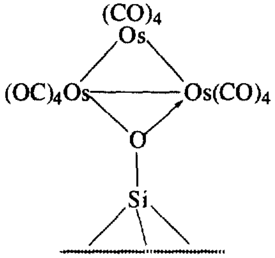
This type of dative Si–O→M interaction may also bear relevance to current studies in surface organometallic chemistry. Dative oxygen→rhodium or oxygen→osmium bonds between grafted organometallic complexes and a silica surface have been proposed by Basset and coworkers [150–152].

3.1. Dynamic behaviour of the Fe-Si-O->M *unit associated with the hemilability of the* $Si(OR)_3$ *ligand*

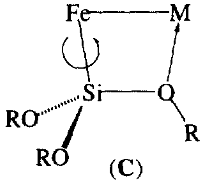
As indicated above, the new type of bonding interaction of type **C** between an iron-bound alkoxysilyl ligand and an adjacent metal centre was first observed with





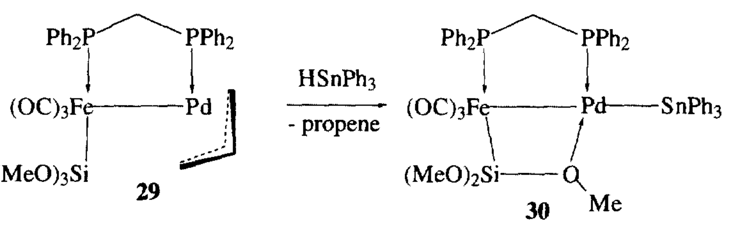


M = Pd [118]. This resulted in surprisingly stable but often kinetically labile four-membered cycle.



(C)

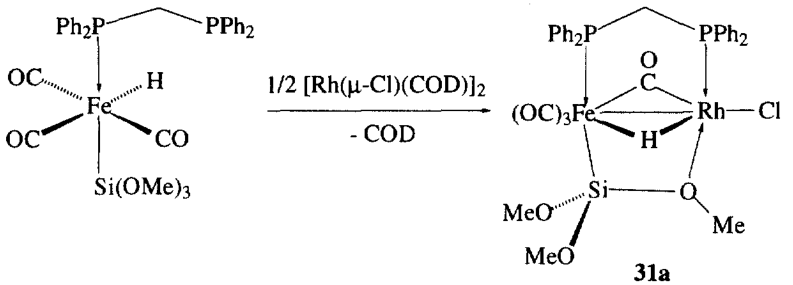
The labile character of the dative oxygen→metal interaction was generally evidenced by variable temperature ^1H NMR spectroscopy. The dynamic exchange between the OR groups results most plausibly from rapid rotation of the silyl ligand about the Fe–Si bond. This is generally clearly shown by ^1H NMR spectroscopy, where two signals in a 1:2 ratio or three signals in a 1:1:1 ratio are observed for the methoxy groups below the coalescence temperature, depending on the molecular symmetry. For example, the high temperature NMR spectrum (toluene) of the structurally characterized Fe–Pd–Sn chain complex **30** — which was prepared from the allyl precursor **29** according to reaction (21) — reveals at 363 K the presence of nine identical protons for the $-Si(OMe)_3$ group. Progressive cooling of the solution broadens this signal until coalescence is reached at ca. 318 K ($\Delta G^* \approx 65$ kJ/mol). A rigid four-membered Fe-Si-O->Pd ring structure with an η^2-μ_2-Si–O bridge exists at 243 K, as shown by the presence of two well-separated singlets for the methoxy protons in a 2:1 ratio [129].



29 **30** (21)

Note that formation of **30** was accompanied by the catalytic formation of Sn_2Ph_6. Various complexes of type **29** and **30** have been shown to be efficient catalysts (or catalyst precursors) for the dehydrogenative coupling of stannanes (see Section 7) [130,131].

In the hydride-bridged Fe–Rh complex **31a** [reaction (22)], the molecular symmetry is lowered compared to that of **30** owing to the presence of a hydride and a carbonyl bridge. Consequently, the methoxy groups are now chemically and magnetically inequivalent below coalescence temperature, thus giving rise to three singlets of relative intensities 1:1:1 [128].



31a (22)

The bromo and iodo derivatives **31b** and **31c** were prepared by halide metathesis reactions and display similar dynamic behaviour. This is illustrated in Fig. 1 for complex **31c**.

The surprisingly strong propensity for forming a dative bond between a relatively hard donor such as the oxygen of a methoxy group and a soft metal centre such as Pd dominates even in cases where a second potential donor ligand could, a priori, compete for intramolecular coordination to the neighbouring metal centre. This was

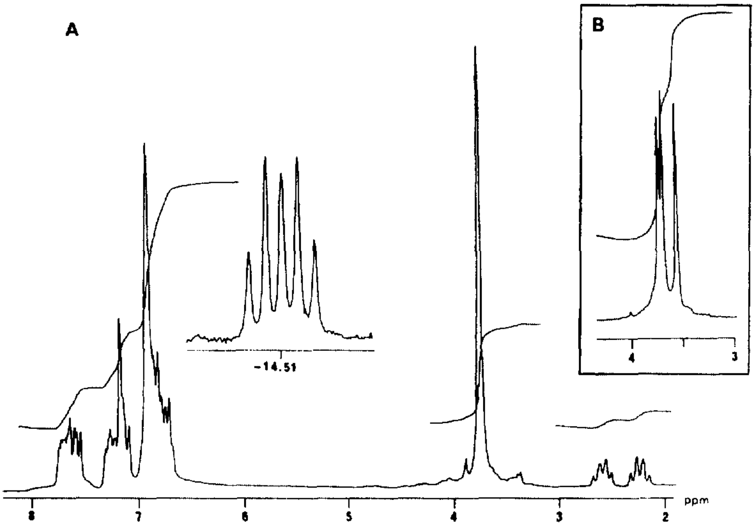
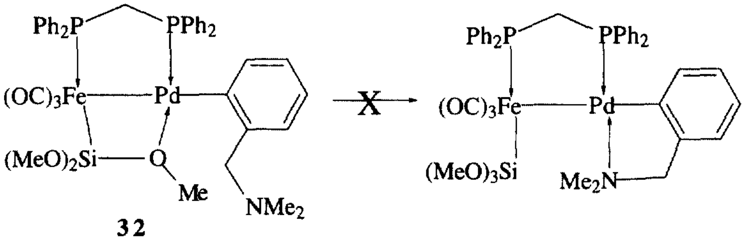


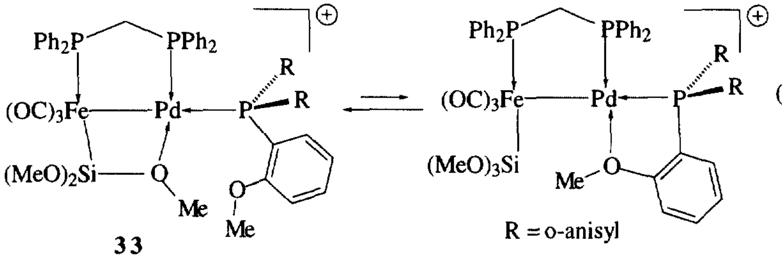
Fig. 1. Variable temperature ^1H NMR spectroscopic study of the dynamic behaviour of the μ_2-η^2-Si–O bridge in $[(OC)_2Fe(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-CO})\{\mu\text{-Si(OMe)}_2(OMe)\}RhI]$ **31c**: (A) at 298 K in C_6D_6; (B) at 253 K in toluene-d_8 for the methoxy protons. The doublet of triplet resonance centred at δ −14.51 is due to the μ-hydride ligand.

evidenced in the reaction of the metalate **13a** with the dinuclear complex $[Pd(C_6H_4CH_2NMe_2)(\mu\text{-}Cl)]_2$ which leads to **32** after opening of the cyclopalladated *N,N*-dimethylbenzylamine chelating ligand [reaction (23)]. NMR studies unambiguously showed the preference for methoxy coordination over formation of a five-membered *C,N*-chelate [153,154].



32

(23)



33

R = o-anisyl

(24)

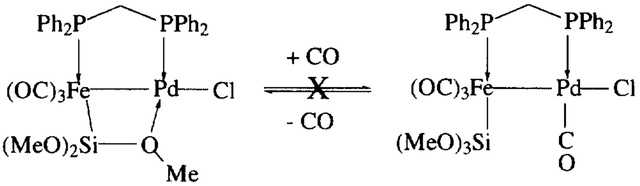
However, in the case of the cationic complex **33** with a Pd-bound *o*-anisylphosphine ligand, preliminary NMR studies indicated that an equilibrium is established between the four- and five-membered ring structures, with the former being favoured at 243 K (ca. 85%) [reaction (24)]. Both examples confirm the strong tendency for establishing the Fe–Si–O→M interaction, even in the presence of intramolecular competitors [155]. The propensity of tris(2,4,6-trimethoxyphenyl)phosphine to behave as a multidentate ligand has also recently been studied on dinuclear Rh–Rh complexes [156].

3.2. Chemical use of the masked coordination site at M

The labile oxygen→metal donor interaction provides the metal M with a masked, potentially vacant, coordination site and this can be exploited in chemical reactivity studies concerned with the fixation and activation of small molecules. We have explored such reactions with CO, isonitriles or olefins with the aim of forming carbon–carbon bonds around a bimetallic template or with stannanes for their dehydrogenative coupling.

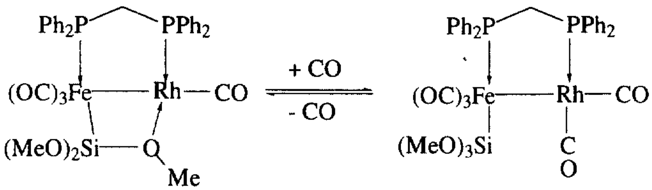
3.2.1. Coordination of CO and CNR ligands

Upon purging a solution of **20** with CO for 20 min no displacement of the methoxy group was evidenced [reaction (25)], whereas the Fe–Rh complex **34** reacted instantaneously with uptake of CO and opening of the four-membered ring $\overline{\text{Fe-Si-O->Rh}}$ [reaction (26)]. IR and NMR studies revealed that **35** readily loses the additional CO ligand under reduced pressure. Renewed CO purging afforded again quantitatively the CO adduct **35**, thus demonstrating the reversible character of this CO uptake [128]. In an analogous manner the Os_3 cluster **36** which displays two $\overline{\text{Os-Si-O->Os}}$ units added two equivalents of CO to yield $[Os_3(\mu\text{-}H)(CO)_{11}\{Si(OEt)_3\}]$ **37**, which lost under a nitrogen purge at 97 °C the two carbonyl ligands to regenerate **36** [reaction (27)] [157].



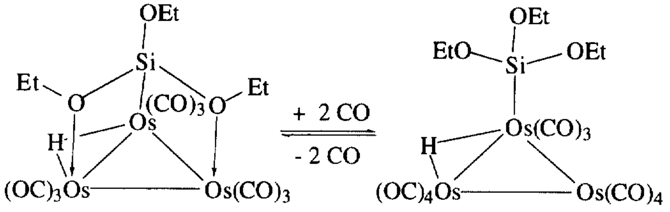
20

(25)



34 **35**

(26)



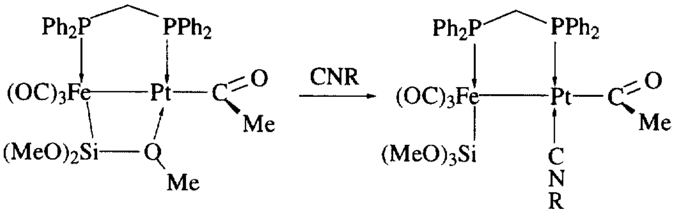
36 **37**

(27)

Addition of an isonitrile ligand to the bimetallic Fe–Pt acyl complex **38**, whose synthesis will be described in the next section, resulted in the formation of the stable adduct **39** [reaction (28)] which has been characterized by X-ray diffraction. Note that in this case no backreaction with CNR dissociation was evidenced [158].

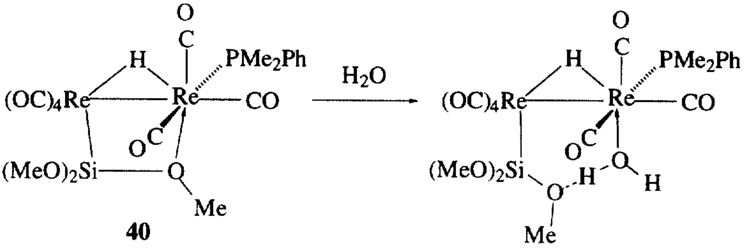
3.2.2. *Reactivity towards H_2O*

A surprising ring opening reaction has been reported by Adams et al. after addition of a stoichiometric amount of water to the dinuclear Re–Re complex **40**.



38 **39** (28)

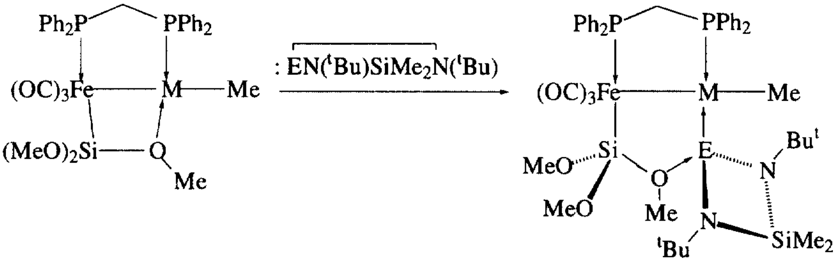
Consistent with our own observations with heterobimetallic systems, no rapid hydrolysis of a Si–OR bond occurred, in contrast to the facile processes involved in sol–gel chemistry. Instead, the water molecule displaced a Re-bound methoxy group to yield the organometallic aquo complex **41**, whose hydrogen bond between the aquo ligand and the alkoxysilyl ligand has been established by an X-ray diffraction study [reaction (29)] [159].



40 **41** (29)

3.2.3. Reactivity towards cyclic bis(amino) germylenes and -stannylenes

Cyclic germylenes and stannylenes of the type $\overline{\mathrm{EN(^tBu)SiMe_2N(^tBu)}}$ (E=Ge, Sn) have been shown to be very versatile reagents towards transition metals and lead to simple ligand substitutions, insertions into metal–carbon bonds or more complex reactions such as tin–tin coupling [160–169]. We were interested in the chemistry of these two-electron donor ligands because of their electronic relationship with carbene and silylene ligands studied by us (see below). Upon addition of a slight excess of these metal(II) amides to the heterodinuclear alkyl complexes **42** and **43**, instantaneous opening of the four-membered $\overline{\mathrm{Fe\text{-}Si\text{-}O\text{->}M}}$ ring occurred to give $[(OC)_3Fe\{\overline{\mu\text{-}Si(OMe)_2(OMe)}\}\{\overline{EN(^tBu)SiMe_2N(^tBu)}\}(\mu\text{-dppm})M(Me)]$ **44** and **45**, respectively, in which the stannylene or germylene ligand is additionally coordinated by a methoxy group as shown in reaction (30) [170]. ^1H NMR investigations in solution at variable temperature revealed that also in this unprecedented five-membered ring structure a rapid exchange of the methoxy groups coordinated to E takes place. Whereas at ambient temperature a single resonance for the methoxy protons was observed, two distinct signals were found in a 2:1 ratio below the coalescence temperature. The free activation energy $\Delta G^{\ddagger}$ has been estimated for the palladium derivatives **44a** and **44b** at 53.6 kJ/mol and 54.7 kJ/mol, respectively and for **45** at 51.3 kJ/mol [170].



(30)

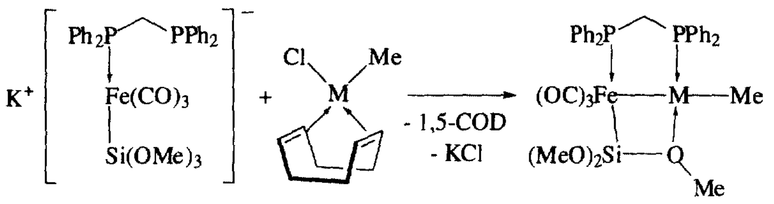
42 M = Pd
43 M = Pt

44a M = Pd, E = Sn
44b M = Pd, E = Ge
45 M = Pt, E = Sn

This intramolecular base-stabilization of the germylene or stannylene ligand may also in part be responsible for the fact that no insertion reaction into the M–methyl bond occurred, despite the close electronic relationship between CO, CNR and these metal(II) amides. The facile insertion of CO and CNR into the metal–alkyl bond of **42** and **43** will be presented in detail in the following section.

4. Migratory insertion reactions

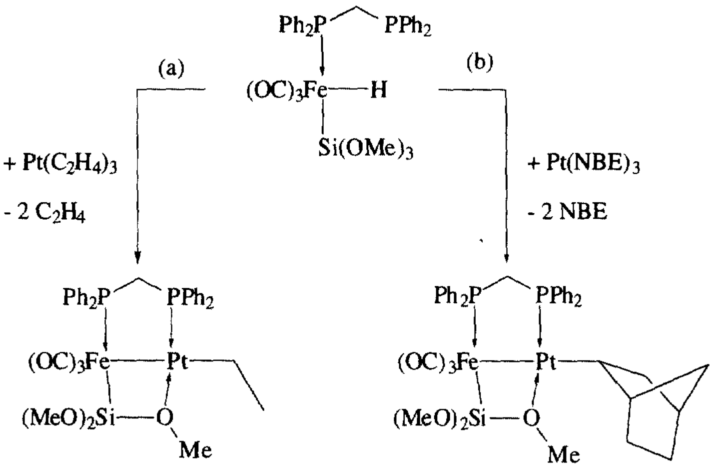
In order to exploit the chemoselective coordination of small molecules that could be used for carbon–carbon coupling reactions, we were interested in preparing new heterobimetallic alkyls and we used different synthetic methodologies to this end. The stable methyl complexes $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})M(Me)]$ (**42**, M = Pd; **43**, M = Pt) were easily prepared by reaction of $[M(Me)Cl(1,5\text{-}COD)]$ with $[Fe\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]^-$ **13a** in THF [reaction (31)], whereas the bimetallic alkyls $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})Pt(R)]$ (**46**, R = Et; **47**, R = norbornyl, C_7H_{11}) were obtained by oxidative addition/insertion reactions between $[HFe\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]$ and $[Pt(C_2H_4)_3]$ or $[Pt(norbornene)_3]$, respectively, in toluene [120,171] [reaction (32)]. In view of the lability of the dative O→Pt bond (see below), the stability of the ethyl derivative **46** towards β-elimination of ethylene is remarkable [172]. Attempts to prepare the palladium analogue of **46** by reaction of $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})PdCl]$ **20** with EtMgBr failed, and only decomposition was observed, probably owing to too rapid β-elimination of ethylene.



13a

42 M = Pd
43 M = Pt

(31)



46

47

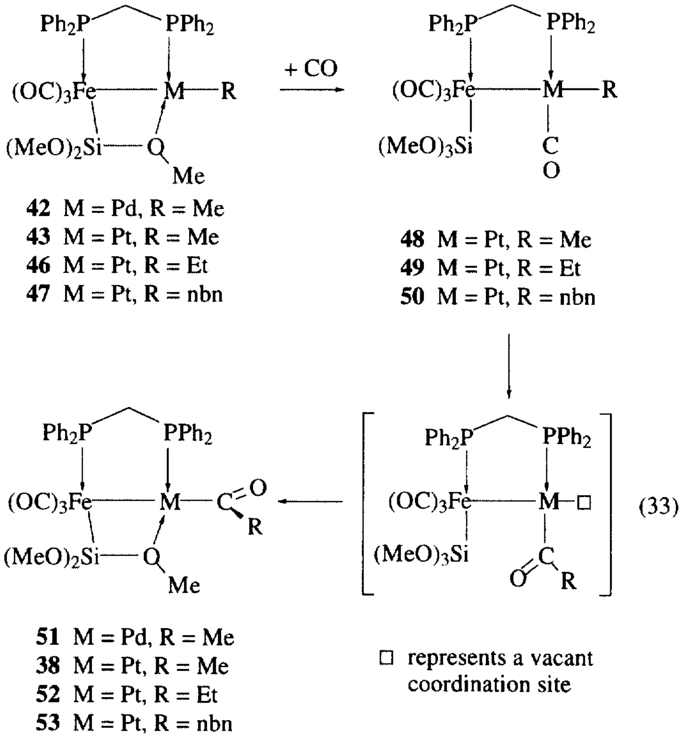
(32)

The σ-bonded alkyl ligands in these stable complexes occupy only one coordination site at M, and this explains the bridging behaviour of the alkoxysilyl ligand which allows the Pd or Pt centre to reach its preferred 16-electron configuration [120].

The migratory insertion of small molecules such as CO, organic isocyanides and olefins into metal–carbon bonds has long been recognized as an elementary step of considerable importance in organometallic chemistry and catalysis [173–178]. Several mononuclear Pd(II) catalytic systems have been described recently which allow stepwise successive insertion reactions (e.g. of CO and olefins leading to polyketone chain growth) [179–192]. Since relatively little is known about insertion reactions involving heterometallic alkyls, perhaps owing to the limited number of such complexes and/or their instability [193–203], complexes **42** and **43** became good candidates for such studies.

4.1. Carbonylation reactions

Carbonylation of the alkyl complexes $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})M(R)]$ (M = Pd, **42**; M = Pt, **43**, **46** and **47**) afforded the corresponding acyl derivatives $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})MC(O)(R)]$ (**51** and **38**, **52** and **53**), respectively [reaction (33)] [120,171]. Whereas insertion of CO into the Pt–C bond of the ethyl derivative **46** is complete after 10 min, it proceeds more slowly with the methyl and norbornyl derivatives **43** and **47**, respectively. (The higher reactivity of Pt–ethyl complexes in CO insertion reactions has recently been noted by Chen et al. [204].)



42 M = Pd, R = Me
43 M = Pt, R = Me
46 M = Pt, R = Et
47 M = Pt, R = nbn

48 M = Pt, R = Me
49 M = Pt, R = Et
50 M = Pt, R = nbn

51 M = Pd, R = Me
38 M = Pt, R = Me
52 M = Pt, R = Et
53 M = Pt, R = nbn

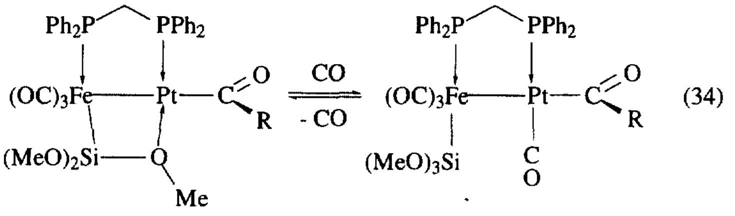
□ represents a vacant coordination site

(33)

Complex **48** could be characterized in the solid state, as a rare example of a stable complex under ambient conditions which displays a CO and an alkyl ligand bound *cis* to each other in a square planar environment [205–209]. Such intermediates are often postulated but rarely observed [209], and special low temperature techniques have sometimes been used to this purpose [183,206]. However, after ca. 30 min, or more slowly in the solid state (in a KBr pellet), acyl formation occurs which liberates a coordination site and restores the dative O→Pt intramolecular interaction, resulting in complex $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})Pt\{C(O)Me\}]$ (**38**).

The *cis*-migratory insertion of the R group should lead to complexes in which the acyl ligand is *trans* to phosphorus. Although we shall discuss later intramolecular "trapping" reactions that support this logical assumption, such an intermediate could not be directly observed. We believe that the very rapid isomerization leading to **38**, and **51–53**, in which the acyl ligand occupies a position *trans* to the metal–metal bond, must be driven, at least in part, by the restoration of the entropically favoured μ_2-η^2-Si–O bridge. With the Fe–Pd–Me complex **42**, only the acyl product **51** could be characterized and isolated. In contrast to most palladium acyl complexes, it is stable with respect to CO deinsertion [207–214]. Similarly, the related Pt–acyl complexes showed no tendency to lose CO by deinsertion, even in refluxing CH_2Cl_2.

Under 1 atm CO, complexes **38** and **52** quantitatively afforded the carbonyl, acyl complexes $[(OC)_3\{(MeO)_3Si\}\overline{Fe(\mu\text{-dppm})Pt}\{C(O)R\}(CO)]$ **54** and **55** [reaction (34)] [120]. The equilibrium of reaction (34) can be displaced depending on the CO partial pressure, and these complexes are easily and quantitatively converted into each other by simple addition or removal of CO. Noteworthy is that removal of CO under reduced pressure only affected the terminal Pt-bound CO (but not the acyl CO), affording pure **38** and **52**.



(34)

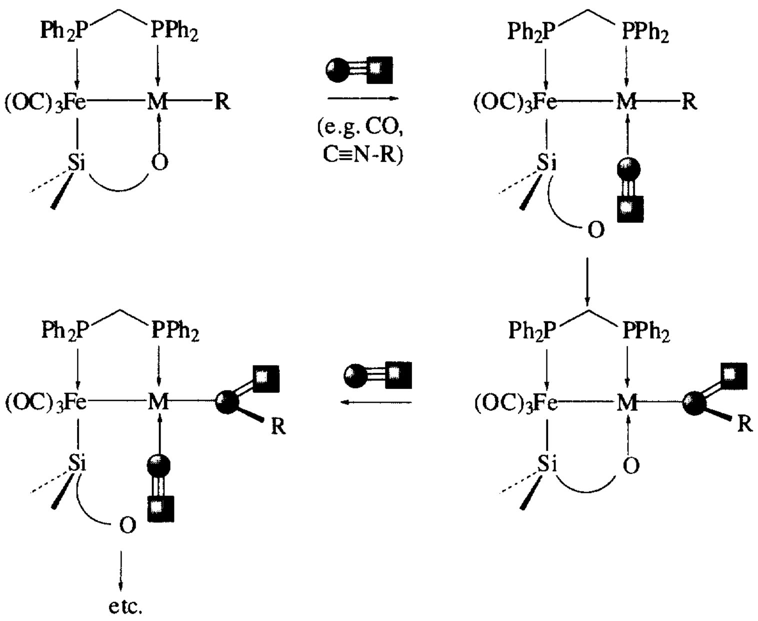
38 R = Me
52 R = Et

54 R = Me
55 R = Et

In general, deinsertion of CO from the acyl ligand is much more frequent with Pd complexes than with the related Pt complexes for which the insertion products are generally stable. Only a few examples have been reported for the complete and rapid room temperature decarbonylation of insertion products in Pt chemistry [172,206,207,215].

In the case of complexes **46** and **52** (R = Et), opening of the μ_2-η^2-Si–O bridge [reactions (33) and (34)] is clearly evidenced by ^1H NMR spectroscopy. Thus, all the successive "opening and closing" steps involving the trimethoxysilyl ligand are easily identified in the Fe–Pt systems. This mechanism also applies to the analogous Fe–Pd complexes, although the much higher reactivity of the latter precludes characterization of all the individual steps. The $^{31}P\{^1H\}$ NMR spectra are very sensitive to the bimetallic nature of these complexes, and also to the bonding mode of the silicon ligand. Further attempts at CO insertion into the Pd–acyl bond of **51**, even under 80 atm pressure, were unsuccessful. Similarly, efforts to insert under mild conditions olefins such as ethylene or norbornene (NBE) (see below) into the newly formed Pt–acyl bond of the Fe–Pt alkyls failed. Note that insertion of norbornene into the Pt–acyl bond of a cationic mononuclear Pt complex has been reported to require nine days to reach completion [216], whereas in the case of palladium the reaction is much faster [214].

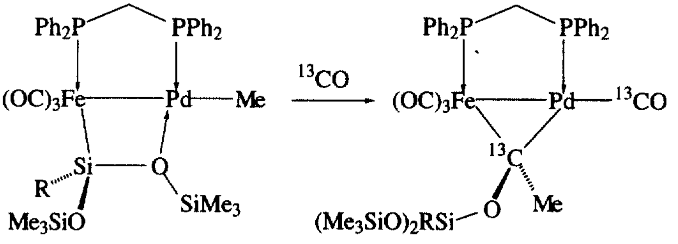
In summary, these heterobimetallic alkyl complexes possess a migrating group R *trans* to a metal–metal bond and contain an intramolecular donor which can function by successive "opening and closing", therefore providing a coordination site in the open state required for the incoming substrate and, in the closed state, the stabilization of the inserted product (Scheme 1) [171].



Scheme 1. Substrate coordination/migratory insertion sequence resulting from the opening and bridging behaviour of the alkoxysilyl ligand (M = Pd, Pt).

4.2. *Reactions of metallasiloxane complexes and CO-induced silicon migration reactions*

The course of the carbonylation reaction of the alkyl complexes **56** containing a siloxane unit, and prepared from their chloro precursors $[(OC)_3Fe\{\mu\text{-}Si(OSiMe_3)_2(OSiMe_3)\}(\mu\text{-dppm})PdCl]$ [217], differed markedly from that of the corresponding $Si(OMe)_3$ derivative. After purging a solution of **56a** for 5 min with CO and then removing the solvent ($CDCl_3$ or hexane), the heterobimetallic siloxycarbene-bridged complex $[(OC)_3Fe(\mu\text{-}C\{OSi(OSiMe_3)_3\}Me)(\mu\text{-dppm})Pd(CO)]$ **57a** was formed in quantitative yield [reaction (35)]. The analogous derivative **57b** was prepared similarly from **56b**, which contains a stereogenic Si centre [218].



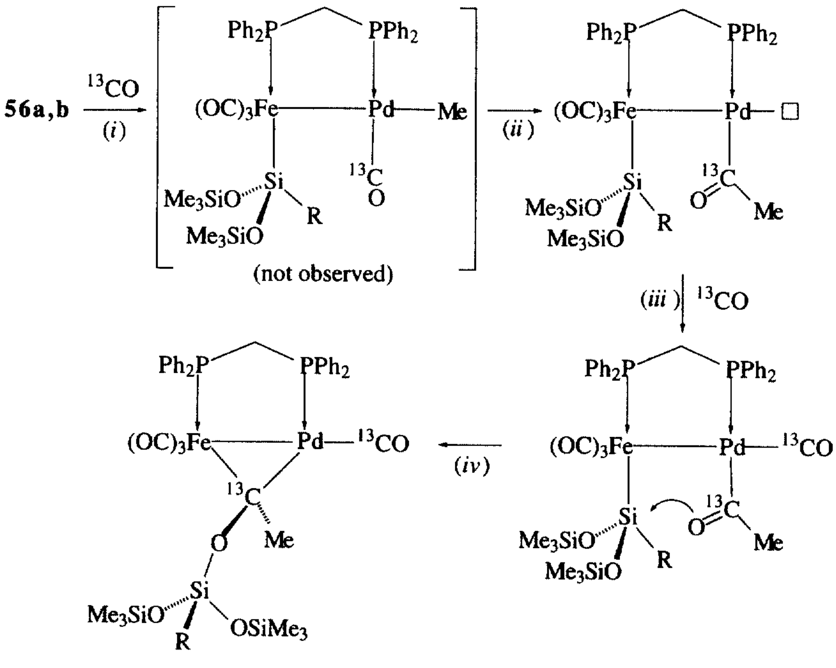
(35)

56a R = OSiMe$_3$
56b R = Me

57a R = OSiMe$_3$
57b R = Me

The presence of a terminal CO ligand on Pd was evidenced in the IR spectrum by a strong ν(CO) band at 2035 cm^{-1}. Labelling experiments using ^{13}C enriched (99%) CO confirmed incorporation of the labelled ^{13}C nuclei as described in reaction (35).

Bridging siloxycarbene complexes do not appear to have been previously isolated, although they have recently been invoked as intermediates in the hydrosilylation reaction of a bridging CO ligand in a dinuclear Ru complex [219]. The formation of complexes **57a,b** can be tentatively rationalized as follows (Scheme 2): (i) displace-



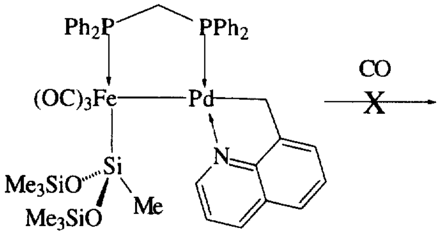
57a R = OSiMe$_3$
57b R = Me

□ represents a vacant coordination site

Scheme 2. Suggested pathway for the formation of the μ-siloxycarbene complexes **57** by carbonylation of **56**.

ment of the donor Si–O→Pd bond by CO; (ii) *cis* migration of the methyl ligand; (iii) occupation of the free coordination site by another CO ligand in an intermediate which has the acyl ligand *syn* to the migrating siloxane moiety; (iv) migration of the siloxane moiety and formation of Fe–C bond (perhaps facilitated by a cyclic transition state involving some dative interaction of the acyl oxygen with silicon) to the acyl oxygen to form a siloxycarbene complex [218]. Note that purging a solution of the chloro complex $[(OC)_3Fe\{\mu\text{-}Si(OSiMe_3)_2(OSiMe_3)\}(\mu\text{-}dppm)PdCl]$ with CO for 15 min produced no change in the IR spectrum, which is consistent with the key role played by CO migratory insertion into the alkyl bond in the rearrangement shown in reaction (35). No acyl intermediate could be observed in the carbonylation of **56a,b** (see Scheme 2). In contrast, remember that in the case of the $Si(OMe)_3$ derivative $[(OC)_3Fe\{\mu\text{-}Si(OSiMe_3)_2(OSiMe_3)\}(\mu\text{-}dppm)PdCl]$ **42**, carbonylation led to the stable acyl complex **51**, which showed no tendency to rearrange, even under prolonged CO exposure.

When the "masked" coordination site at palladium is occupied by a stronger ligand, coordination of CO is prevented and no migratory insertion of the alkyl group was observed. Consequently, no rearrangement into a bridging siloxycarbene ligand occurred. This was evidenced in the case of the Fe–Pd complex **58** in which the nitrogen donor atom of an 8-methylquinoline chelate remains coordinated to Pd [217], even under CO (1 atm).

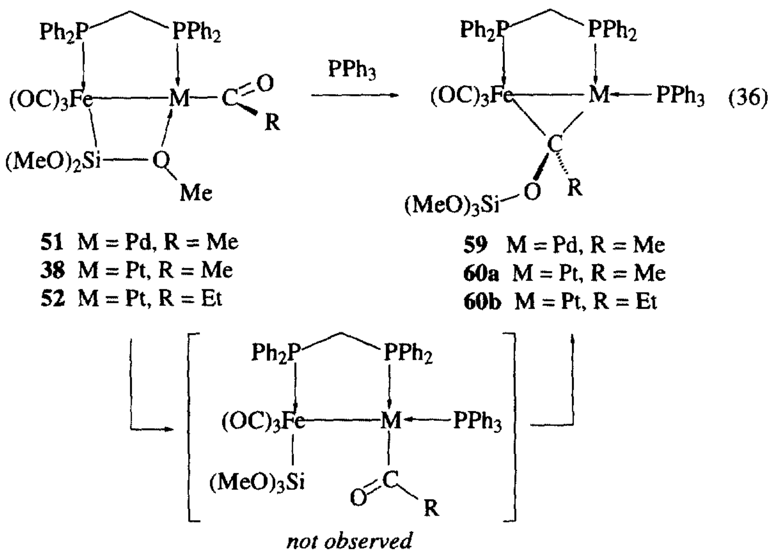


58

The absence of Si migration during the synthesis of the alkoxysilyl complexes **38** and **51–53** according to reaction (33) appears to be due to the preferred formation of a μ_2-η^2-Si–O bridge. The contrasting behaviour of the $-Si(OMe)_3$ and the $-Si(OSiMe_3)_3$ derivatives may be assigned to the more electropositive character of the central Si atom in the latter case since $OSiMe_3$ substituents are less electron donating than methoxy groups. However, carbene formation may be observed in the $Si(OMe)_3$ case, provided a strong donor ligand such as PR_3 is present [reaction (36)] (see below).

4.3. *Phosphine-induced formation of bridging siloxycarbene complexes*

Reaction of a donor ligand like PR_3 to the Pd or Pt centre of the bimetallic acyl complexes **38** and **51** led to the formation of the μ-siloxycarbene complexes **59** and **60a** [reaction (36)] [220].



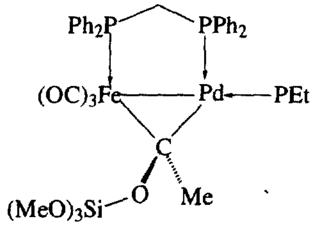
(36)

51 M = Pd, R = Me
38 M = Pt, R = Me
52 M = Pt, R = Et

59 M = Pd, R = Me
60a M = Pt, R = Me
60b M = Pt, R = Et

not observed

Whereas complex **59** is rather labile, its PEt_3 analogue **61** was more stable and was obtained quantitatively. Note that the use of the more basic phosphine PEt_3 also accelerated the rate of this phosphine-induced silyl migration reaction [220].



61

The structures of **59–61** were proposed on the basis of solution IR and multinuclear NMR spectroscopic data and confirmed by an X-ray diffraction study (Fig. 2) of the derivative $[(OC)_3\overline{Fe\{\mu\text{-}C(Et)OSi(OMe)_3\}(\mu\text{-dppm})Pt}(PPh_3)]$ **60b**, the synthesis of which was also performed according to reaction (37). The existence of a metal–metal bond [*d*(Fe–Pt) = 2.506(1) Å] confers their usual 16e and 18e counts to the Pt and Fe centres. The bridging carbene ligand (with a stereogenic carbon atom) is symmetrically situated between the metals, with Fe–C(1) and Pt–C(1) distances of 2.066(7) and 2.074(7) Å, respectively (Fig. 2) [220].

There are two possible roles for the phosphine ligand: (i) it increases the basicity of the acyl oxygen, which compensates for the less electropositive character of the Si centre in alkoxysilyl vs. siloxy complexes, thus favouring Si migration; (ii) it "pushes" and maintains the acyl ligand *trans* to phosphorus, a position that the bulkier PR_3 ligand will not occupy, long enough to allow Si migration to occur.

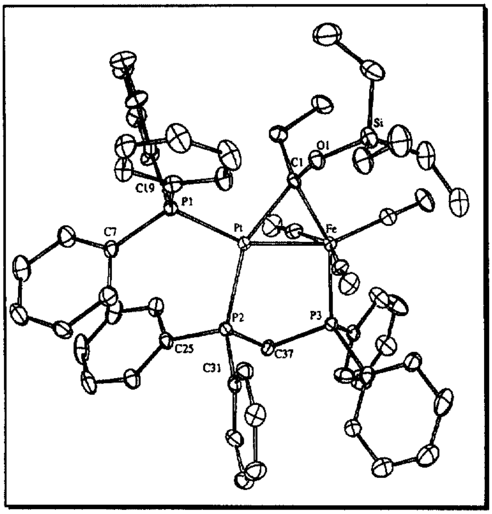


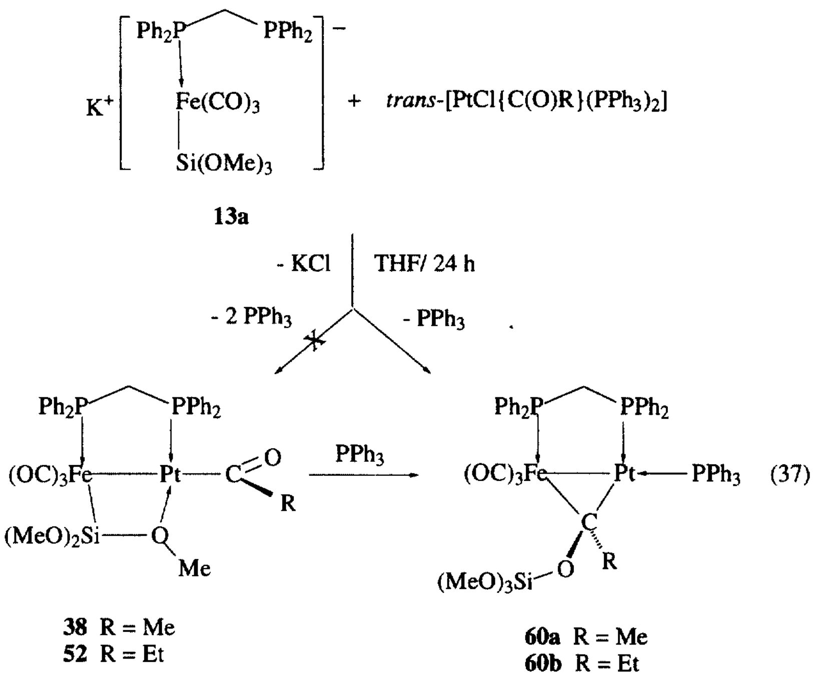
Fig. 2. View of the molecular structure of the μ-siloxycarbene complex **60b**.

As in the case of the silicon–oxygen coupling reactions observed with the mononuclear acyl–silyl complex *cis*-$[(OC)_4Fe\{C(O)Me\}(SiMe_3)]$ (which rearranged rapidly via a 1,3 silatropic shift to afford the siloxycarbene complex $[(OC)_4Fe{=}C(Me)(OSiMe_3)]$ [221]) or suggested with $[HCo\{C(O)Me\}(SiR_3)(CO)_3]$ [222], the formation of a strong silicon–oxygen bond is assumed to be the driving force for this rearrangement.

It is interesting to compare the reactivity of **51** and **38** with phosphines and isonitriles. In the latter case opening of the O→M bridge was observed, without any further rearrangement [reaction (28)]. This behaviour is similar to that of CO and contrasts with that of phosphine ligands, which may be explained by steric reasons.

The μ-siloxycarbene complexes **60a,b** could also be synthesized by reaction of the metalate $K[Fe\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]$ **13a** with *trans*-$[MCl\{C(O)R\}(PPh_3)_2]$ (R = Me, Et) [reaction (37)]. In the case of platinum, the reaction was performed at 293 K in THF for 24 h and the stable μ-siloxycarbene complexes $[(OC)_3\overline{Fe\{\mu\text{-}C(R)OSi(OMe)_3\}(\mu\text{-}dppm)Pt}(PPh_3)]$ (**60a**, R = Me; **60b**, R = Et) were isolated in ca. 75% yield. The heterobimetallic acyls **38** and **52** were not observed, which indicates that they are not intermediates in this reaction, since their reaction with PPh_3 to give **60a,b** has been independently shown to require a few hours [220].

These findings suggest that during the synthesis of the Fe–Pd and Fe–Pt μ-siloxycarbene complexes **59** and **60a,b** an intermediate having the acyl ligand *syn* to silicon is formed in which silyl migration from Fe to O(acyl) occurs. We have, however, no direct spectroscopic proof for this acyl intermediate, but evidence that the C–O unit found in the carbene ligand stems from the acyl group was provided by ^{13}C labelling experiments [220].



(37)

38 R = Me
52 R = Et

60a R = Me
60b R = Et

4.4. Insertion reactions with isonitriles

By analogy with CO, the migratory insertion of organic isonitriles into late transition metal–carbon bonds has been much investigated [173,174,223–227]. In

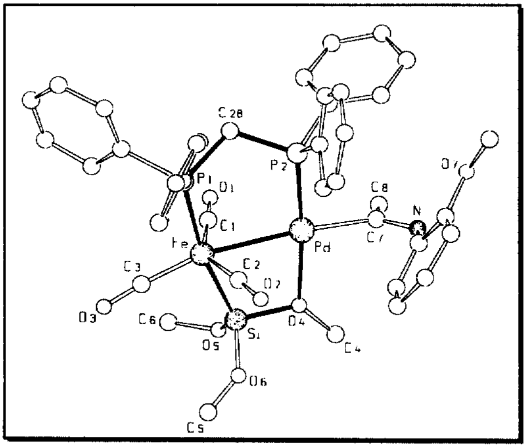
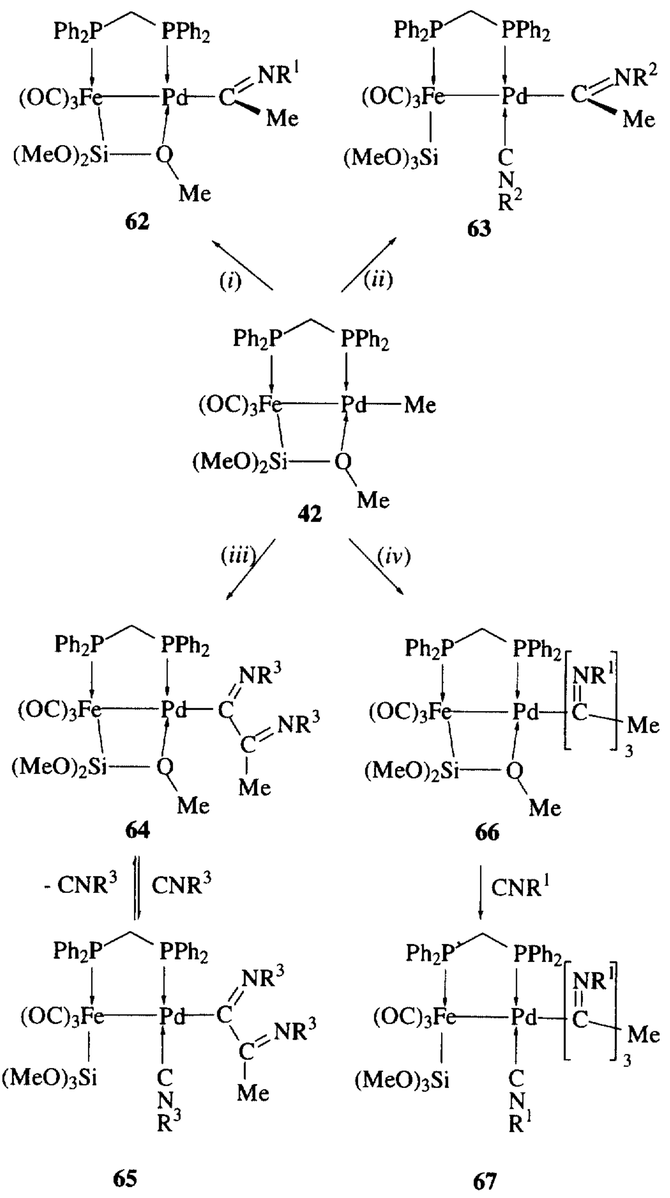


Fig. 3. View of the molecular structure of **62**. Selected distances (Å) and angles (°): Fe–Pd 2.668(3), Fe–Si 2.244(4), Pd–O(4) 2.178(8), Pd–C(7) 2.028(2); Pd–C(7)–N 129.8(9), C(7)–N–C(9) 122.5(11).



Scheme 3. Reactions in CH_2Cl_2, −10 to 25 °C. (i) 1 equiv. $C{\equiv}NR^1$ [$R^1{=}C_6H_4$(o-OMe)], (ii) 2 equiv. $C{\equiv}NR^2$ [R^2=t-Bu], (iii) 2 equiv. $C{\equiv}NR^3$ [$R^3{=}C_6H_3Me_2$-2,6], (iv) 3 equiv. $C{\equiv}NR^1$.

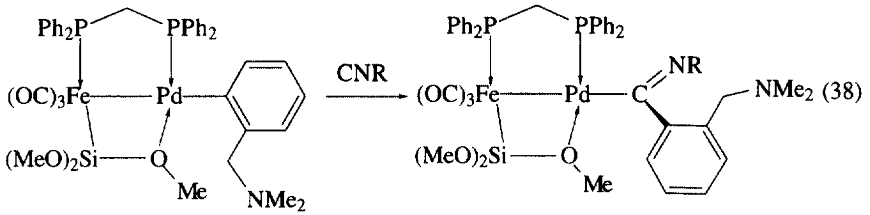
contrast to CO, $C{\equiv}NR$ molecules readily lead to successive multiple insertion and formation of oligomeric or polymeric compounds. Recent studies by Takahashi and coworkers have shown that a multiple insertion (living polymerization) of ca. 100

aromatic isonitrile units can be achieved using the alkyne-bridged heterobimetallic system [$Cl(Et_3P)_2Pt–C{\equiv}C–Pd(PEt_3)_2Cl$] [228,229]. The interest in polymeric isonitrile chains [poly(iminomethylenes)] stems in part from the physico-chemical properties of these polymers and their helix-like conformation, which allows their use i.a. as chiral material for chromatographic separations [230–232].

With our own bimetallic alkyl and aryl complexes, we were interested to examine the reactivity of organic isonitriles which could a priori result in site-selective CO substitution at the $Fe(CO)_3$ moiety, or insertion into the M–carbon bond affording iminoacyl derivatives analogous to the acyl complexes presented in the previous section. Thus, we reacted **42** with isonitrile ligands such as C≡N-(*o*-anisyl), C≡N-*t*-Bu or C≡N-(2,5-xylyl) [171]. Reaction with one equivalent of C≡N-(*o*-anisyl) yielded the imino acyl complex **62**, analogous to **51** (Scheme 3 and Fig. 3). The molecular structure of **62** shows that the insertion of C≡N-(*o*-anisyl) occurred with conservation of the four-membered Fe-Si-O->Pd unit. This spontaneous isomerization of the iminoacyl ligand from a position *trans* to phosphorus to *trans* to the Fe–Pd bond allows in principle successive reactions that can operate by opening of the dative O→Pd bond.

Reaction of **42** with two equivalents of C≡N-*t*-Bu selectively gave **63** whereas with the more reactive C≡N-(2,6-xylyl), bis-insertion occurred readily to give selectively **64** possessing a σ-bound 1,4-diaza-3-methylbutadiene-2-yl ligand. In the presence of excess C≡N-(2,6-xylyl), an equilibrium was established with **65** which contains a Pd-bound terminal isonitrile [$\nu(CN) = 2173\ cm^{-1}$] in place of the dative O→Pd bond. The reaction of **42** with two equivalents of C≡N-(*o*-anisyl) gave a mixture of mono-, di- and tri-insertion products. Selective tris-insertion leading to **66** was achieved when three equivalents of C≡N-(*o*-anisyl) were used. Further addition of isonitrile opens again the dative O→Pd interaction to give **67** [$\nu(CN) = 2186\ cm^{-1}$], en route to the next migratory insertion similar to that observed with mononuclear palladium complexes [223–229]. The sequence of reactions shown in Scheme 3 follows the general pattern depicted in Scheme 1.

Similar reactivity was observed for Fe–Pd–aryl complexes. Insertion of one equivalent of C≡N-(*o*-anisyl) or C≡N-(2,6-xylyl) [reaction (38)] into the Pd–C_{sp2} bond of complex **32** afforded the iminoacyl complexes **68** [153,154]. In both **32** and **68**, the SiO→Pd interaction is preferred over coordination of the dimethylamino group which would have led to a five- or six-membered chelate ring, respectively.

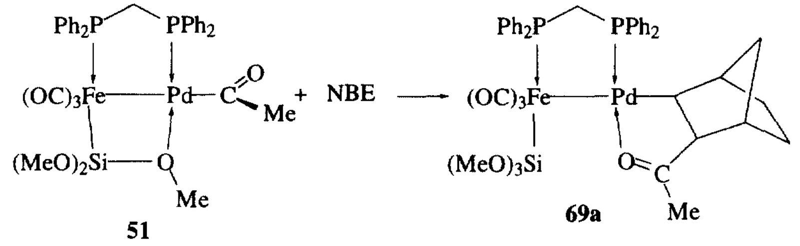


32 **68** (38)

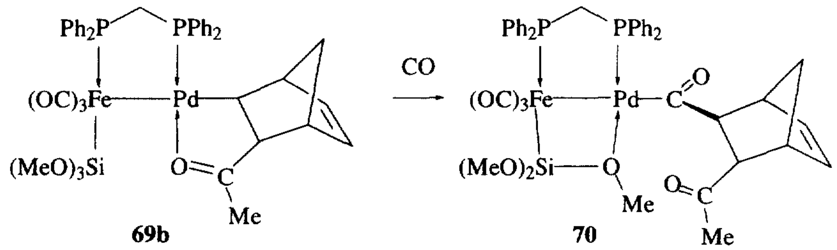
R = $C_6H_4(o\text{-}OMe)$, $C_6H_3Me_2\text{-}2,6$

4.5. *Migratory insertion reactions of CO and olefins*

Olefin insertion into the Pd–acyl bond of **51** occurred quantitatively after 3 h in the presence of norbornene (NBE) to give **69a**. Its ^1H NMR spectroscopic data indicate that this product resulted from *cis* addition of Pd–C(O)Me across the *exo* face of norbornene [reaction (39)] [171]. The IR spectroscopic data confirm the expected coordination of the acyl group to palladium, resulting in a five-membered chelate rather than in an Fe-Si-O->Pd four-membered ring.

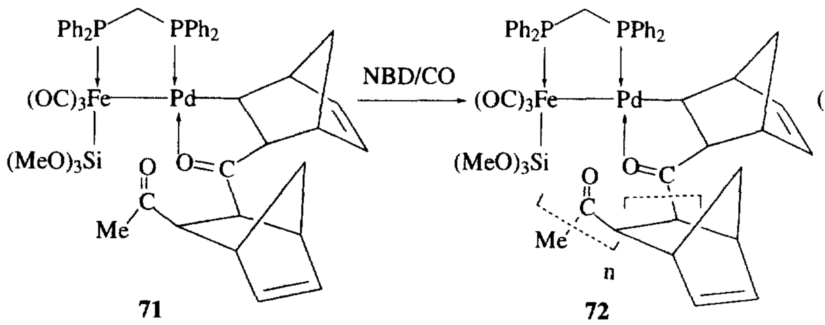


51 **69a** (39)



69b **70** (40)

A similar result was obtained with the more reactive norbornadiene (NBD) substrate. Further CO insertion into the Pd–C bond of **69b** took place under a CO atmosphere and stable **70** was isolated and fully characterized [reaction (40)]. Renewed insertion of norbornadiene led to **71**. Since olefin insertion into the Pd–acyl bond is thermodynamically preferred over CO insertion, whereas CO insertion into the Pd–alkyl bond is kinetically favoured over olefin insertion, a perfect alternation results in the insertion sequence and leads to polyketone chain growth. Product **72** contains an oligomeric chain with alternating CO and NBE units, but its exact length is not yet known [reaction (41)].



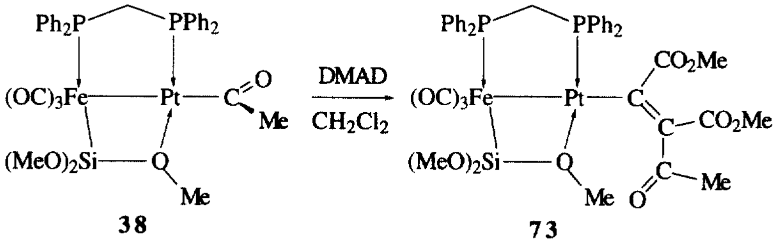
71 **72** (41)

The products with $n=2$, 3 have been characterized by IR and ^1H and ^{13}C NMR spectroscopic methods. Note that mononuclear complexes related to **72** with $n=$ 0–3 have recently been characterized [184,185,210–212,214]. No olefin insertion was observed in the case of the Fe–Pt–acyl complex **38** (ethylene, NBD, CH_2Cl_2, 20 °C).

The mechanism of all these insertion reactions follows a sequence which contains the elementary steps involved in CO migratory insertion (Scheme 1): opening of the labile SiO→Pd bond, coordination of the substrate, *cis* migration, isomerization and closing of the $\overline{\text{Fe-Si-O->Pd}}$ ring. Although five-coordinate intermediates have not been detected and need not be invoked in this mechanism, their involvement in the course of the displacement of the O→M bond cannot be ruled out.

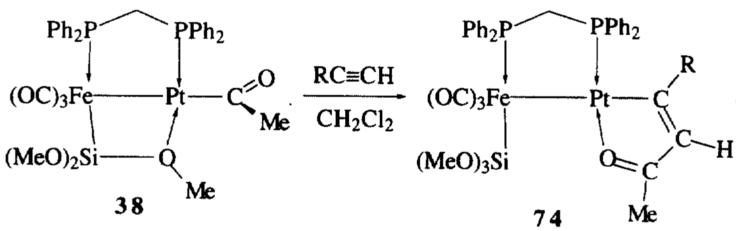
4.6. *Insertion reactions of alkynes*

Addition of MeO(O)C–C≡C–C(O)OMe (DMAD) to a solution of **38** led to another type of reactivity [reaction (42)]. In contrast to the situation encountered with the isonitrile ligands, the alkyne readily inserted into the Pt–acyl bond to afford the alkenyl complex **73**. The η^2-μ_2-Si–O bridge is maintained in this complex [158].



(42)

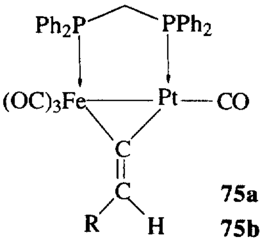
A more complex reaction occurred upon treatment of **38** with 1-alkynes such as phenylacetylene or *t*-butylacetylene. In a first step, insertion of the alkyne afforded the insertion products **74** in which the oxygen of the former acyl group is coordinated by a dative bond to platinum, forming a five-membered chelate, reminiscent of that encountered in the olefin-insertion products $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-dppm})Pd\{C_7H_{10}C(=O)Me)\}]$ **69a**.



(43)

Mononuclear alkenylketone complexes which display a ketonic–metal interaction resulting in a five-membered chelate have also been obtained after phenylacetylene insertion in molybdenum– and tungsten–acyl bonds and have been structurally characterized in the case of the insertion of PhC≡CH into the Ni–C(O)R bond of *trans*-$[NiCl\{C(O)CH_2SiMe_3\}(PMe_3)_2]$ [233–236].

In the presence of an excess of HC≡CR a transformation which is mechanistically not yet fully understood led to cleavage of the iron–silicon bond of **74** and formation of the μ-vinylidene complexes **75a,b**. ^{13}C NMR experiments using **38**, which has been previously ^{13}C labelled at the acyl carbon atom, demonstrated that the carbonyl ligand attached to the platinum centre of **75a,b** stems from the acyl unit [158].



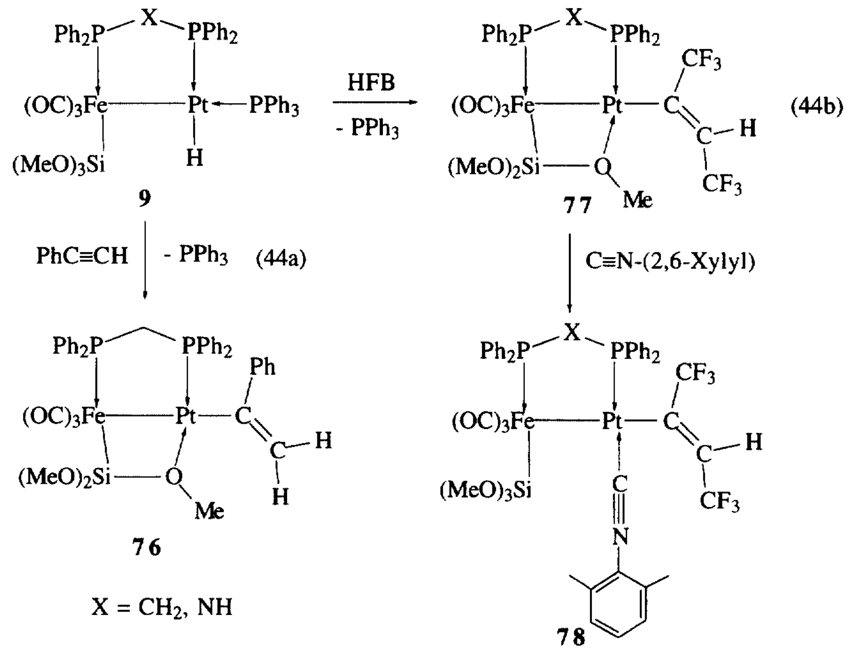
75a R = Ph
75b R = Bu^t

5. Alkyne insertion reactions into metal–hydride bonds

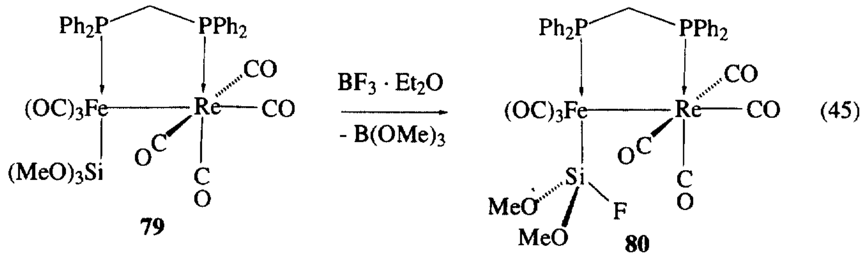
The (reversible) insertion of olefins into metal–hydride bonds represents a fundamental reaction in organometallic chemistry. Similarly, the insertion of alkynes RC≡CR into L_nM–H bonds offers a route to metal–carbon bonds and leads in general to vinyl complexes of the type L_nM–C(R)=C(H)R [237–243]. Cyclic four-centre transition states have been discussed for this insertion reaction [244]. Reaction of the bimetallic silyl-substituted Fe–Pt–H complexes **9** already presented in reaction (12) with 1-alkynes led to regioselective alkyne insertion into the Pt–H bond with the C–R unit forming the α-carbon of **76** [reaction (44a)]. In addition, the platinum-bound PPh_3 ligand is displaced and a four-membered Fe-Si-O->Pt cycle is formed. In a similar manner, insertion of hexafluorobutyne (HFB) afforded the vinyl complex **77** [reaction (44b)]. The *trans* configuration of the CF_3 groups has been established by a recent X-ray diffraction study performed on the isonitrile adduct **78**.

6. Fluorination of the $Si(OMe)_3$ group

Since we were interested in extending the novel bonding mode encountered in our bimetallic $Si(OR)_3$-substituted systems to other potentially ligating substituents of the silyl moiety, we probed the possibility of exchanging the alkoxy groups by fluorine atoms. The fluorination of silyl groups has already been successfully applied by other groups on mononuclear silyl complexes [245–247]. Reaction of the Fe–Re complex **79** with one equivalent of $BF_3 \cdot Et_2O$ led to replacement of only one methoxy

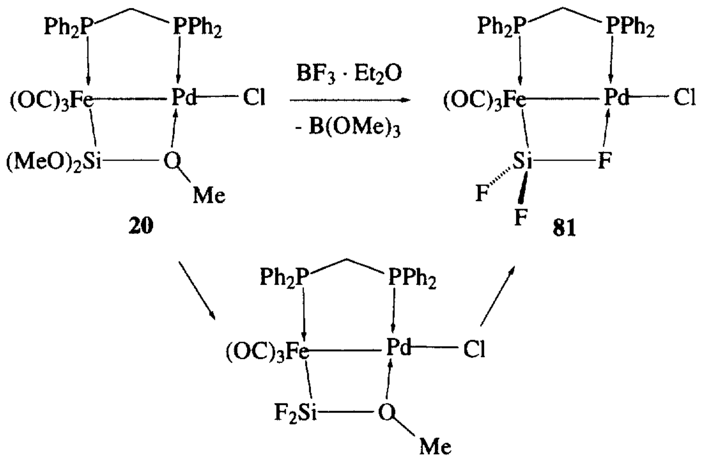


group of the $Si(OMe)_3$ ligand by fluorine and afforded the stable complex $[(OC)_3\{(MeO)_2FSi\}Fe(\mu\text{-dppm})Re(CO)_4]$ **80** [reaction (45)] [248].



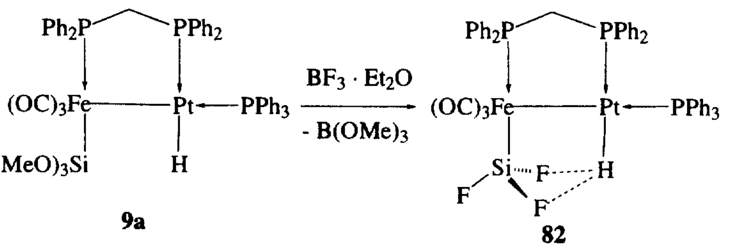
The fully fluorinated Fe–Pd complex **81** possessing a four-membered μ_2-η^2- Fe-Si-F->Pd unit could only be characterized by spectroscopic methods due to a competing rupture of the Fe–Si bond. During the course of the reaction, progressive substitution of the methoxy groups afforded partially fluorinated intermediates [reaction (46)] [249].

A stable SiF_3 derivative was, however, isolated upon fluorination of **9a**. A single crystal diffraction study performed on this bimetallic hydride complex **82** revealed a weak intramolecular interaction between the hydride ligand and two F atoms of the SiF_3 ligand (bifurcated hydrogen bond) [H···F 2.39(7) and 2.50(6) Å]. NMR



(46)

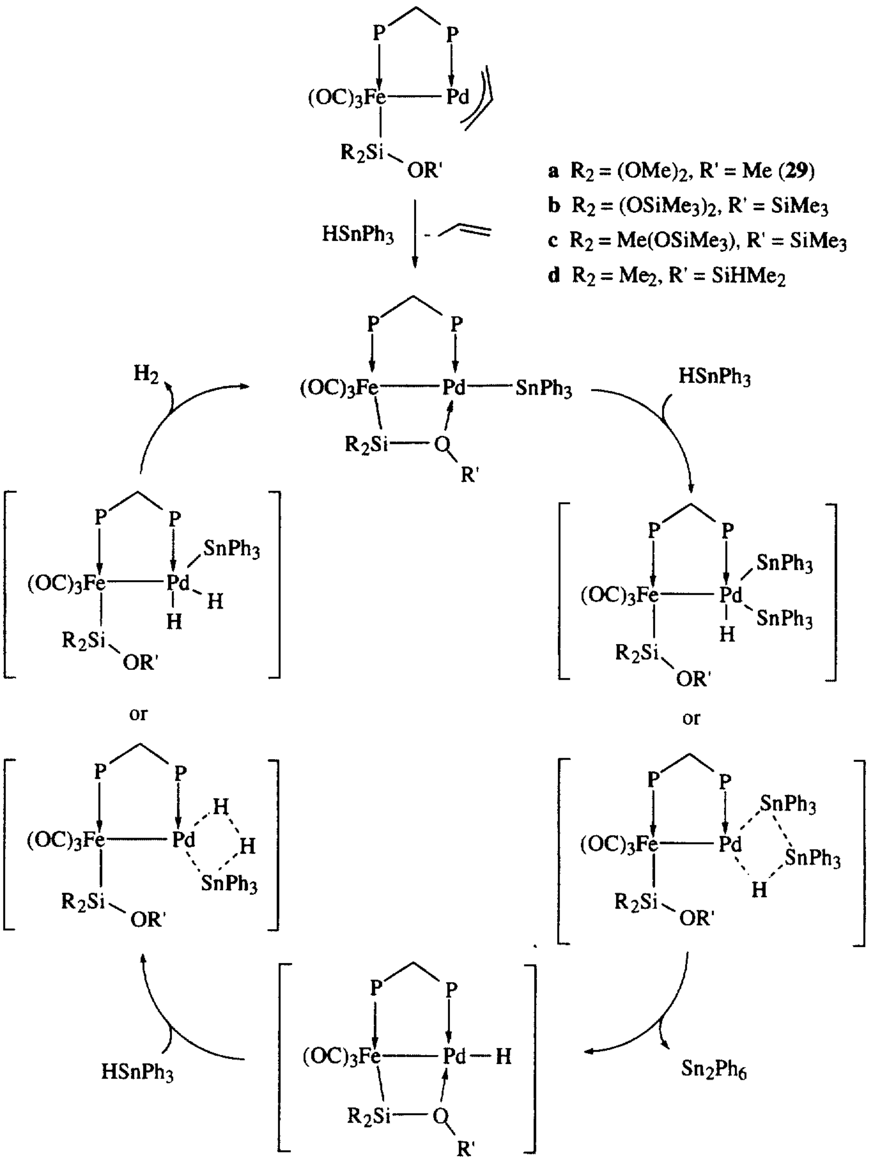
studies indicated that even in solution an interaction between the hydride and the SiF_3 ligand is retained [249].



(47)

7. Catalytic dehydrogenative coupling of stannanes

During our studies on the reactivity of the bimetallic allyl complex **29** (see Section 3.1), we investigated the reaction with $HSnPh_3$ which afforded the trinuclear complex **30** [reaction (21)]. Concomitant production of Sn_2Ph_6 was observed and this led us to examine in more detail the catalytic properties of these complexes. We found that the trinuclear Fe–Pd–Sn complex is involved in the catalysis. By varying the nature of the assembling ligand bridging the two metals, the substituents at silicon and the stannanes, we observed very efficient catalysis, with turnover numbers and turnover frequencies up to 2×10^5 and 3×10^7 h^{-1}, respectively, in the case of HSn^nBu_3 [130,131]. The cycle was suggested to involve either successive oxidative addition/reductive elimination steps with opening and closing of the alkoxysilyl bridge, or a σ-bond metathesis-type mechanism, as summarized in Scheme 4.

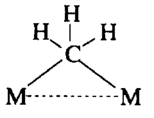


a $R_2 = (OMe)_2$, $R' = Me$ (**29**)
b $R_2 = (OSiMe_3)_2$, $R' = SiMe_3$
c $R_2 = Me(OSiMe_3)$, $R' = SiMe_3$
d $R_2 = Me_2$, $R' = SiHMe_2$

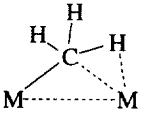
Scheme 4. Suggested mechanisms for the dehydrogenative coupling of stannanes catalyzed by bimetallic Fe–Pd complexes [131].

8. Intramolecular silicon migration from one metal to another

Intramolecular transfer reactions of alkyl groups from one metal centre to another in bimetallic systems have been studied by several groups. These reactions may involve the existence of intermediates or transition states with bridging alkyl groups of type **D** or **D′** (with an agostic C–H interaction). In several cases, the bridging 2e–3c bonding mode of the μ-alkyl ligand has been confirmed by X-ray diffraction [196,202,203,250–254].

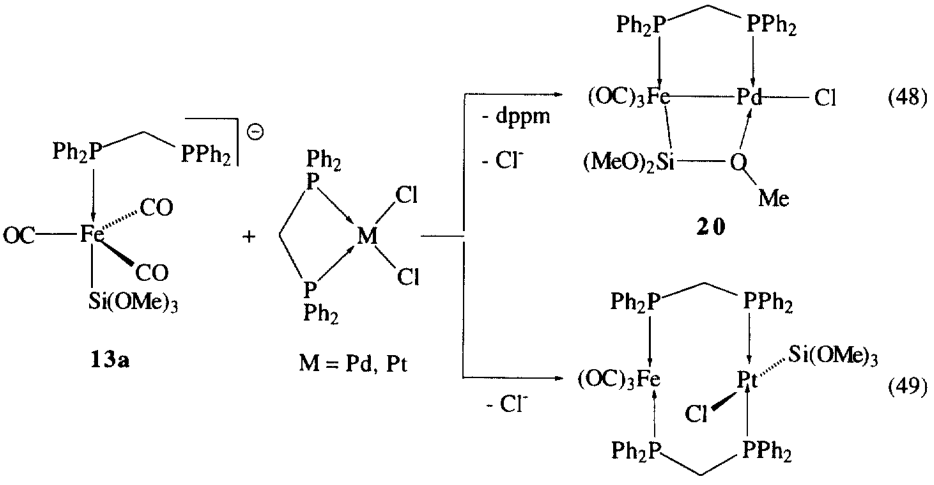


(D)



(D′)

We observed the first examples of transfer reactions of silyl groups in different bimetallic Fe–Pt systems, where a silyl group coordinated to iron migrated onto platinum. Upon reaction of the metalate **13a** with [$PdCl_2(\eta^2$-dppm)], the chelating dppm ligand was surprisingly liberated and the Fe–Pd complex **20** isolated as the sole product [reaction (48)]. Unexpectedly, when **13a** was reacted with [$PtCl_2(\eta^2$-dppm)] under similar reaction conditions, the rearranged product **83** possessing a platinum-bound $Si(OMe)_3$ ligand was isolated in high yields [reaction (49)] [255].



83

The structure suggested for **83** has been corroborated by multinuclear NMR experiments. For example, the ^{13}C NMR spectrum of **83** exhibits a singlet for the Pt-bound $Si(OMe)_3$ ligand at δ 49.6, which is flanked by platinum satellites due to a ^3J(Pt–C) coupling of 16 Hz. Further proof is provided by the ^{29}Si INEPT spectrum shown in Fig. 4, which displays a broadened singlet centred at δ −45.6, which is strongly coupled to the ^{195}Pt nucleus with a ^1J(Pt–Si) coupling of 1821 Hz.

When solutions of the phosphido-bridged iron–platinum complexes containing a three-electron μ_2-diaryl(or dialkyl)phosphido bridging ligand in place of the four-electron donor μ-dppm ligand were purged with CO, a completely different behaviour

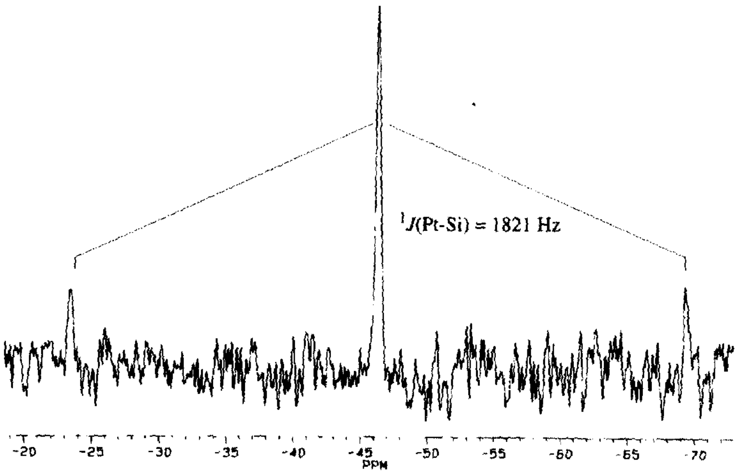
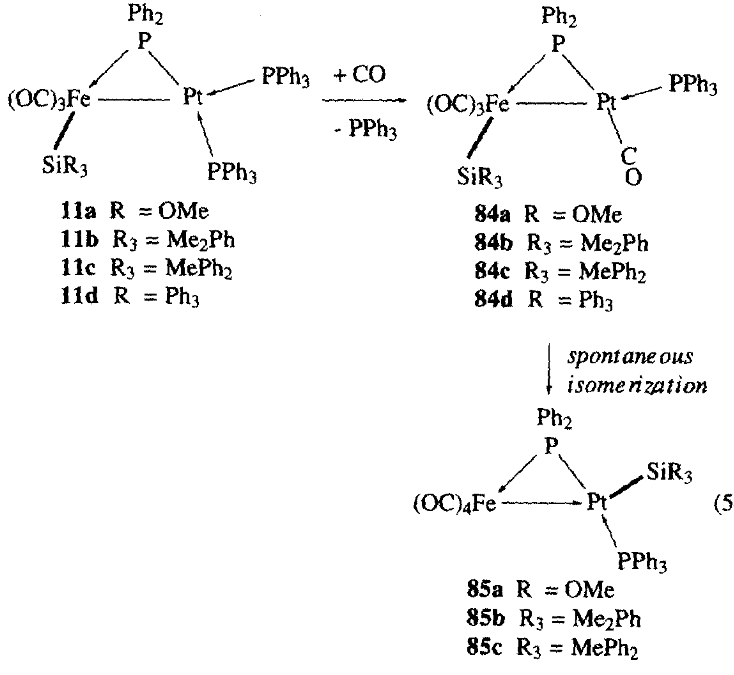


Fig. 4. ^{29}Si INEPT spectrum of complex **83** in $CDCl_3$ at room temperature.

of the silyl ligand was observed. When CO was bubbled through a solution of complexes **11**, selective substitution of the PPh_3 ligand *trans* to the phosphido bridge occurred, leading to **84**. This was followed by an unexpected, quantitative rearrangement in solution to isomers **85** in which the Si atom is now bonded to Pt, whilst the Pt-bound CO ligand has migrated to the Fe centre [reaction (50)] [256].



11a R = OMe
11b R_3 = Me_2Ph
11c R_3 = $MePh_2$
11d R = Ph_3

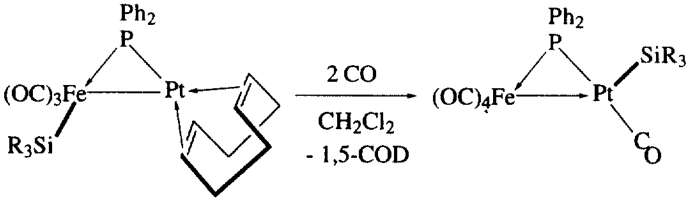
84a R = OMe
84b R_3 = Me_2Ph
84c R_3 = $MePh_2$
84d R = Ph_3

85a R = OMe
85b R_3 = Me_2Ph
85c R_3 = $MePh_2$

(50)

The result of this dyotropic-type rearrangement was established by the X-ray structure analysis of **85a**. The rate of this unprecedented silyl shift appears to depend mainly upon the steric requirements of the SiR_3 group. In the case of the $Si(OMe)_3$ ligand, migration is completed within approximately 1 h, whereas for the $SiMe_2Ph$ group ca. 5 h are required and for the even bulkier $SiMePh_2$ group more than one day was needed, respectively. The $-SiPh_3$ derivative **84d**, which was also structurally characterized, did not rearrange [121].

However, carbonylation of the more reactive 1,5-COD complexes $[(OC)_3(R_3Si)\overline{Fe(\mu\text{-}PPh_2)Pt}(1,5\text{-}COD)]$ **12a,b** yielded $[(OC)_4\overline{Fe(\mu\text{-}PPh_2)Pt}(CO)(SiR_3)]$ **86a,b** within minutes, irrespective of the nature of the SiR_3 ligand: even $SiPh_3$ was now found to migrate from iron to platinum [reaction (51)]. Again, NMR spectroscopy proved very valuable in monitoring these reactions; in particular ^{29}Si NMR allowed the determination of $^1J(Si\text{–}Pt)$ couplings, e.g. 2117 Hz in complex **86a** ($\delta = -26.8$ vs. TMS) whereas a $^2J(Si\text{–}Pt)$ coupling of 49 Hz was found in **12a**.

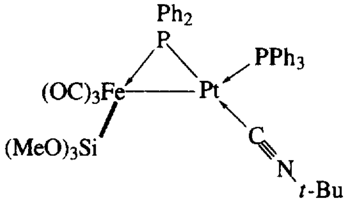


(51)

12a R = OMe
12b R = Ph

86a R = OMe
86b R = Ph

We also examined the possibility of inducing silyl migration in the phosphido-bridged complexes **11** by using isonitriles instead of CO, but found no evidence for it, irrespective of the nature of the SiR_3 group and of the stoichiometry, steric and electronic nature of the various isonitriles used. Instead, stereoselective phosphine substitution occurred leading to **87**. However, the enhanced reactivity of the 1,5-COD complexes **12** allowed the silyl transfer of an Fe-bound SiR_3 group to the adjacent platinum centre to be promoted under mild conditions: addition of two equivalents of t-BuNC afforded $[(OC)_3Fe(t\text{-}BuNC)\overline{Fe(\mu\text{-}PPh_2)Pt}(CN\text{-}t\text{-}Bu)(SiR_3)]$ (**88**) [257,258].



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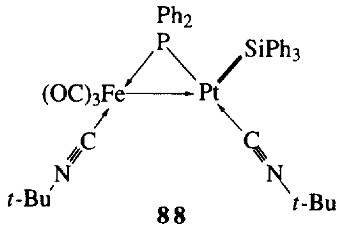
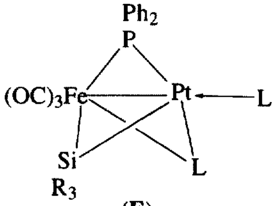


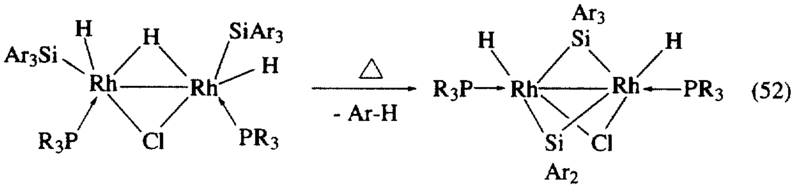
88

The study of the CO-induced silyl migration reaction in a 1:1 mixture of complexes **12a** and $[(OC)_4\overline{Fe(\mu\text{-}PCy_2)Pt}(SiPh_3)(CO)]$ revealed that only **86a** and $[(OC)_4\overline{Fe(\mu\text{-}PCy_2)Pt}(SiPh_3)(CO)]$ were formed. This indicates that the silyl transfer reaction occurs in an intramolecular manner [257,258]. One may speculate about an intermediate (or transition state) of type **E** possessing a bridging μ-SiR_3 group to account for this mutual ligand exchange.



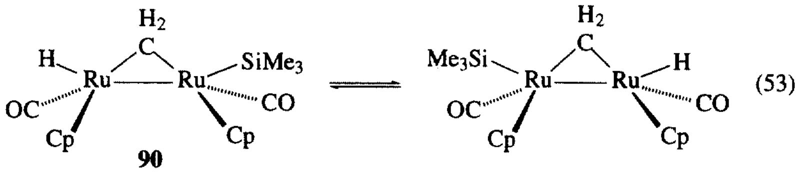
(E)

Unusual bridging bonding modes for a –SiR_3 group have already been structurally established in borane [259] and, more recently, in the polynuclear copper complex $[Li(THF)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$ [260] and in the dirhodium complex $[P(^iPr)_3Rh(H)(\mu\text{-}Cl)(\mu\text{-}SiAr_2)(\mu\text{-}SiAr_3)Rh(H)P(^iPr)_3]$ **89** prepared according to reaction (52) [261].



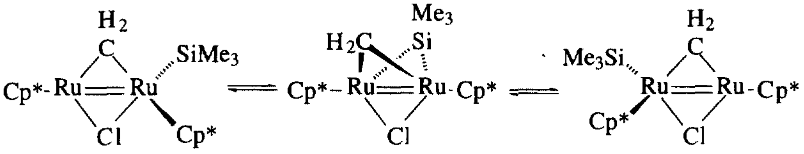
89a Ar = Ph
89b Ar = C_6H_4-*p*-F

These results nicely support our mechanistic considerations about the migration of silyl ligands from one metal to another. Recent studies by Girolami and Akita et al. on dinuclear $SiMe_3$-substituted Ru–Ru complexes have concluded that the silyl ligand could reversibly flip from one metal centre to another via a μ_2-SiR_3 intermediate [reaction (53)] [262–264].



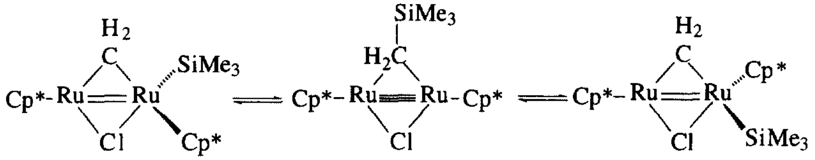
90

Girolami's diruthenium complex **91** exhibits a dynamic behaviour that was explained by reversible migration of the silyl group between the two Ru centres in the low temperature regime [reaction (54a)] and reversible migration to the bridging methylene group in the high-temperature dynamic process [reaction (54b)] [264].
Studies are in progress to determine the parameters which control our first examples of silicon migration reactions between two different metal centres.



91 **91**

(54a)



(54b)

9. New mono- and bimetallic silylene complexes

Since silylenes :SiXY have been recognized as transients (even the most stable one SiF_2 has a lifetime of only 150 s at 25 °C and 0.2 Torr), the search for such divalent and two-coordinated species amenable to isolation has shown no sign of waning [265]. Factors that may contribute to their stability have been analysed and it was suggested in 1986 that a NH_2 substituent would be very effective, a stabilization of 22.3 kcal/mol being calculated for $Si(NH_2)_2$ relative to SiH_2 [266]. The bis(amino)silylene $:\overline{\mathrm{SiN(^tBu)SiMe_2N}}\mathrm{(^tBu)}$ was detected in an argon matrix in 1992 [267], and the first thermally stable free silylene, bis(amino)silylene $:\overline{\mathrm{Si[N(^tBu)CH{=}CHN}}\mathrm{(^tBu)]}$, was prepared in 1994 with the help of additional aromatic stabilization [268]. The electronic structure of the latter has recently been discussed [269–271]. Electron diffraction was used to establish its structure in the vapour phase, whereas the structure of the crystalline bis(amino)silylene $:\overline{\mathrm{Si[\{N}}\mathrm{(CH_2{}^tBu)\}_2C_6H_4\text{-}1,2]}$ was established by X-ray diffraction and reported in 1995 [272].

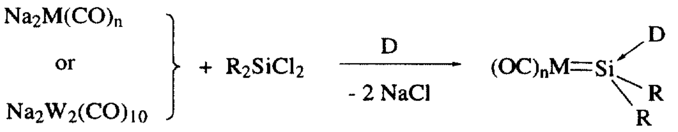
Let us recall now some of the specific features associated with the metal–silylene functionality. That the question "Does a silylene complex exist?" could be raised by theoreticians in 1983 indicates quite clearly that it was not that trivial to think of the heavier analogues of the well-known metal-carbenes as being stable entities [273]. The energy of the M=Si bond for the hypothetical complex $[(OC)_5Cr{=}Si(OH)H]$ was calculated to be only 29.6 kcal/mol, against 44.4 kcal/mol for the M=C of the corresponding hypothetical complex $[(OC)_5Cr{=}C(OH)H]$. Therefore, the search for stable silylene complexes became an exciting challenge. Whereas the first metal–silylene complexes were reported in 1977 by Schmid and Welz [274], the structural characterization by X-ray diffraction methods of stable mononuclear silylene complexes was only achieved in 1987–1988 [275–283]. This triggered an increasing interest in this chemistry, which had been somewhat neglected when compared to that of the corresponding carbene, germylene and stannylene complexes. Let us just mention here the recent first insertion of a silylene into M–N bonds (M = Ge, Sn, Pb) [284].

Furthermore, it is now widely accepted and often well established experimentally that silylene complexes play a key role as intermediates in a number of stoichiometric or catalytic reactions, often of considerable industrial interest [21,22,27,39,64,67,70–72,116,278,285–297]. The role of surface-bound silylenes in the direct process for the selective heterogeneously catalyzed synthesis of $SiMe_2Cl_2$ has been confirmed by trapping experiments with butadiene [298]. It is now clear that metal–silylene complexes display a rich and often unexpected chemistry, as nicely shown in recent review articles [285–289].

9.1. Synthesis of base-stabilized metal–silylene complexes

Before going into some new chemistry with mono- and bimetallic silylene complexes, it may also be appropriate to recall that the first silylene metal complexes to be isolated contained an additional donor ligand bound to the silicon atom. This remains typical for the vast majority of those known today. The following examples of synthetic reactions will serve to illustrate this point and provide a condensed overview of preparative routes to base-stabilized metal–silylene complexes:

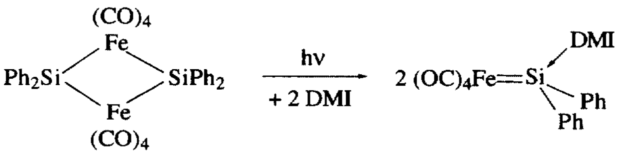
- reaction of carbonylmetalates with halogenosilanes, which provide a very efficient access to this class of compounds [reaction (55)] [276–282]:



(55)

M = Cr, n = 5; M = Fe, n = 4;
M = Ru, n = 4; M = W, n = 5
R = *eg*. Me, t-BuO, t-BuS, MesO, Cl
D = THF, $OP(NMe_2)_3$

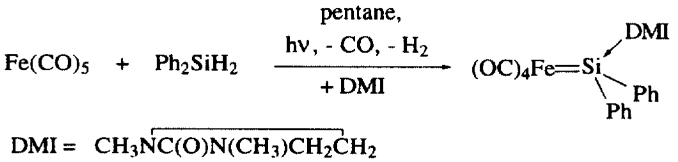
- cleavage of a silylene-bridged dinuclear complex in the presence of a Lewis base [reaction (56)] [299–302]:



(56)

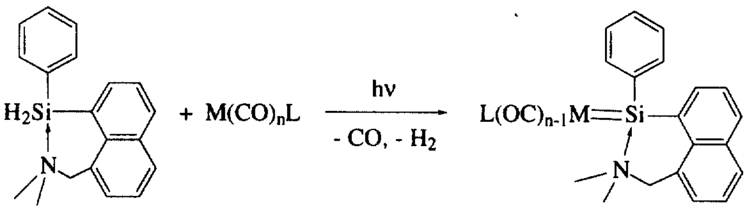
DMI = $CH_3NC(O)N(CH_3)CH_2CH_2$

- oxidative addition of a secondary silane to a zero-valent metal carbonyl complex [reaction (57)] [299–302]:



(57)

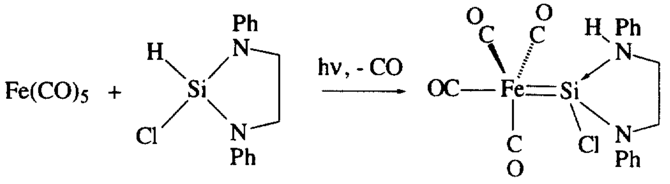
- oxidative addition to a zero-valent metal carbonyl complex of a secondary silane containing a donor function that is susceptible to lead to intramolecular stabilization [reaction (58)] [299–303]:



(58)

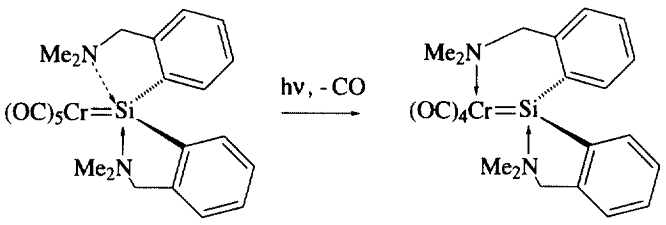
M = Fe, n = 4, L = CO
M = Mn, n = 3, L = MeCp

- ligand rearrangement in the coordination sphere of the silicon atom. This can occur via the in situ formation of the donor ligand, as shown in reaction (59):



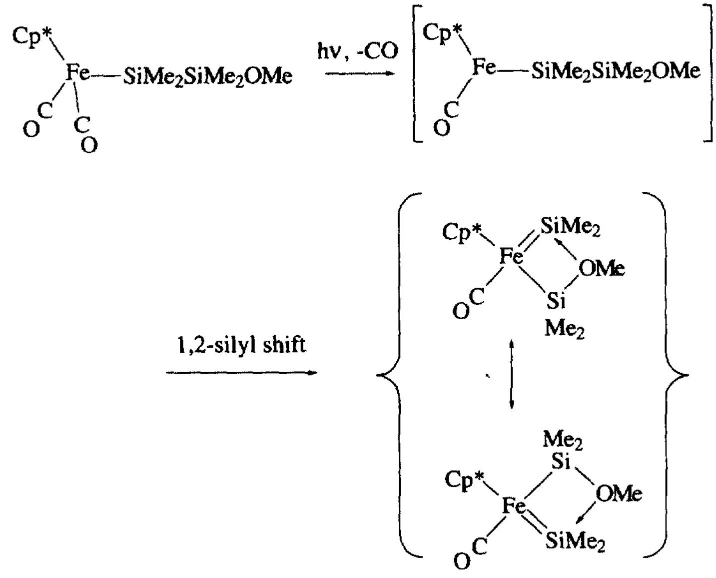
(59)

(this method was used by Schmid and Welz to prepare the first examples of metal–silylene complexes [274]; these labile complexes were characterized by analytical and spectroscopic methods) or by a photochemically-induced 1,2-shift of the donor [303], as in reaction (60):



(60)

- metal–disilanyl rearrangements involving 1,2-silyl shifts which have allowed Ogino and coworkers to prepare new alkoxysilyl(silylene), and later aminosilyl(silylene) transition metal complexes [reaction (61)] [148,149,283,304–310]:

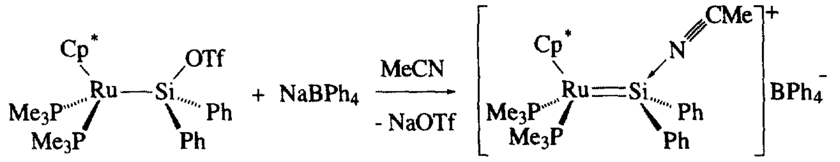


(61)

- CO substitution reaction in the presence of a base [reaction (62)] [311]:

$$AuCl(CO) + Si(\pi\text{-}C_5Me_5)_2 \underset{-CO}{\xrightarrow{\text{base}}} AuCl[Si(\sigma\text{-}C_5Me_5)_2 \cdot \text{base}] \qquad (62)$$

- substituent displacement at silicon [reaction (63)] [275,312]:



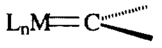
(63)

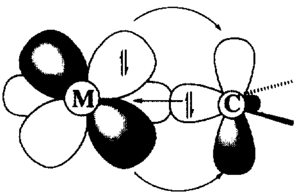
- trapping of a reactive silylene with metal complexes [reaction (64)] [313]:

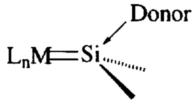
$$(TPP)Os + \overline{Me_2CMe_2CMe_2Si} \xrightarrow{THF} (TPP)Os{=}SiMe_2(THF) + Me_2C{=}CMe_2 \qquad (64)$$

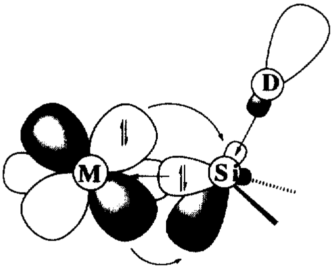
TPP = *meso*-tetra-*p*-tolylporphyrine

A comparison between the bonding of a carbene and a silylene fragment to a metal is appropriate to explain the propensity of metal–silylene complexes to exist in a donor-stabilized form. The description of the M=C double bond in metal carbenes involves dative σ/π interactions between singlet fragments. The π backbonding between the metal and the silylene ligand is much weaker than in the carbene case, making this ligand behave rather like a σ donor [314]. This allows a stabilizing interaction to develop with an additional Lewis base [315].



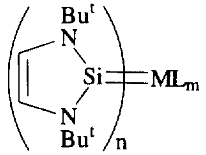




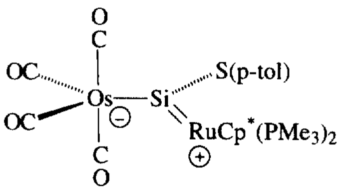


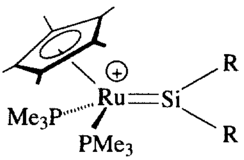
9.2. Synthesis of base-free metal–silylene complexes

It is only very recently that non-donor-stabilized (base-free) metal silylenes have been characterized [316–321]. These include the following examples:

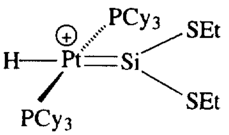


n = 2, M = Ni
n = 1, M = Cr, Fe



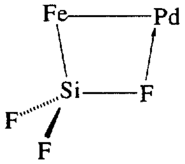


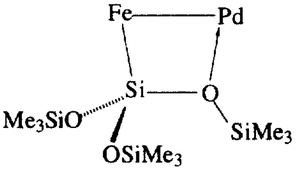
R = Me, Ph, SEt, S(p-Tol)

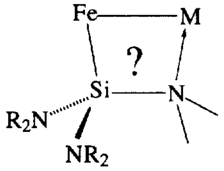


These observations generated considerable interest because of the paradigm associated with the "necessity" of donor stabilization. This will perhaps explain our surprise when we came across a base-free metal–silylene complex that furthermore behaves like an electron donor towards an electron deficient metal centre (see below)! Indeed, reactivity studies with metal–silylene complexes are still rather limited, although their Lewis acid character is generally well documented [310,312,316–319,322,323].

Our studies on the alkoxysilyl and siloxy–metal complexes led us to speculate whether other substituents at silicon could also lead to the occurrence of hemilabile interactions with the adjacent metal since only the $-SiF_3$ and the siloxyl ligands $-Si(OSiMe_3)_3$ have been found able to bridge between iron and palladium [217,218,249].

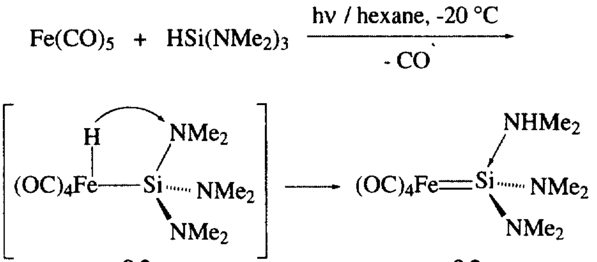






Nitrogen donors were particularly attractive since it also appeared that the reactivity of tris(amino)silanes towards transition metals had not yet been examined, although tris(amino)silyl complexes have been obtained indirectly [324]. The amino substituents would be expected to have a considerable influence on the properties of the metal–silicon bond.

Following the approach used by Schmid and Welz in reaction (59), we prepared the amine-stabilized bis(dimethylamino)silylene complex $[Fe(CO)_4\{Si(NMe_2)_2(NMe_2H)\}]$ (**93**) by oxidative addition of the Si–H bond of $HSi(NMe_2)_3$ to the photochemically generated $Fe(CO)_4$ fragment [325]. The suggested hydrido, tris(dimethylamino)silyl intermediate complex **92** was not observed, owing to more favourable migration of its acidic proton to the more basic nitrogen atom [reaction (65)].



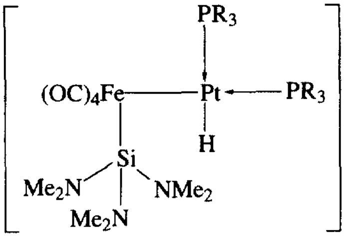
(65)

92
not observed

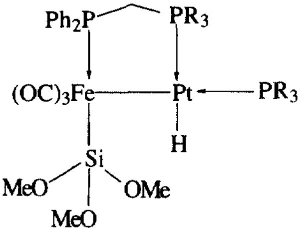
93

However, we reasoned that in case **92** would exist in equilibrium with **93** or have a sufficiently long lifetime to be trapped by a metal reagent, a reaction with $[Pt(C_2H_4)(PR_3)_2]$ (R = Ph, *p*-tolyl) could lead to insertion of the 14e $Pt(0)L_2$ fragment into the Fe–H bond and yield complex **94**. This hypothetical complex would be related to **9** that has previously been characterized [reaction (12)] [118].

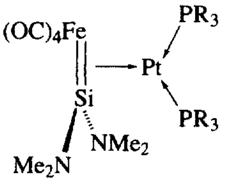
To our surprise, however, the product obtained from the reactions of **93** with $[Pt(C_2H_4)(PR_3)_2]$ (R = Ph, *p*-tolyl) had lost the amine ligand. We assigned structure **95a** to this new complex on the basis of analytical and spectroscopic data [325].



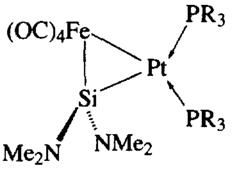
94
not observed



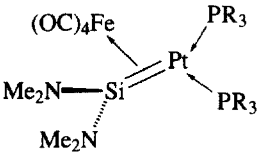
9



95a

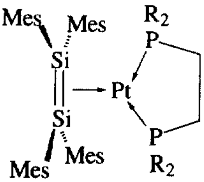


95b



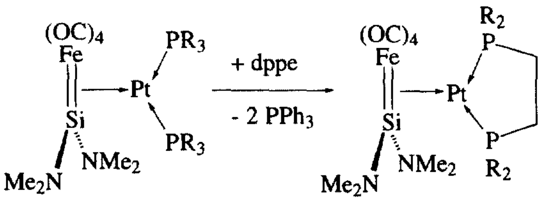
95c

Thus, the dimethylamine ligand of **93** and the Pt-bound ethylene ligands have been displaced, leading to new bimetallic silylene complexes. The resulting silylene complex is now stabilized by an electron-acceptor fragment (i.e. PtL_2) instead of an electron-donor group, as observed in most cases (see above). Viewed from the platinum centre, the silylene fragment behaves like the ethylene ligand of its precursor complex $[Pt(C_2H_4)(PR_3)_2]$. In the absence of a crystal structure determination, alternative bonding descriptions for this complex include **95b**, a dimetalla-silacyclopropane complex and **95c**, with a formal Pt=Si double bond donating electron density to the $Fe(CO)_4$ moiety. This illustrates nicely the isolobal analogy between these moieties and the disilene ligand, which has also been coordinated to a PtL_2 fragment as in **96** [326,327].



96

The stability of complex **95** towards external donor ligands is remarkable as addition of one equivalent of dppe leads exclusively to substitution of the PPh_3 ligands [reaction (66)].

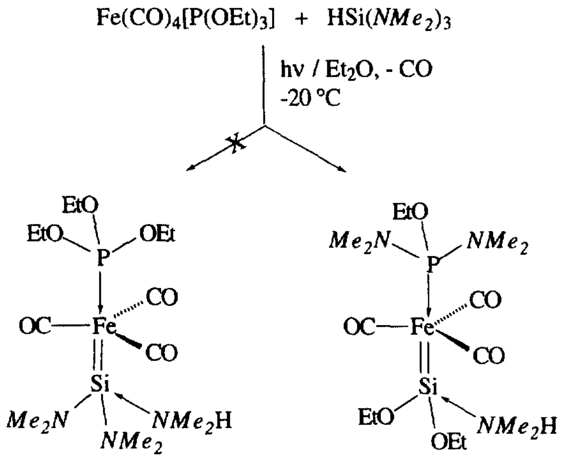


95a **97**

(66)

9.3. *Metal-mediated ligand redistribution reactions between silicon and phosphorus*

In order to evaluate the influence of an increased electron density at the iron centre on the bonding and reactivity of bimetallic silylene complexes such as **95**, we investigated the photochemically-induced oxidative addition reaction of $[Fe(CO)_4\{P(OEt)_3\}]$ with $HSi(NMe_2)_3$ [reaction (67)].

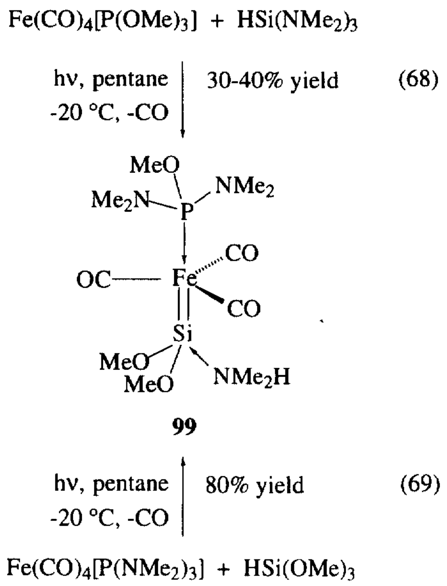


98

(67)

To our great surprise, this led to the amine-stabilized iron–silylene complex **98** in which two ethoxy groups on phosphorus have exchanged with two amino groups on silicon. We checked that this unprecedented rearrangement was metal-promoted [325]. We observed a similar reaction with $[Fe(CO)_4\{P(OMe)_3\}]$ [reaction (68)]. Since **99** was only obtained in ca. 30–40% yield (based on $^{31}P\{^1H\}$ NMR of the reaction mixture), we attempted an alternative synthesis based on the reaction of $[Fe(CO)_4\{P(NMe_2)_3\}]$ with $HSi(OMe)_3$ [reaction (69)]. It also led to **99** but in ca. 80% yield [328]. These cross-experiments indicate that the subtle balance between the oxophilicity of the phosphorus and silicon centres may lead to highly selective substituent exchange reactions.

For the reaction between $[Fe(CO)_4\{P(OR)_3\}]$ and $HSi(NMe_2)_3$, we suggest the sequence of steps shown in Scheme 5 to account for these remarkable rearrangements.



(a) Oxidative addition of $HSi(NMe_2)_3$ to the fragment $Fe(CO)_3[P(OR)_3]$ generated photochemically from $[Fe(CO)_4\{P(OR)_3\}]$.

(b) Proton migration towards the more basic site in the molecule, i.e. a nitrogen atom from the amino substituents at silicon, leading to an amine-stabilized iron–silylene complex.

(c) Reversible decoordination of the dimethylamine ligand to form a base-free silylene complex.

(d) 1,3-Migration of the OMe group from phosphorus to silicon.

(e) Coordination of the dimethylamine ligand to the resulting phosphinidene ligand.

(f) Proton migration towards the more basic site of the molecule, i.e. a nitrogen atom of the amino substituents at silicon, leading again to an amine-stabilized iron–silylene complex.

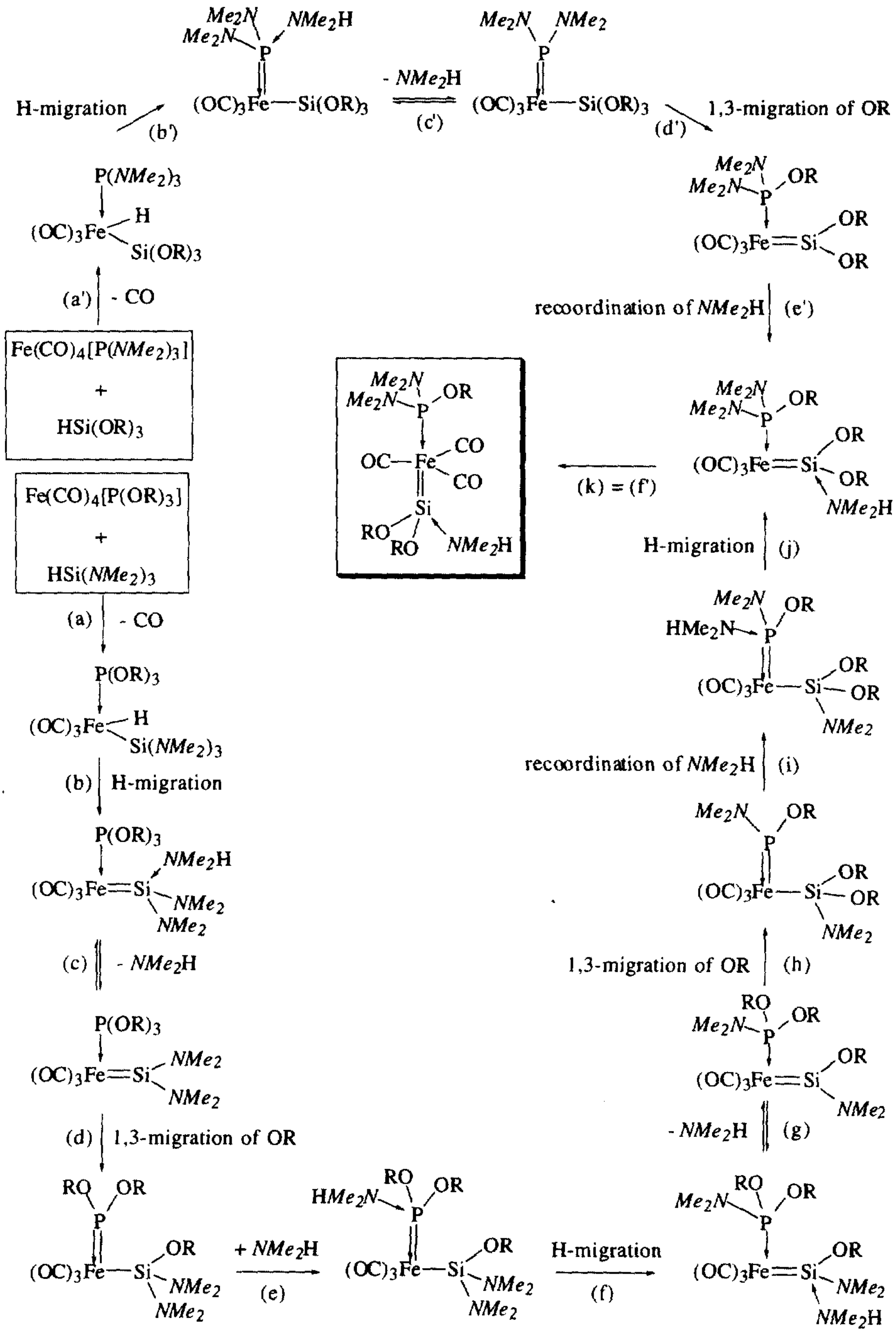
Then repetition of the same processes (g–j) until the thermodynamic product is formed after a *cis–trans* isomerization (k) of the phosphorus and silicon ligands.

The driving force for the migration reactions most probably resides in the formation of two Si–O bonds. It is known that the energy of a Si–N bond in an aminosilane is ca. 320 kJ/mol and thus ca. 100 kJ/mol lower than that of a Si–O bond [329].

The fact that complex **99** was also obtained from the reaction between $[Fe(CO)_4\{P(NMe_2)_3\}]$ and $HSi(OR)_3$ results from the competing oxophilicity of phosphorus and silicon and may be explained by a sequence of steps similar to those above.

(a′) Oxidative addition of $HSi(OR)_3$ to the fragment $Fe(CO)_3[P(NMe_2)_3]$ generated photochemically from $[Fe(CO)_4\{P(NMe_2)_3\}]$.

(b′) Proton migration to a basic nitrogen substituent at phosphorus.

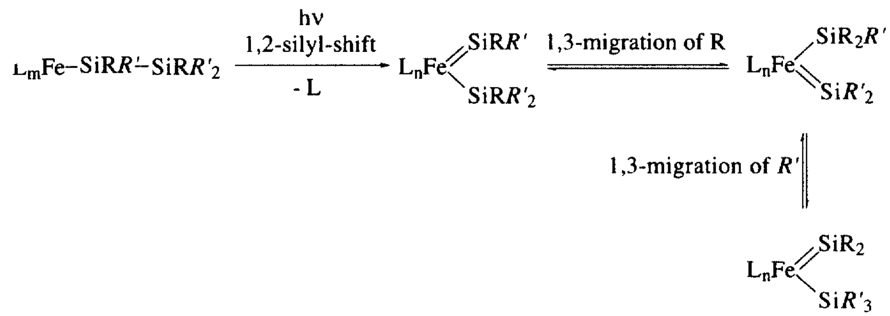


Scheme 5. Suggested mechanism for the iron-promoted redistribution of substituents between phosphorus and silicon.

(c′) Reversible decoordination of the resulting dimethylamine ligand.
(d′) 1,3-Migration of the OR group from silicon to the resulting phosphinidene ligand.
(e′) Coordination of the dimethylamine ligand to silicon.
(f′) *Cis–trans* isomerization of the product.

This leads to the desired product in fewer steps than in the previous case, since only one methoxy group has to migrate from silicon to phosphorus. Consequently, a higher product yield should be, and is indeed, observed in this case.

The 1,3-migrations suggested in steps (d), (h) and (d′) may be compared with those discussed for silyl(silylene) complexes which contain a $R_3Si{-}M{=}SiR_2$ linkage [27,307,308,330,331]. Related steps may explain redistribution reactions of alkyl groups between silyl and silylene ligands (Scheme 6) [332–336].



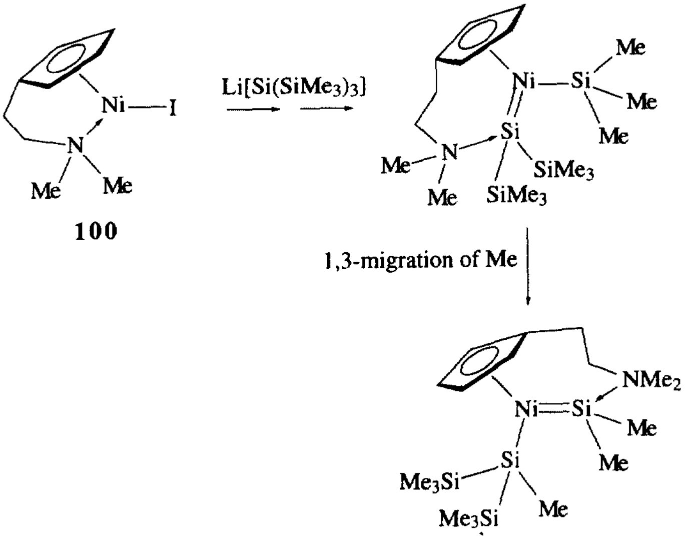
Scheme 6. Redistribution of alkyl groups between silyl and silylene ligands.

It is noteworthy that another reaction possibly involving a 1,3-migration has recently been reported for a nickel complex. Complex **101** would result from **100** by 1,3-migration of an alkyl group of $-SiMe_3$ to the silylene fragment $Si(SiMe_3)_2$ [reaction (70)] [337].

Related 1,3-migrations have also been suggested for complexes containing a $R_nE{-}M{=}E'R_m$ moiety with element combinations such as Ge and Ge [338,339], Si and Ge [338,340], Ge and Sn [341], or Sn and P [reaction (71)] [342].

9.4. Some recent silylene–stannylene chemistry

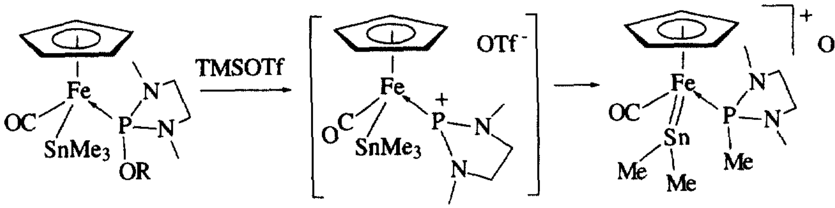
Various sites are potentially available for reactivity studies in the base-stabilized iron–silylene complexes **98** and **99** and, in collaboration with Veith, we became interested in combining some silylene and stannylene chemistry by using a class of cyclic stannylene reagents, such as $\overline{SnN(^tBu)SiMe_2N(^tBu)}$, which display a rich chemistry. They could lead with **98** or **99** to ligand displacement, insertion or addition reactions [160–170]. The reaction of **98** or **99** with one equivalent of $\overline{SnN(^tBu)SiMe_2N(^tBu)}$ in toluene at room temperature yielded quantitatively (^1H NMR) complexes for which analytical and spectroscopic data clearly showed the presence of the expected Fe-, Sn-, Si-, P- and N-containing fragments. Despite



100

101

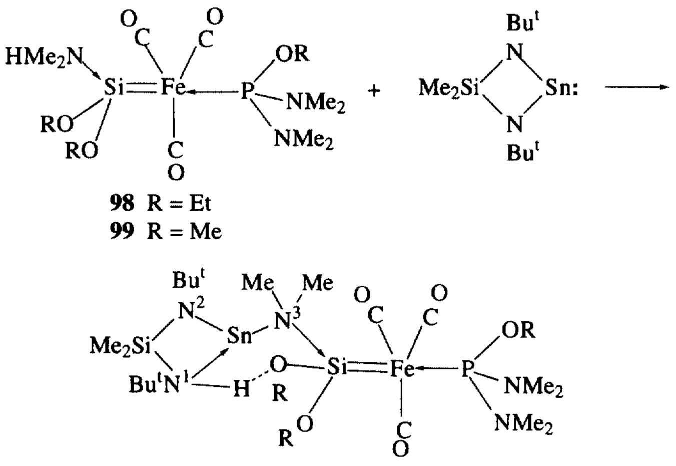
(70)



(71)

the use of IR and $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy, an X-ray diffraction study was necessary to fully ascertain the bonding in these molecules [reaction (72)] [343]. A $S_n \overset{\leftarrow}{=} N$ bond of the stannylene reagent [164] has formally inserted in the NH bond of the silylene unit $HMe_2N \rightarrow Si$. A dynamic behaviour in solution, with $\Delta G^{\ddagger} = 48.9$ kJ/mol, was evidenced for this complex which could result from pyramidal inversion at tin, or from breaking of the N(3)→Si bond followed by rotation of the NMe_2 group about the Sn–N(3) axis, inversion at N(3) and recoordination.

To account for this highly selective reaction, we suggest initial addition of the N–H bond to the polar $S_n \overset{\leftarrow}{=} N$ bond of **98**, **99**. Formal 1,2-addition of an X–H bond ($X = C_5H_5$, Cl, Br, I) to an amino stannylene reagent has been observed previously [164,169]. An alternative displacement of the amine by the stannylene ligand followed by insertion of the amine into the Si–Sn bond appears unlikely, also on steric grounds. It is also interesting to note that the stannylene reagent did not displace the silylene unit from the Fe centre to give an iron–stannylene complex, whereas Sn(IV) reagents can readily displace an iron–silyl bond [344–346]. Complexes **102** and **103** are new members of the family of amine-stabilized metal–silylene complexes. The reactive N–H bond of **98**, **99** is replaced by a less reactive



98 R = Et
99 R = Me

102 R = Et
103 R = Me

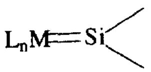
(72)

Sn–N–H...O system. Accordingly, a second equivalent of stannylene did not react with complexes **102** or **103**.

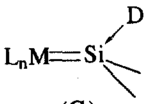
In conclusion, a large variety of silylene coordination complexes are now available. As discussed above, the vast majority are monometallic, with only very few of the "non-stabilized" type (**F**), in contrast to the neutral carbonyl complexes (**G** and **H**) [276–282,289], the Ru cationic complexes (**I**) and the intramolecularly-stabilized complexes (**J–L**) which may undergo dynamic behaviour when competition between two donor functions occurs as in **K**. A new class of heterobimetallic silylene complexes has now been discovered in which the silylene functionality behaves as an electron donor (**M**), resulting in a reverse behaviour ("umpolung") when compared to all the previous cases. Although considerable progress has been made in recent years towards the development of synthetic methods and a better understanding of the electronic structure, properties and reactivity of silylene complexes, much remains to be done in this very active and promising field of research.

10. The first bridging aminosilyl ligand

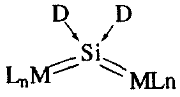
When we observed that deprotonation of the N–H bond of **99** with excess KH in THF restored the basicity at the metal centre and afforded the metalate complex $K[Fe(CO)_3\{P(OMe)(NMe_2)_2\}\{Si(OMe)_2(NMe_2)\}]$ (**104**), it became clear that a new, interesting reagent was available for the synthesis of bimetallic complexes [328]. Reaction of this metalate with $[CuCl(PPh_3)]_4$ at low temperature in a 1:1 Fe/Cu stoichiometry yielded $[(OC)_3\{(Me_2N)_2(MeO)P\}\overline{Fe\{\mu\text{-}Si(OMe)_2(\underline{NMe_2)\}}Cu}(PPh_3)]$ **105** without any further rearrangement of the ligands [reaction (73)]. Complex **105** was characterized by X-ray diffraction [Fe–Cu = 2.530(2) Å, Si–N =



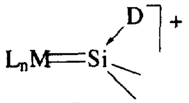
(F)



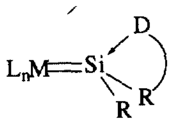
(G)



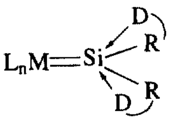
(H)



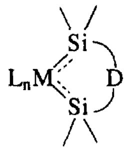
(I)



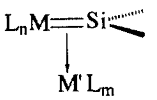
(J)



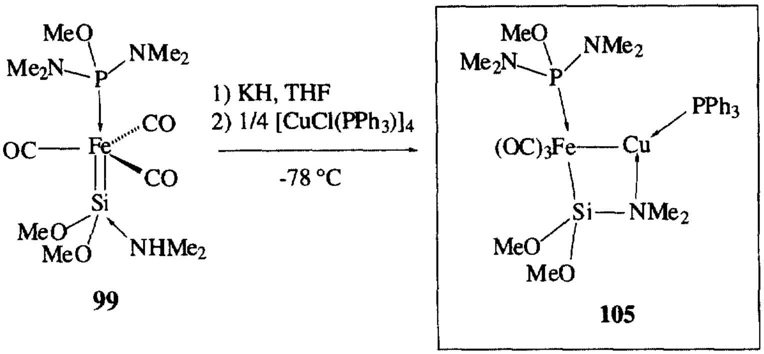
(K)



(L)



(M)



99

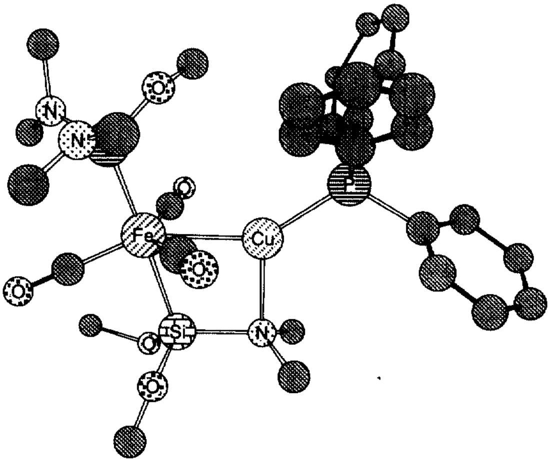
105

(73)

1.793(4) Å, N–Cu = 2.15 1(4) Å]. It provides the first example of a bridging aminosilyl ligand and this significantly extends the scope of the studies performed with tris(alkoxysilyl) ligands. That the amino group on silicon rather than either of the alkoxy groups binds to the copper atom may be explained by its higher basicity.

11. Conclusions and perspectives

We have seen that bimetallic complexes containing silyl ligands may be tailored to display unique structures and reactivity patterns that are directly related to a subtle interplay between the metals and the ligands. Unique features result from unusual μ_2-η^2-Si–O, or in only one case so far, μ_2-η^2-Si–N bonding interactions between the silicon-containing ligand and the bimetallic core. The hemilabile behaviour of the bridging $-Si(OR)_3$ ligand in Fe–Pd and Fe–Pt alkyl complexes allowed controlled insertion reactions of organic isonitriles, alkynes and CO/olefins to be



performed under mild conditions into the preformed metal–carbon bond. As a result of silicon migration from Fe to the oxygen atom of an acyl ligand bound to an adjacent Pd or Pt centre, new bridging siloxycarbene complexes have been isolated. By altering the nature of the assembling ligand (μ-PR_2 vs. μ-dppm) but keeping the metals and the silyl ligand unchanged, we found a completely different chemistry and discovered the first example of intramolecular silyl migration from one metal to another. Finally, the use of aminosilyl ligands led to the synthesis of new silylene complexes, to unprecedented metal-mediated substituent exchange reactions between phosphorus and silicon involving silylene intermediates, and to the characterization of the first complex containing a bridging aminosilyl ligand. There is no doubt that the rich chemistry associated with the presence of silicon ligands in bi- or polymetallic complexes will lead to more exiting results.

Acknowledgements

We are very grateful to the students and coworkers cited in the references for their dedicated and enthusiastic contribution to this research and to Professor H. Ogino (Sendai, Japan) for discussions. We acknowledge support from the Centre National de la Recherche Scientifique (Associate Research Position for M.K.), the Ministère de la Recherche et de l'Enseignement Supérieur, the Deutsche Forschungsgemeinschaft (M.K.), the Ministère des Affaires Etrangères (Paris) and the Deutscher Akademischer AustauschDienst (Bonn) (PROCOPE), the Commission of the European Communities (CHRX-CT93-0277), the Fondation Nationale Alfred Kastler (Académie des Sciences) and Johnson Matthey plc for a generous loan of $PdCl_2$ and $PtCl_2$.

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