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Review

Group 10 transition-metal complexes with metal–silicon bonds derived from 1,2-disilylbenzenes and bis(2-silylphenyl)silane

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Contents

Abstract

This article provides an account of the group 10 transition-metal complexes with metal–silicon bonds formed by the reaction of hydrosilanes with group 10 transition-metal complexes, with particular emphasis on the unique chemistry of 1,2-disilylbenzene, 1-dimethylsilyl-2-silylbenzene and bis(2-silylphenyl)silane. These hydrosilanes provide sterically less congested bidentate and tridentate silyl ligands and make

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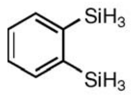
it possible to stabilize a number of unusual mono-, di- and trinuclear poly(silyl) group 10 metal complexes including those of high formal valence state.

Keywords: Hydrosilane; Silicon; Silyl; Silylene; Platinum; Palladium; Nickel

1. Introduction

The chemistry of transition-metal complexes with metal–silicon bonds has rapidly grown during the last two decades and the pace of progress is still increasing, associated mainly with catalysis involving silicon compounds toward organic synthesis and silicon-based materials [1]. As basic science, the chemistry of silyl–metals is intriguing in its own right, in view of comparison with organometallic complexes. There are various methods of formation of silyl–metal complexes, including: (1) reaction of anionic silyl species ($LiSiR_3$, etc.) with transition-metal halides, (2) reaction of anionic transition-metal species with halosilanes and (3) oxidative addition of Si–X (X = H, halogen, Si, C, etc.) bonds toward transition-metal precursors, etc. Among these methods, the reaction of hydrosilanes with transition-metal precursors has been most widely exploited [2]. A number of review articles on silyl–transition-metal complexes have already been published [2–11].

This article mainly deals with our recent results on the reaction of group 10 metal complexes with three hydrosilanes, 1,2-disilylbenzene **1**, 1-dimethylsilyl-2-silylbenzene **2** and bis(2-silylphenyl)silane **3**, unique precursors of bidentate and tridentate silyl ligands. These hydrosilanes display metal-dependent reactivity that reveals the formation of unusual complexes that cannot be produced with other hydrosilanes. An overview of the silyl group 10 metal complexes derived from hydrosilanes is also provided in Section 2.



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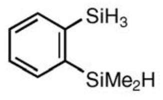

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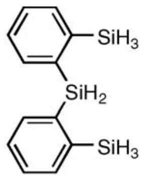

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Group 10 metal complexes are the most widely used catalysts for the transformation of silicon compounds such as hydrosilylation, bis-silylation and dehydrocoupling reactions, initiated by the discovery of Speier's catalyst for hydrosilylation reaction of alkenes in 1957 [1b,12]. The first isolated example of silyl-group 10 metal complex, *trans*-$Pt(SiMe_3)Cl(PEt_3)_2$, was synthesized by the reaction of *cis*-$PtCl_2(PEt_3)_2$ with $Hg(SiMe_3)_2$ in 1966 by Glockling and Hooton [13], 10 years later than Wilkinson's report on the first silyl–transition-metal complex, $Fe(SiMe_3)Cp(CO)_2$, in 1956 [14]. The reaction of hydrosilanes with transition-metal complexes has been used for the synthesis of silyl–transition-metal species from the early stage of their history; the first silylnickel complex, $Ni(SiCl_3)Cp(CO)$, was synthesized by the reaction of $HSiCl_3$ with $[NiCp(CO)]_2$ in 1967 [15].

The number of hydrogens bound to the silicon atom significantly influences the reaction of hydrosilanes with group 10 metal complexes. The reaction of tertiary hydrosilanes ($HSiR_3$) is relatively simple and usually forms mono(silyl)metal(II) and/or bis(silyl)metal(II) complexes. On the other hand, primary (H_3SiR, R = alkyl, aryl, halogen, alkoxy, etc.) and secondary (H_2SiR_2) hydrosilanes often generate a more diverse range of products because primary and secondary hydrosilanes have more than one reactive Si–H bond and/or are less sterically hindered than tertiary hydrosilanes. During the last decade considerable progress has been achieved in the silyl group 10 metal chemistry of primary and secondary hydrosilanes, including hydrosilanes **1**–**3**.

In this article, the following abbreviations are used: dmpe, 1,2-bis(dimethylphosphino)ethane; depe, 1,2-bis(diethylphosphino)ethane; dcpe, 1,2-bis(dicyclohexylphosphino)ethane; dppe, 1,2-bis(diphenylphosphino)ethane; cod, 1,4-cyclooctadiene; Cy, cyclohexyl.

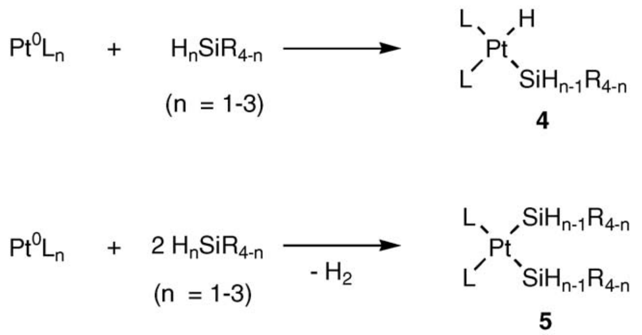
2. Reaction of hydrosilanes with group 10 transition-metal complexes—an overview

2.1. Reaction with platinum complexes

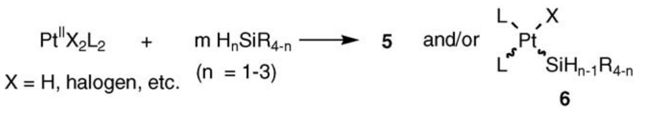
Among silyl–transition-metal complexes, those of platinum have been most extensively studied. This is not only because (silyl)platinum complexes generally have higher stability than the corresponding palladium and nickel complexes but also because platinum complexes are the most widely used catalysts for the hydrosilylation reaction since the discovery of the Speier's catalyst [12]. The number of group 10 transition-metal complexes with metal–silicon bonds registered in the Cambridge Structural Database reflects the research activity with each metal; 119, 34 and 18 complexes are found for platinum, palladium and nickel, respectively [16].

2.1.1. Mono(silyl)platinum(II) and bis(silyl)platinum(II) complexes

The reaction of tertiary hydrosilanes with platinum(0) complexes usually produces *cis*-(silyl)(hydrido)platinum(II) **4** and/or *cis*-bis(silyl)platinum(II) complexes **5**; the latter are formed by the reaction of the former with a second molecule of hydrosilane via an oxidative addition/reductive elimination sequence (Scheme 1) [17]. Steric bulkiness of ligands on the platinum complexes as well as that of substituents on the hydrosilanes affect the selectivity to **4** and **5**; bulkier ligands and substituents favor the formation of **4**. In the case of primary and secondary hydrosilanes, bis(silyl)platinum(II) complexes **5** are commonly formed [17a,18], while the formation of stable (silyl)(hydrido)platinum(II) complexes **4** is rather

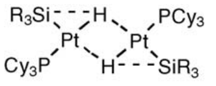


Scheme 1.



Scheme 2.

limited [17d,19] because sterically less hindered complexes **4** derived from primary and secondary hydrosilanes can easily react with a second molecule of hydrosilane to form complexes **5**. Platinum(II) complexes are also commonly used as precursors for the preparation of bis(silyl)platinum(II) complexes **5**, *trans*-**5** and mono(silyl)platinum(II) complexes **6** (Scheme 2) [20]. Formation of μ-hydrido-bridged dinuclear complexes **7** is reported in the reaction of monophosphine platinum(0) complex, $\mathrm{Pt(CH_2{=}CH_2)_2(PCy_3)}$ with $\mathrm{HSiR_3}$ [21].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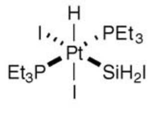
2.1.2. Mono(silyl)platinum(IV) complexes

During the formation of bis(silyl)platinum(II) complexes, (silyl)platinum(IV) intermediates are expected to be involved. Although platinum(IV) complexes, usually hexacoordinate, are abundantly found in platinum chemistry, (silyl)platinum(IV) species are generally unstable since (silyl)platinum(IV) species are often sterically more congested than other organoplatinum(IV) and four-coordinate square-planar platinum(II) species. Only in exceptional cases, where steric congestion is somehow mitigated and/or stabilization by chelating ligands is applied, such (silyl)platinum(IV) species can be spectroscopically detected as intermediates or can be isolated as stable complexes. For instance, Ebsworth and co-workers spectroscopically characterized mono(silyl)platinum(IV) complexes **8** and **9** formed, respectively, by the reaction of *trans*-$\mathrm{PtI_2(PEt_3)_2}$ with $\mathrm{H_3SiI}$ and by the reaction of *trans*-$\mathrm{PtH_2(PCy_3)_2}$ with $\mathrm{H_3SiCl}$ or $\mathrm{H_3SiSiH_3}$ at low temperature [22]. A similar mono(silyl)platinum(IV) complex **10** is also observable at low temperature in the reaction of *cis*-$\mathrm{PtH_2(dcpe)}$ with $\mathrm{H_2MeSiSiMeH_2}$ [23]. A thermally- and air-stable mono(silyl)platinum(IV) complex **11** can be synthesized by the reaction of $\mathrm{Pt^{IV}Tp'Me_2H}$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with $\mathrm{HSiEt_3}$ and its structure was confirmed by X-ray diffraction [24]. Protonation of **11** with $\mathrm{[H(OEt_2)][BAr_4]}$ (Ar = 3,5-$\mathrm{(CF_3)_2C_6H_3}$) affords a cationic five-coordinate (silyl)platinum(IV) complex **12a** [25]. Complexes **12a** and its analogues **12b** and **12c** can also be prepared by the reaction of a cationic platinum(II) complex **13** with hydrosilanes.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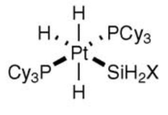
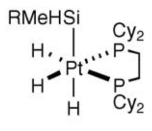
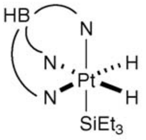

9 (X = Cl or $\mathrm{SiH_3}$)


10 (R = $\mathrm{SiMeH_2}$)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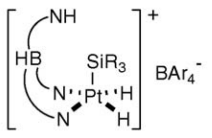
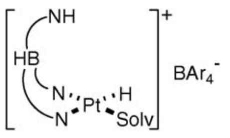

12a: $\mathrm{R_3 = Et_3}$
12b: $\mathrm{R_3 = Ph_3}$
12c: $\mathrm{R_3 = Ph_2H}$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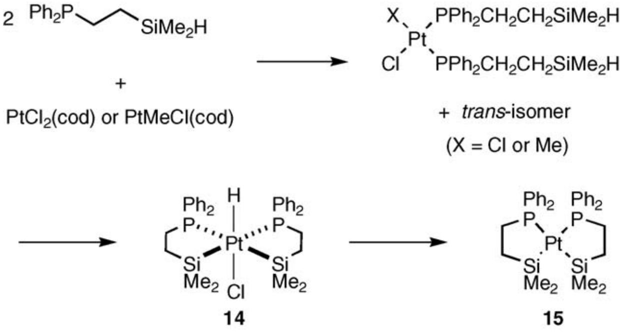
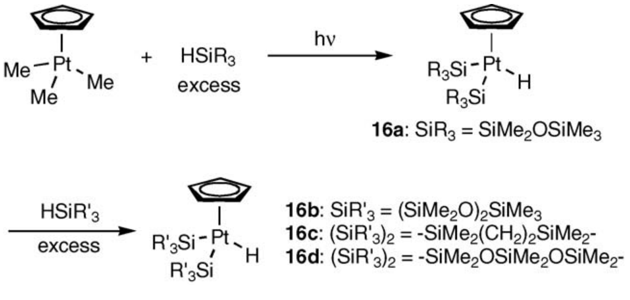
2.1.3. Bis(silyl)platinum(IV) complexes

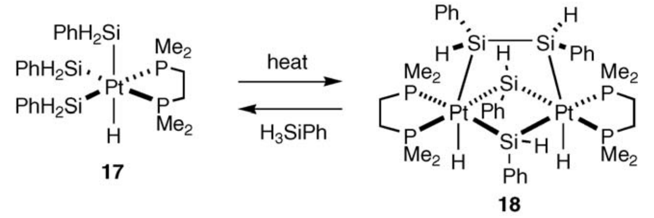
A bis(silyl)platinum(IV) complex, **14**, was observed as an intermediate in the reaction of $\mathrm{Ph_2PCH_2CH_2SiMe_2H}$ with $\mathrm{PtCl_2(cod)}$ or PtMeCl(cod) to form bis(silyl)platinum(II) complex **15** (Scheme 3) [26]. In this reaction, formation of platinum(IV) intermediate **14** was confirmed by NMR study, ^{31}P NMR spectroscopy of which shows a signal with a low ^1J(Pt–P) value (1084 Hz) typical for Pt(IV) species. A thermally stable and isolable bis(silyl)platinum(IV) complex **16a** can be prepared by the photolysis of $\mathrm{Pt^{IV}CpMe_3}$ in the presence of an excess of hydrosilane (Scheme 4) [27]. Complex **16a** is a useful precursor



Scheme 3.



Scheme 4.



Scheme 5.

for the synthesis of similar bis(silyl)platinum(IV) complexes **16b–d** by silane exchange reaction.

2.1.4. *Tris(silyl)platinum(IV) complexes*

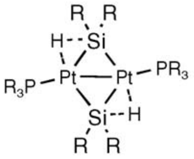
A tris(silyl)(hydrido)platinum(IV) complex **17** can be obtained as a thermally stable complex by the reaction of a bis(silyl)platinum(II) complex, $[Pt(SiH_2Ph)_2(dmpe)]_2(\mu\text{-}dmpe)$, with H_3SiPh [18b]. Thermolysis of complex **17** induces a Si–Si bond formation to form dinuclear complex **18** consisting of two platinum(IV) centers bridged by two μ-silylenes and one μ-disilanylene. Complex **18** goes back to **17** upon treatment with 4 equiv of H_3SiPh with extrusion of $H_2PhSiSiPhH_2$ (Scheme 5). It is interesting to note possible relevance of this interconversion to the catalytic dehydrocoupling reaction of hydrosilanes.

2.1.5. *Tetrakis(silyl)platinum(IV) complexes*

Tetrakis(silyl)platinum(IV) complexes are formed by the reaction of hydrosilanes **1** or **2** with platinum(0) complexes. This and related chemistry will be discussed in Sections 3 and 4.

2.1.6. *μ-Silylene-bridged multinuclear platinum complexes*

(Silyl)platinum(II) species derived from primary and secondary hydrosilanes can be easily transformed to multinuclear complexes with bridging silylene ligands that are not observed in the reaction of tertiary hydrosilanes. Treatment of $Pt(CH_2{=}CH_2)_2(PCy_3)$ with H_2SiR_2 forms μ-silylene-bridged dinuclear complexes **19** [28]. Note that the same procedure using tertiary hydrosilanes affords μ-hydrido-bridged dinuclear complex **7**, as already described [21]. Another type of dinuclear complexes **20** can be synthesized by the reaction of primary hydrosilanes with $PtCl_2(PR_3)_2$ in the presence of Na [29]. Complexes **19** consist of a $(Pt–Si)_2$ four-membered cycle with bridging hydrogen forming Pt···H···Si three center two electron bonds. In addition, the structural feature of complexes **19** is characterized by a short Pt···Pt diagonal distance. On the other hand, the $(Pt–Si)_2$ four-membered cycle of complexes **20** comprises two bis(phosphine)platinum units and has a short diagonal Si···Si distance. Recently several reports have described the detailed study of these types of complexes including variations of **19** such as complexes **21** and **22** [30]. The Si···Si distances determined by X-ray diffraction (2.55–2.73 Å) in complexes belonging to the category of **20** are almost the same as or shorter than the longest Si–Si single bond found in $^tBu_3Si–Si^tBu_3$ (2.70 Å) [31] and one may expect some bonding interaction between these silicon atoms. However, recent theoretical calculations on model complexes suggest such bonding interaction is weak in the platinum complexes [32].



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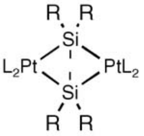

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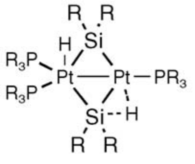

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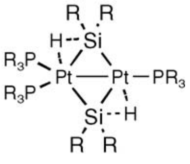

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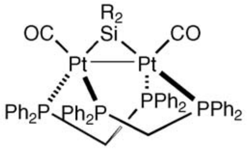
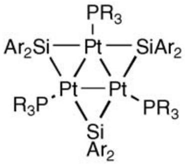
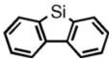
The reaction of secondary hydrosilanes with $Pt_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2$ (dppm = bis(diphenylphosphino)methane) gives mono-μ-silylene-bridged dinuclear complexes **23** [33]. Triangular trinuclear μ-silylene-bridged complexes **24a** and **24b** can be prepared by the thermolysis of a bis(silyl)platinum(II) complex, *cis*-$Pt(SiHPh_2)_2(PMe_3)_2$ [34], at 100 °C or by the reaction of silafluorene with $Pt(CH_2{=}CH_2)(PPh_3)_2$ at room temperature [30f,30i]. In the latter reaction, a (silyl)(hydrido)platinum(II) species was observed as an intermediate and a dinuclear complex of type **21** can be also isolated.



23 ($R_2 = Me_2, Et_2, Ph_2, MePh$)



24a: R = Me, Ar = Ph
24b: R = Ph, $SiAr_2$ =

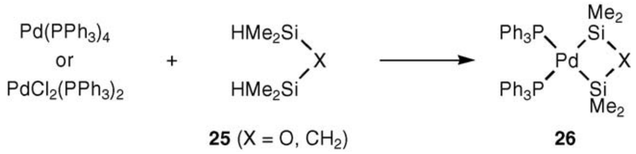


2.2. *Reaction with palladium complexes*

Palladium complexes are used as catalysts for a number of transformations of silicon compounds including hydrosilylation, bis-silylation, redistribution, silylation of organic halides, etc. [1c,1d,1f]. However, as their high catalytic activity in the diverse reactions implies, (silyl)palladium species are often too unstable to be isolated, which has hampered the detailed study on these species.

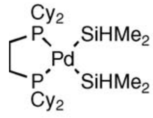
2.2.1. *Mono(silyl)palladium(II) and bis(silyl)palladium(II) complexes*

The complexes most frequently generated in the reaction of hydrosilanes with palladium(0) or palladium(II) complexes are bis(silyl)palladium(II) complexes [35–40]. These complexes can be stabilized by introduction of a chelating structure or halogen substitution to the silicon center to allow isolation. *cis*-$Pd(SiHPh_2)_2(PPh_2Me)_2$, formed by the reaction of $PdMe_2(PPh_2Me)_2$ with H_2SiPh_2, is not stable enough to be isolated [37]. Stable bis(silyl)palladium(II) complexes



Scheme 6.

26 can be synthesized by the reaction of Pd(0) or Pd(II) complexes with chelating hydrosilanes **25** (Scheme 6) [35]. $Pd(SiCl_3)_2(PPh_3)_2$, obtained by the reaction of $Pd(PPh_3)_4$ with $HSiCl_3$ or $Cl_3SiSiCl_3$, is an isolable complex, which exemplifies the stabilization by chlorine [36]. Secondary hydrosilanes also afford bis(silyl)palladium(II) complexes; complex **27** is the first structurally characterized (silyl)palladium complex by X-ray crystallography, which is stabilized by using a bulky chelating phosphine ligand [38a]. Complexes **28** [39] and **29** [40] are other examples of stable bis(silyl)palladium(II) complexes prepared by the reaction of hydrosilanes and palladium(II) or palladium(0) precursors.



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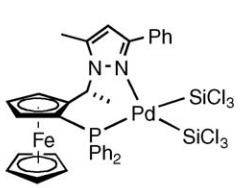

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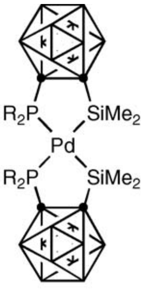

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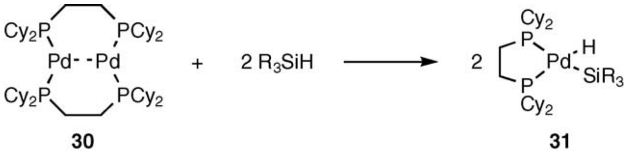
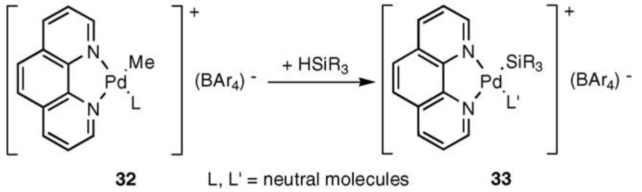
The formation of bis(silyl)palladium(II) complexes probably takes place via oxidative addition–reductive elimination sequences and intermediacy of (silyl)(hydrido)palladium(IV) species is expected as the formation of the platinum analogues suggests (vide supra). Although no (silyl)(hydrido)-palladium(IV) intermediate has been isolated or even detected spectroscopically, participation of such species may be supported by an analogous tetrakis(silyl)palladium(IV) complex being isolated (see Section 3.2).

Mononuclear (hydrido)(silyl)palladium(II) species appear to be readily generated upon treatment of a palladium(0) complex with a hydrosilane. In contrast to the platinum chemistry, in which such species are abundant, the first isolated example, complexes **31** stabilized by bulky dcpe ligand, was reported only very recently (Scheme 7) [41].

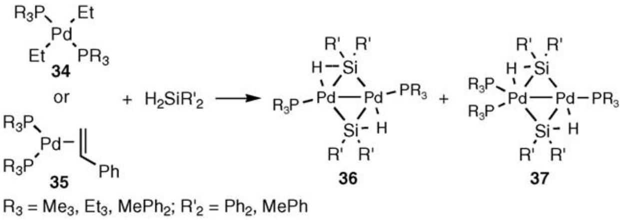
Cationic mono(silyl)palladium(II) complexes **33** can be prepared by the reaction of tertiary hydrosilanes with cationic methylpalladium(II) complexes **32** (Scheme 8) [42].



Scheme 7.



Scheme 8.

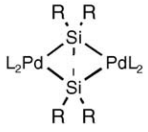


Scheme 9.

2.2.2. μ-Silylene-bridged dinuclear palladium complexes

As was seen with platinum complexes, palladium cases also form dinuclear complexes in the reaction of primary and secondary hydrosilanes. Thus, the reaction of *trans*-$Pd^{II}Et_2(PR_3)_2$ **34** or Pd^0(styrene)$(PR_3)_2$ **35** with secondary hydrosilanes affords dinuclear complexes **36** (Scheme 9). In the reaction of *trans*-$Pd^{II}Et_2(PMe_3)_2$ and H_2SiPh_2, unsymmetrical complex **37** is also produced in addition to **36** [43]. These products are palladium analogues of dinuclear complexes **19** and **22**. To date, however, complex **38**, analogous to platinum complex **20** with a short diagonal Si···Si distance has not been reported. In contrast to platinum complex **20**, palladium complex **38** is predicted to have significant bonding interaction between Si atoms according to the theoretical calculations [32].

Pd–Pt mixed-metal dinuclear complexes **39**–**41** can be synthesized by treatment of Pt-bound Si–H species, *cis*-$Pt(SiHPh_2)_2L_2$ (L_2 = dmpe, $(PEt_3)_2$), with Pd(0) complexes such as $Pd(PCy_2)_2$ or $Pd(PEt_3)_3$ [44].



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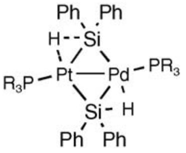

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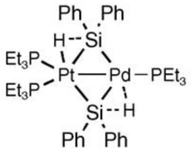

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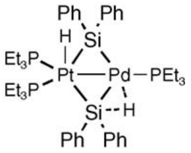

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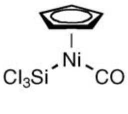
2.3. Reaction with nickel complexes

Nickel complexes catalyze the reactions of hydrosilanes such as hydrosilylation [1b,45], bis-silylation [46] as well as dehydrocoupling reactions [47]. However, only a very limited number of isolated (silyl)nickel complexes are known. In particular, stable complexes formed from primary and secondary hydrosilanes are reported only for hydrosilanes **1**–**3** (see Sections 3.3, 4.3 and 5.3). Mono(silyl)- and bis(silyl)nickel complexes are obtained by the reaction of tertiary hydrosilanes with nickel complexes [15,46b,48] and structurally characterized examples, **44**–**47**, are shown below.



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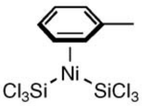

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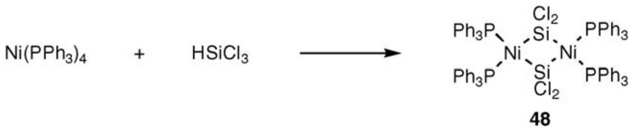
47

The reaction of $Ni(PPh_3)_4$ with Ph_nSiH_{4-n} ($n=1$–3) afforded highly colored complexes, which were presumed to be bis(silyl)nickel(II) complexes, $Ni(SiH_{3-n}Ph_n)_2(PPh_3)_2$ ($n=1$–3) [49]. However, their structural characterization could not be attained due to their pyrophoric nature as well as probable paramagnetism. When $HSiCl_3$ was used in place of Ph_nSiH_{4-n}, μ-$SiCl_2$-bridged dinuclear complex **48** was obtained although no spectroscopic characterization was provided (Scheme 10).



Scheme 10.

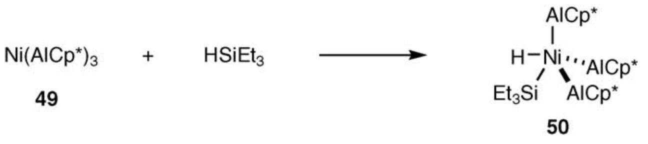
Recently, the first example of a (silyl)(hydrido)nickel(II) complex has been reported; the reaction of a nickel(0) complex **49**, which has an exotic ligand AlCp* (Cp* = η^5-pentamethylcyclopentadienyl), with $HSiEt_3$ affords complex **50** as a thermally stable complex (Scheme 11) [50].

3. Reaction of 1,2-$C_6H_4(SiH_3)_2$ with group 10 metal complexes

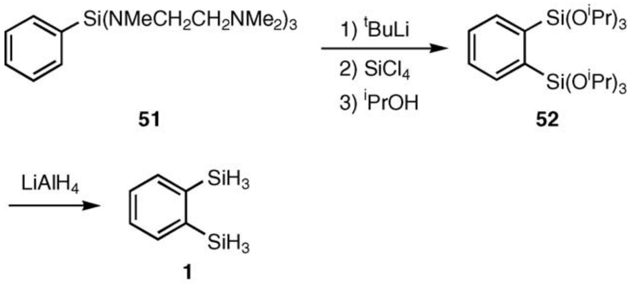
3.1. *Reaction with platinum complexes*

Disilylbenzene **1** is readily prepared by selective *ortho*-lithiation of (aminosilyl)benzene **51** developed by Tamao et al. [51] and subsequent reduction of **52** with $LiAlH_4$ (Scheme 12) [52]. Schmidbaur and co-workers have reported two alternative methods, one using the selective cleavage of the Si-(*p*-tolyl) bonds in 1,2-$C_6H_4[SiH_2(p\text{-tolyl})]_2$ with TfOH as a key reaction [53] and the other by the bis-silylation using $(EtO)_3SiOSi(OEt)_3$ and 1,2-dibromobenzene [54].

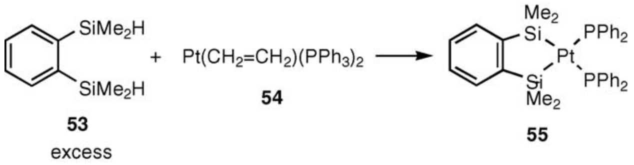
The reaction of 1,2-bis(dimethylsilyl)benzene **53** with $Pt(CH_2{=}CH_2)(PPh_3)_2$ **54** affords a bis(silyl)platinum(II) complex **55** exclusively (Scheme 13) [17c]. Complex **55** is thermally stable and no further reaction of **55** with hydrosilane **53** takes place. On the other hand, the reaction of the same platinum complex **54** with 2.2 equiv of 1,2-disilylbenzene **1** at room temperature exclusively produces complex **56**, the first example of tetrakis(silyl)platinum(IV) complex (Scheme 14) [52].



Scheme 11.

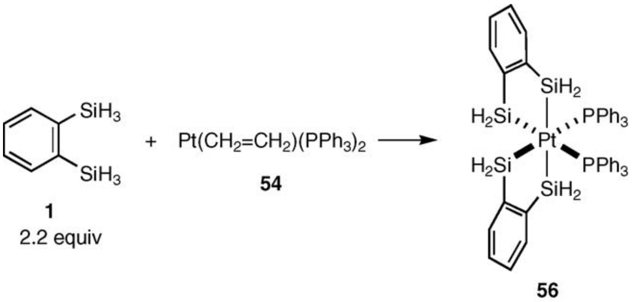


Scheme 12.

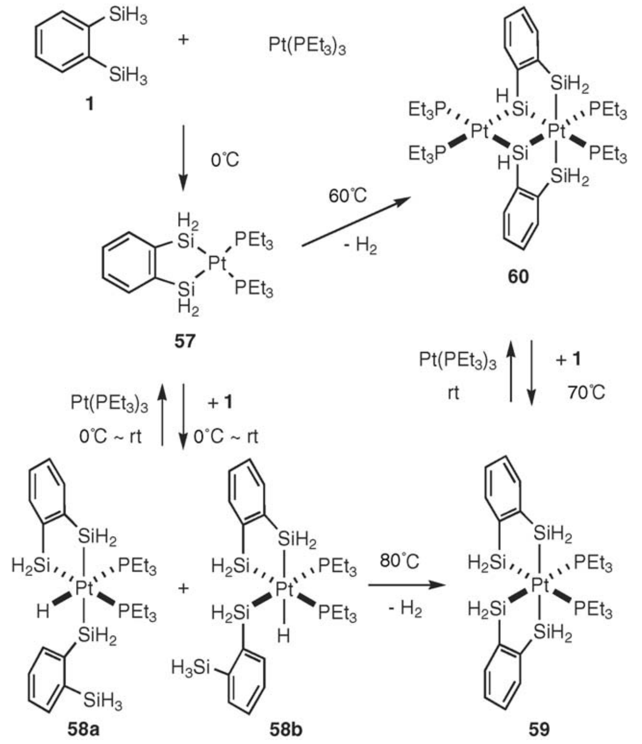


Scheme 13.

The detailed reaction pathways leading to tetrakis(silyl)-platinum species can be clearly traced by using $Pt(PEt_3)_3$ as summarized in Scheme 15. Hydrosilane **1** reacts with 1 equiv of $Pt(PEt_3)_3$ at 0 °C to give a bis(silyl)platinum(II) complex **57**. In contrast to complex **55**, sterically less hindered **57** can easily react with another molecule of **1** to form an isomeric mixture of tris(silyl)(hydrido)platinum(IV) complexes **58a** and **58b**, the core structures of which are similar to complex **17** formed from H_3SiPh, although formation of stereoisomers of **17** was not described [18b]. Different from complex **17**, thermolysis of complexes **58a** and **58b**, which have a free SiH_3 group in the close proximity of platinum, induces intramolecular dehydrocyclization to form a tetrakis(silyl)platinum(IV) complex **59**, a PEt_3 analogue of complex **56**. In the absence of another molecule of **1**, complex **57** dimerizes to form mixed-valent $Pt^{II}Pt^{IV}$ complex **60**. Its molecular structure determined by X ray diffraction (Fig. 1) reveals a short diagonal Si···Si distance (2.72 Å), suggesting that the complex is classified into the category of dinuclear complexes **20**. In ^{31}P NMR spec-



Scheme 14.



Scheme 15.

troscopy, complexes **56**, **58a**, **58b**, **59** and **60** display low ^1J(Pt–P) values (1078–1316 Hz), typical for (silyl)platinum(IV) species. In complex **58a**, ^1J(Pt–P) values clearly reflect stronger trans influence of silyl ligand than hydrido ligand; ^1J(Pt–P) value for the phosphorous *trans* to the silyl ligand is 1220 Hz while the value is 1624 Hz for the phosphorous *trans* to the hydrido ligand. ^{195}Pt NMR spectroscopy is also useful to diagnose the valence state of (silyl)platinum species; ^{195}Pt NMR chemical shifts for Pt(IV) nuclei of complexes **56**, **58a**, **58b**, **59** and **60** are observed in a high field region (between −6176 and −6855 ppm), while those for (silyl)platinum(II) species are reported at ca. −5500 ppm or lower. Similar high field values are also reported for bis(silyl)platinum(IV) complexes **16a–d** [27]. Summary of ^{195}Pt NMR data is given in Table 5.

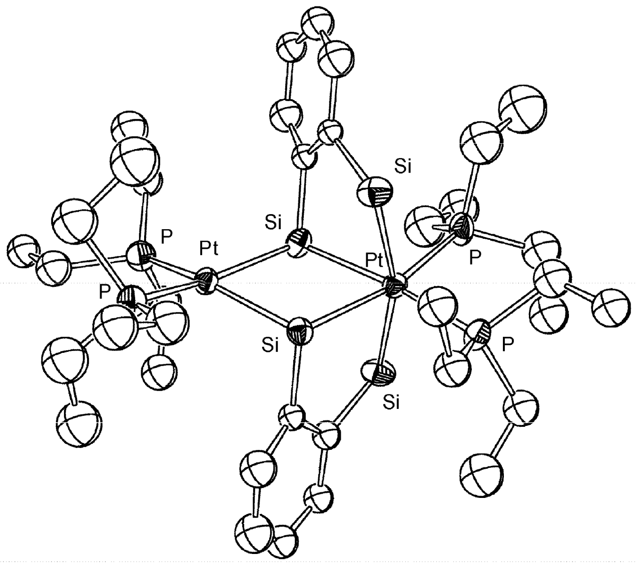
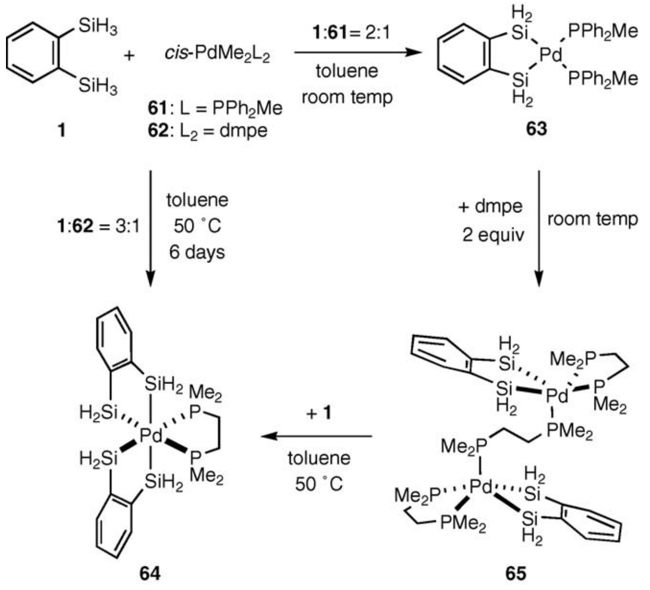


Fig. 1. Molecular structure of complex **60** (30% probability level). Hydrogen atoms are omitted for clarity.

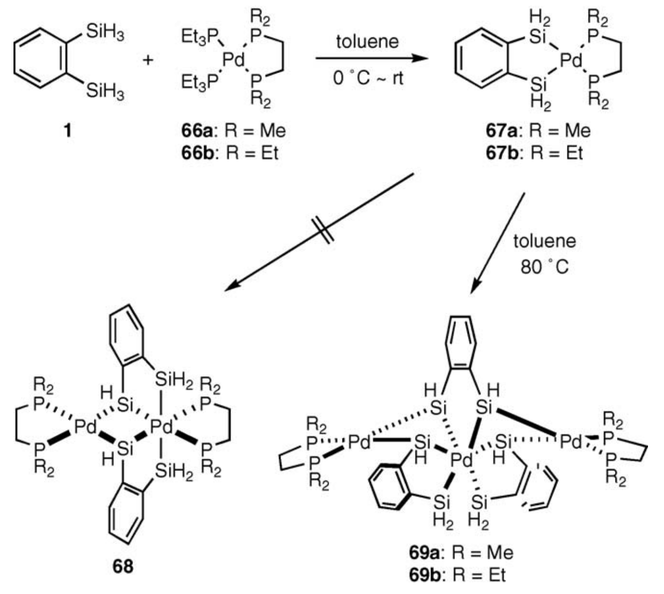
3.2. Reaction with palladium complexes

The reaction of hydrosilane **1** with dimethylpalladium(II) complex **61** in 2:1 ratio takes place at room temperature to give bis(silyl)palladium(II) complex **63**. As compared with *cis*-Pd$(SiHPh_2)_2(PPh_2Me)_2$ that has the same local configuration with non-chelating silyl ligands [37], complex **63** has a sufficiently high thermal stability to allow isolation and structural characterization by X-ray diffraction [55]. A similar reaction of hydrosilane **1** with palladium complex **62** in 3:1 ratio slowly takes place at 50 °C to give tetrakis(silyl)palladium(IV) complex **64**, the first example of (silyl)palladium(IV) complex (Scheme 16) [56]. Monitoring the reaction progress by NMR spectroscopy shows signals of bis(silyl)palladium(II) complex **67a** generated as a transient intermediate. The quantity of **67a** does not exceed 15% among the total palladium species, suggesting that complex **67a** is more reactive toward hydrosilane **1** than complex **62**. Initial attempts to isolate intermediate **67a** were not successful but its μ-dmpe dimer **65** was obtained by phosphine exchange reaction of complex **63** with 2 equiv of dmpe. As expected, complex **65** reacts with hydrosilane **1** to give complex **64** quantitatively at 50 °C.

Extensive exploration for a more straightforward synthetic procedure for complex **67a** has revealed that palladium complex **66a** is the starting complex of choice. Thus, treatment of **66a** or **66b** with hydrosilane **1** furnishes bis(silyl)palladium(II) complexes **67a** or **67b** cleanly. Although platinum complex **57** dimerizes to form mixed-valent dinuclear complex **60**, thermolysis



Scheme 16.



Scheme 17.

of palladium complexes **67a** and **67b** at 80 °C does not give dinuclear complex **68**, but instead affords novel trinuclear complexes **69a** and **69b**, respectively (Scheme 17) [57,58]. X-ray structure analysis revealed that the central palladium atoms in **69a** and **69b** no longer retain the chelating phosphine ligand, but are coordinated by six silicon atoms. Fig. 2 shows the molecular structure of complex **69a**. Two Pd1–SiH$_2$ (the atomic numbering refers to that in Fig. 2) distances (average 2.351(3) Å for **69a** and 2.356(3) Å for **69b**) are comparable to the known Pd–Si distances while four Pd1–SiH distances (2.437(3)–2.562(3) Å, average 2.483(3) Å for **69a**, and 2.420(3)–2.521(2) Å, average 2.468(2) Å for **2b**) are unusually long. On the other hand, Si3···Si6 and Si4···Si5 distances are unusually short (average of Si3···Si6 and Si4···Si5 distances, 2.539(4) Å for **69a** and 2.551(3) Å for **69b**). This suggests the possibility of an alternative description of the complex as bis(silyl)bis(η^2-disilane)palladium(II) **70**. The formation of σ-bond complexes of Si–H bonds is well known, while that of Si–Si bonds is unprecedented [10]. According to two independent theoretical calculations on the structure of **69a** and **69b**, considerable bonding interactions are present between Si3 and Si6, and also Si4 and Si5 [59,60]. Therefore, model **70** is probably a more realistic description of the coordination mode.

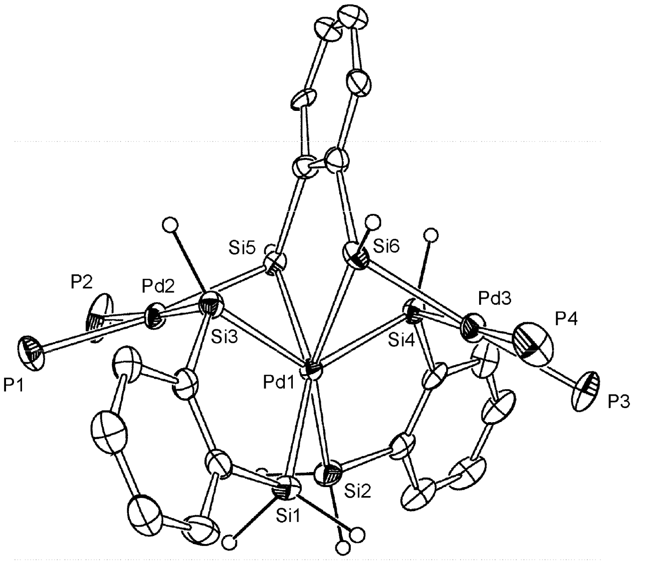
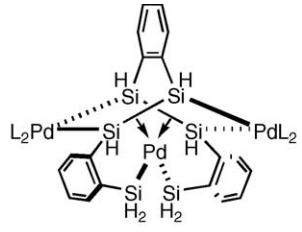


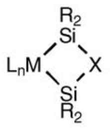
Fig. 2. Molecular structure of complex **69a** (30% probability level). Carbon atoms bound to phosphorous atoms and hydrogen atoms bound to carbon atoms are omitted for clarity.



70

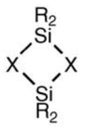
Nickel complexes **81a** and **81b** have also relatively short Si···Si contacts although they are much longer than those in **69a** and **69b** (see Section 3.3). It is known that metaladisilacyclobutanes **71** bridged by oxygen or nitrogen atoms have short Si···Si distances [35a,61]. Related cyclodisiloxanes **72** [62] and cyclodisilazanes **73** [63] also have short Si···Si distances, while no bonding interactions are suggested in **72** and **73** by NMR experiment [64] and by theoretical calculations [65]. Recent reports by Nikonov et al. on their niobium complex **74** suggest partial bonding interaction between the Si atoms in their complexes [66].

The formation of complexes **69a** and **69b** is quite interesting, whatever the real structure is. We can now consider without hesitation that, during catalytic processes such as a dehydrocoupling reaction, up to six silicon atoms can gather together in the coordination sphere of one transition-metal center.

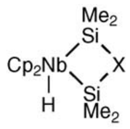


71

X = O, NR'
M = Pt, Ir, W, etc.



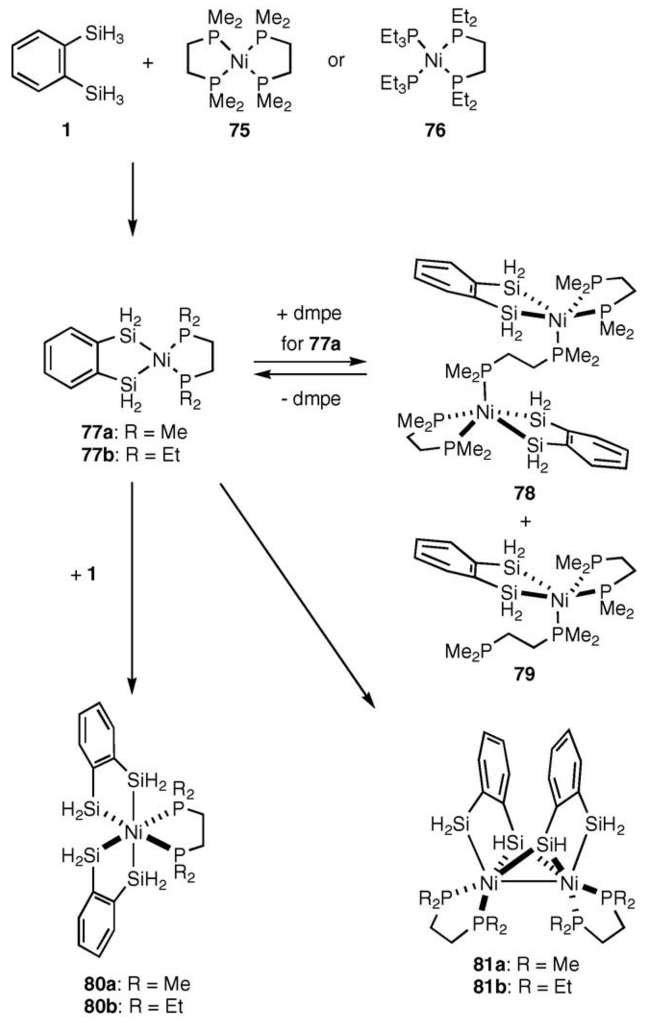
72 (X = O)
73 (X = NR')



74

3.3. Reaction with nickel complexes

As mentioned in Section 2.3, (silyl)nickel complexes are generally less stable than the corresponding (silyl)platinum complexes. Introduction of chelating phosphine ligands increases the stability of (silyl)nickels and makes it possible to isolate various (silyl)nickel complexes from hydrosilane **1**. Two equivalents of **1** slowly reacts with Ni(dmpe)$_2$ **75** at 80 °C to form tetrakis(silyl)nickel(IV) complex **80a**, similar to the platinum



Scheme 18.

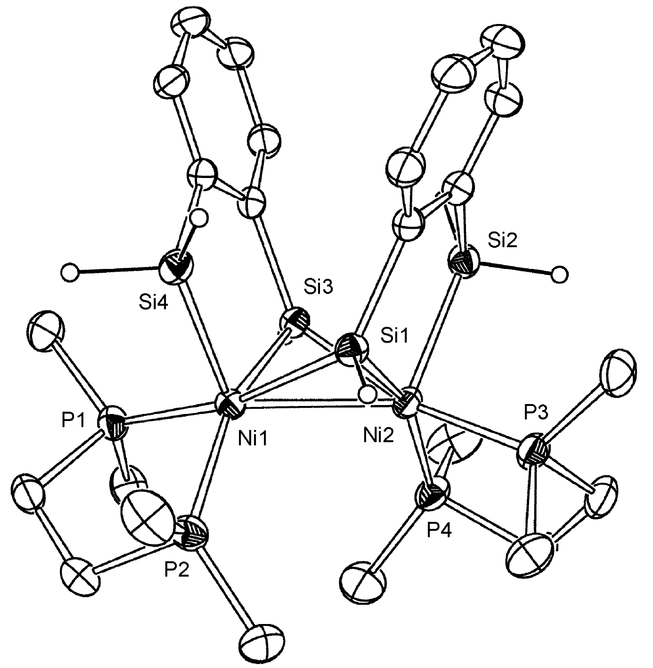


Fig. 3. Molecular structure of complex **81a** (30% probability level). Hydrogen atoms bound to carbon atoms are omitted for clarity.

complexes **56**, **59** and the palladium complex **64**, as a final product (Scheme 18) [67]. Complex **64** is the first example of (silyl)nickel(IV) complex. (Silyl)nickel(IV) species have been proposed as intermediates in nickel-catalyzed or -mediated reactions [68]. Nickel(IV) complexes are generally less stable than the lower valent nickel species, in particular in organonickel and related complexes. Isolated examples of organonickel(IV) complexes are very limited [69].

During the formation of **80a**, two five-coordinate bis(silyl)nickel(II) species **78** and **79** can be seen as intermediates by ^{31}P NMR spectroscopy. The same reaction of **1** with **75** in 1:1.5 ratio afforded the bis(silyl)nickel(II) complexes as major products, from which complex **78** can be isolated. The structures of complexes **78** and **80a** were confirmed by X-ray diffraction. Under the present reaction conditions, three bis(silyl)nickel(II) complexes, **77a**, **78** and **79**, are probably in equilibrium and the formation of **80a** is envisioned to take place through **77a**, although the presence of four-coordinate complex **77a** is not clearly detected by NMR spectroscopy of the reaction mixture due presumably to the low equilibrium concentration. Dissociation of the bridging phosphine ligand in **78** is conceivable since, in ^{31}P NMR spectroscopy, heating a toluene-d_8 solution of **78** induces signal broadening only for the bridging phosphine ligand at 40 °C.

Different from bis(silyl)platinum(II) complex **57** and bis(silyl)palladium(II) complexes **67a** and **67b**, which respectively afford the mixed-valent dinuclear complex **60** and the trinuclear complexes **69a** and **69b**, thermolysis of bis(silyl)nickel(II) complex **78** at a temperature of 80 °C or higher results in the formation of a new type of dinuclear complex **81a** [70]. Fig. 3 shows the molecular structure of complex **81a** determined by X-ray diffraction. Complex **81a** has a puckered μ-silylene-bridged four-membered ring with a short diagonal Ni–Ni distance (2.6658(7) Å). Each of the formal nickel(III) centers is ligated by three Si atoms. Another interesting feature of the complex **81a** is the short Si···Si distances (Si1···Si4 2.693(2) Å, Si2···Si3 2.685(1) Å, the atomic numbering refers to that in Fig. 3), which is almost the same as the longest Si–Si single bond [31]. This structural feature is presumed to be relevant to the bond formation between silicon atoms as discussed in Section 4.3.

Another similar dinuclear complex **81b** can be more readily formed at lower temperature than **81a**; the reaction of **1** with **76** in 1:1.05 ratio takes place even at room temperature to form **81b** as a main product together with a small amount of tetrakis(silyl)nickel(IV) complex **80b**. The difference in the reactivity is presumably associated with the extent of involvement of the five-coordinate species like **78** and **79**. In the reaction of **1** with **75**, five-coordinate species **78** and **79** are indeed formed and, to synthesize **81a**, heating is needed to (re)generate more reactive four-coordinate species **77a**. On the other hand, in the reaction of **1** with **76**, **77b** generated initially is probably reluctant to interact with bulkier depe and PEt$_3$ ligands and hence, dimerizes to **81b** straightforwardly even at room temperature.

4. Reaction of 1,2-$C_6H_4(SiMe_2H)(SiH_3)$ with group 10 metal complexes

4.1. Reaction with platinum complexes

1-Dimethylsilyl-2-silylbenzene **2**, a hybrid of 1,2-bis-(dimethylsilyl)benzene **53** and 1,2-disilylbenzene **1**, can be prepared by a procedure similar to that for **1** (Scheme 12) by replacing $SiCl_4$ with Me_2SiCl_2 [70].

Reaction of hydrosilane **2** with platinum(0) complexes with chelating phosphine ligands, **82a**, **82b**, **83a** or **83b**, in 1:1 ratio proceeds at 0 °C ~ room temperature to form expected bis(silyl)platinum(II) complexes **84a** or **84b** as major products. However, different from related bis(silyl)platinum complexes **55** and **57**, complexes **84a** and **84b** have proved to be in equilibrium with their dimers **85a** and **85b**, respectively, in solution (Scheme 19) [71]. Although monomers **84a** and **84b** are the major species in solution, crystallization of the mixture afforded only the dimers. Fig. 4 shows the molecular structure of dimer **85b**. Dimers **85a** and **85b** possess a μ-silylene-bridged Pt_2Si_2 four-membered ring with a short diagonal Si···Si distance and therefore are classified in the category of complex **20**. Complexes **85a** and **85b** consist of two tris(silyl)(hydrido)platinum(IV) centers and are similar to the Tilley's complex **18**, although the latter complex is not in equilibrium with monomeric species. When crystalline dimers **85a** and **85b** are dissolved in THF-d_8, monomer to dimer ratios are 95/5 for dmpe complexes and >99/1 for depe complex. Although the monomers **84a** and **84b** could not be isolated as crystalline forms, addition of excess of dmpe resulted in the formation of μ-dmpe-bridged dimer **86** as a crystalline compound.

In the dimerization reaction of bis(silyl)platinum(II) complex **57** forming mixed-valent $Pt^{II}Pt^{IV}$ dimer **60**, a complex similar to **85a** and **85b** is a possible intermediate leading to the mixed-valent species by dehydrogenation reaction. Therefore, thermolysis of **85a** was examined. Indeed, the dehydrogenation reaction did take place on the thermolysis of **85a** in toluene at 100 °C. However, the product is not a mixed-valent $Pt^{II}Pt^{IV}$ dimer similar to **60**, but a new type of dimer, **87**, consisting of two formal Pt^{III} centers [72]. Complex **87** is rather similar to Ni^{III} dimers **81a** and **81b**. Unlike complexes **81a** and **81b**, however, complex **87** is not C2-symmetric and two [1,2-$C_6H_4(SiMe_2)(SiH_2)$] ligands are bound to the platinum centers unsymmetrically. During the thermolysis of complex **85a**, a small amount of dinuclear complex **88** crystallized out from the reaction mixture and its structure was determined by X-ray diffraction [72]. The oxygen source for the formation of complex **88** is not clear. The formation of cyclodisiloxane ring is unexpected since such species are still very rare and formation of such species in the reactions starting with a $–SiH_2–$ unit with the aid of transition-metal has never been documented [62,73].

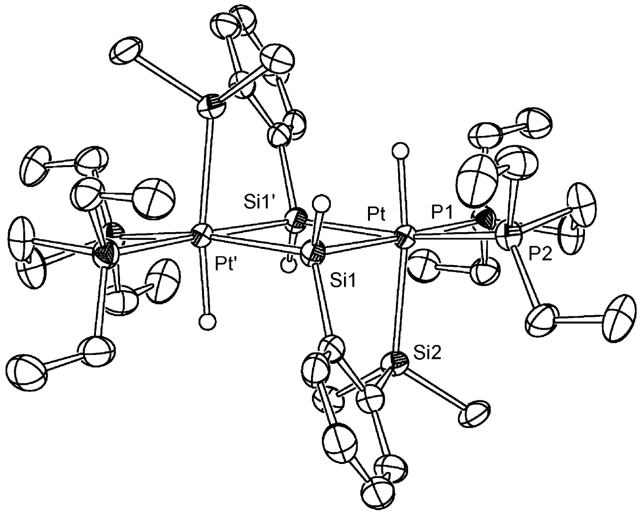
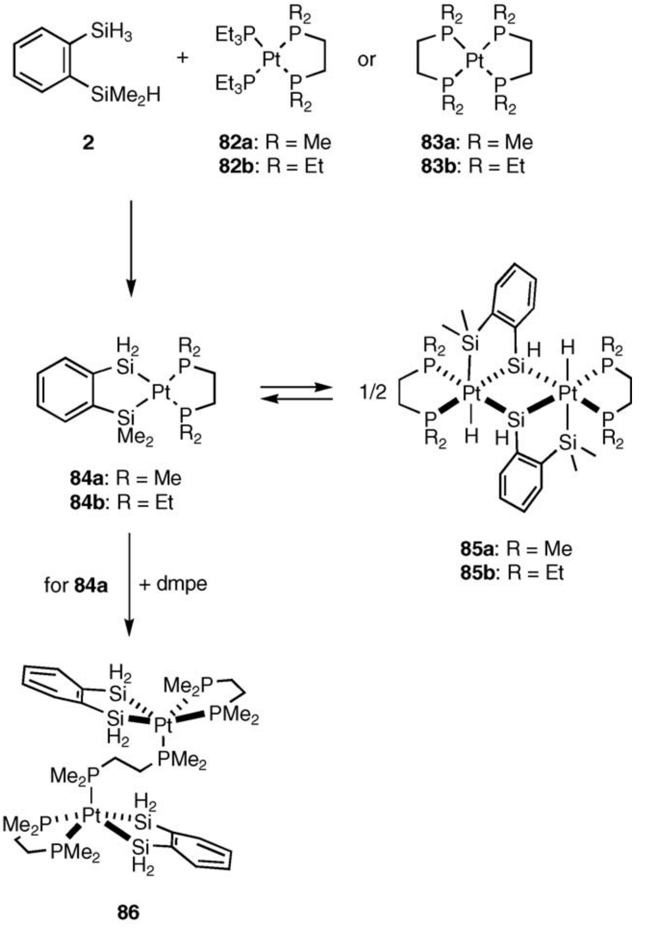
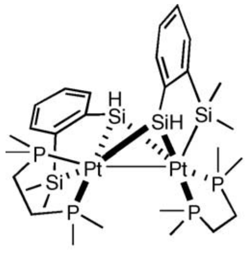


Fig. 4. Molecular structure of complex **85b** (50% probability level). Hydrogen atoms bound to carbon atoms are omitted for clarity.



Scheme 19.



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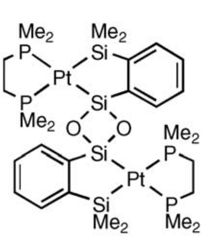

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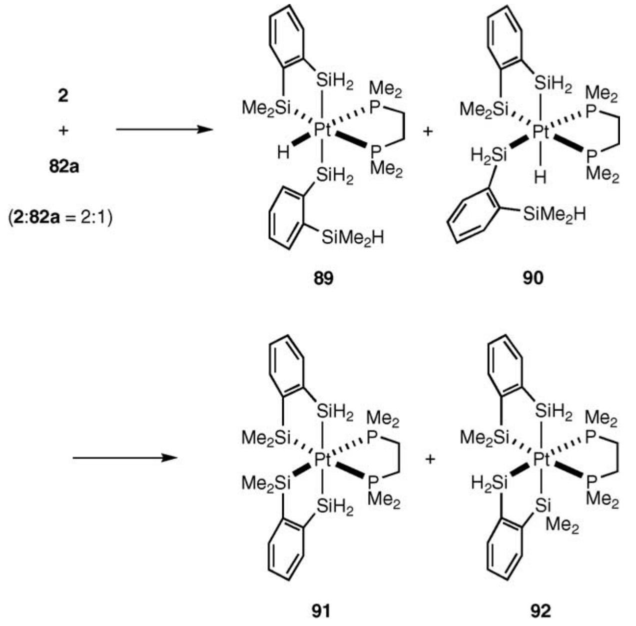
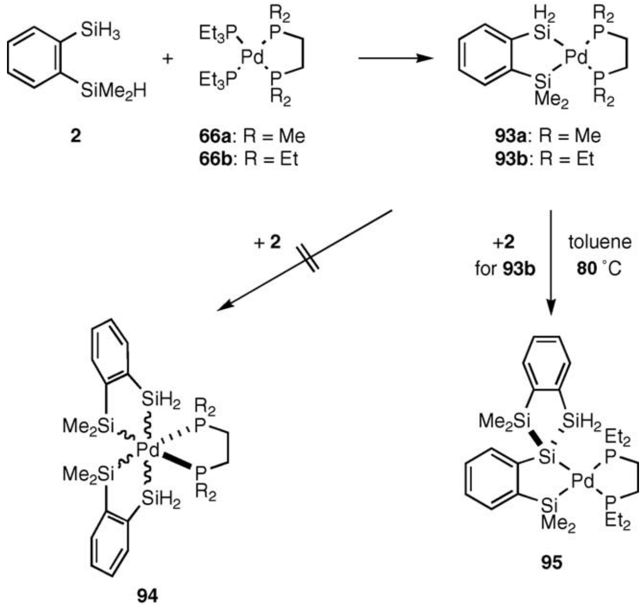


Scheme 20.



Scheme 21.

The reaction of hydrosilane **2** with platinum complex **82a** in 2:1 ratio proceeds similarly to the reaction of **1** with platinum(0) phosphine complexes (Scheme 20). At 0 °C ∼ room temperature, tris(silyl)(hydrido)platinum(IV) complexes **89** and **90**, similar to complexes **58a** and **58b**, are selectively formed among eight possible isomers. Due presumably to higher steric congestion, dehydrogenative cyclization of **89** and **90** to tetrakis(silyl)platinum(IV) complexes **91** and **92**, respectively, is much more difficult than that of **58a** and **58b** to **59**, but slowly takes place at 100 °C [71].

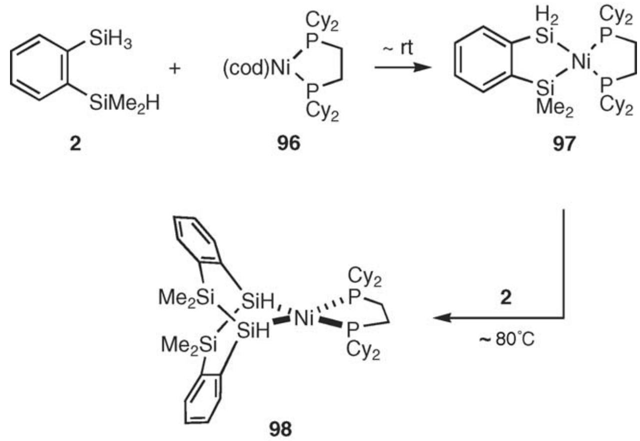
4.2. Reaction with palladium complexes

Palladium complexes **66a** and **66b** react with hydrosilane **2** in 1:1 ratio at 0 °C ∼ room temperature to form bis(silyl)palladium(II) complexes **93a** and **93b**, respectively, in high yields (Scheme 21) [74]. Unlike the platinum analogues **84a** and **84b**, complexes **93a** and **93b** are not prone to dimerize and hence can be isolated as such. Further reaction of **93b** with hydrosilane **2** takes place in toluene at 90 °C. The product isolated in high yield is not tetrakis(silyl)palladium(IV) complex **94** similar to complex **64**, but an unexpected bis(silyl)palladium(II) complex **95** [74]. Complex **95** is formed by dehydrocoupling reaction between the SiH_2 group of complex **93b** and a second molecule of hydrosilane **2**. Repeated oxidative addition/reductive elimination sequences may explain the formation of complex **95**, although other mechanisms, e.g., σ-bond metathesis, are also possible.

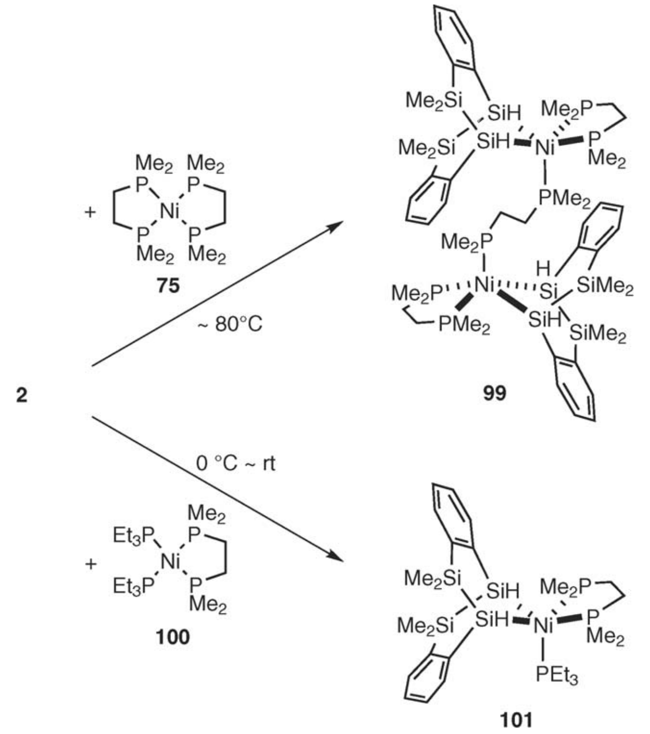
4.3. Reaction with nickel complexes

The reaction of hydrosilane **2** with a nickel(0) phosphine complex in 1:1 ratio gives expected bis(silyl)nickel(II) complex, while further reaction of the Ni(II) complex with hydrosilane **2** is different from those found with the corresponding platinum and palladium complexes (Scheme 22). Bis(silyl)nickel(II) complex **97** was isolated as a thermally stable complex in the reaction of hydrosilane **2** with dcpe complex **96** [75]. Complex **97** further reacts with **2** to form a new bis(silyl)nickel(II) complex **98** but not a tetrakis(silyl)nickel(IV) complex similar to complexes **80a** and **80b**. As found in palladium complex **95**, complex **98** also has two new Si–Si bonds, but the structures of **95** and **98** indicate that the Si–Si bond formation has proceeded to an entirely different direction, depending on the central metals. In the reaction of dmpe complexes **75** and **100** with **2** in 1:2 ratio, five-coordinate bis(silyl)nickel(II) complexes **99** [70] and **101** are formed, respectively, which have the same silyl ligand as complex **98** (Scheme 23). Fig. 5 shows the molecular structure of complex **99**.

As mentioned in Section 3.3, in the dinuclear nickel complexes **81a** and **81b**, two Si···Si distances (Si1···Si4 and Si2···Si3) are quite short. One can view these complexes as a snapshot immediately before the Si–Si bond formation within the dinuclear framework, although such Si–Si bond formation does not proceed as far as **81a** and **81b** are concerned. However,

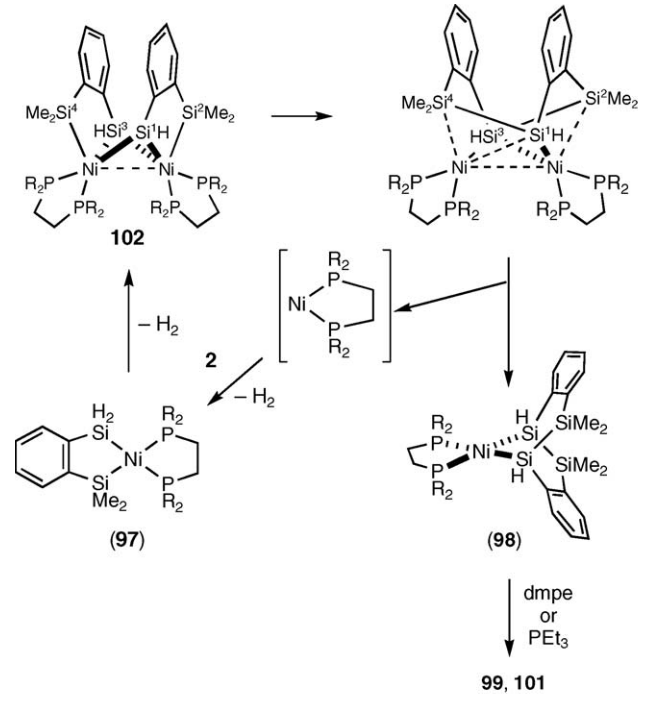


Scheme 22.

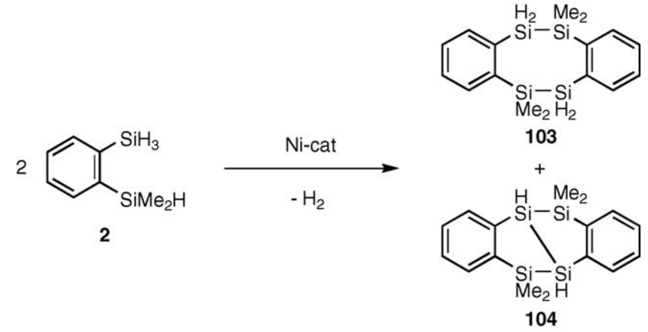


Scheme 23.

if a Si–Ni bond is somehow weakened, e.g., by introducing to silicon a methyl group in place of hydrogen, the bond formation becomes more realistic as is indeed observed with hydrosilane **2**. Scheme 24 illustrates a plausible mechanism for the formation of complexes **98**, **99** and **101**. It assumes a dimerization of complex **97** to **102**, which is basically a replica of the dimerization of complexes **77a** and **77b** to **81a** and **81b**, respectively. Although we have been unable to detect complex **102**, we believe that its involvement as transient intermediate can be safely assumed in view of the formation of isolable complexes **81a** and **81b**. Formation of Si1–Si4 and Si2–Si3 bonds in the framework of **102** and simultaneous release of a [Ni($PR_2CH_2CH_2PR_2$)] fragment produce the observed product **98**. The release of a [Ni($PR_2CH_2CH_2PR_2$)] fragment is likely to be assisted by the attack with hydrosilane **2** to regenerate complex **97**. In the reactions starting with dmpe derivatives **75** and **100**, coordination of free phosphine ligands present in the reaction mixture follows the formation of complexes similar to **98**, leading to the final products **99** and **101**.



Scheme 24.



Scheme 25.

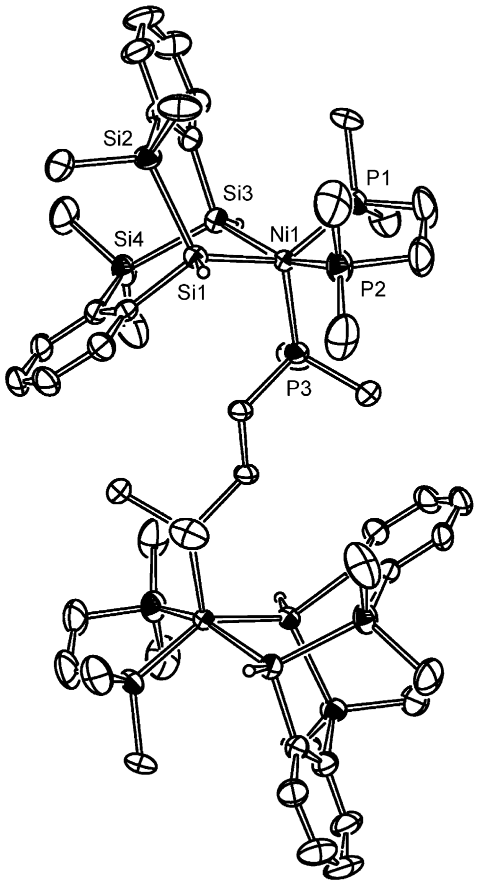


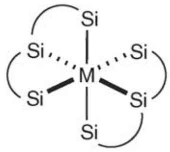
Fig. 5. Molecular structure of complex **99** (30% probability level). Hydrogen atoms bound to carbon atoms are omitted for clarity.

If reductive elimination forming Si–Si bond or silyl ligand exchange reaction takes place in complexes **98**, **99** or **101**, one can expect a catalytic dimerization reaction of hydrosilane **2**. Indeed, such catalytic reaction takes place in the presence of a catalytic amount of **97** or **98** to form dimers **103** and **104** (Scheme 25) [75].

5. Reaction of (2-SiH$_3$C$_6$H$_4$)$_2$SiH$_2$ with group 10 metal complexes

5.1. Reaction with platinum complexes

Bis(2-silylphenyl)silane **3** was designed as a precursor of tridentate silyl ligand with minimal steric congestion. Although attempted reactions have been unsuccessful, introduction of two molecules of **3** to a metal center may lead to hexasilyl complex **105**, which is similar to the core structure of trinuclear palladium complexes **69a** and **69b**. On the other hand, hydrosilane **3** is envisioned to stabilize a wide range of tris(silyl)(hydrido)metal(IV) complexes **106**, which have been found only for platinum. Exploration along this line has indeed uncovered the formation of such species and/or related species formed via such complexes. As observed with hydrosilanes **1** and **2**, the chemistry of hydrosilane **3** also displays metal-dependent diversity.



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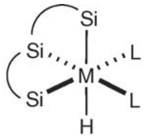
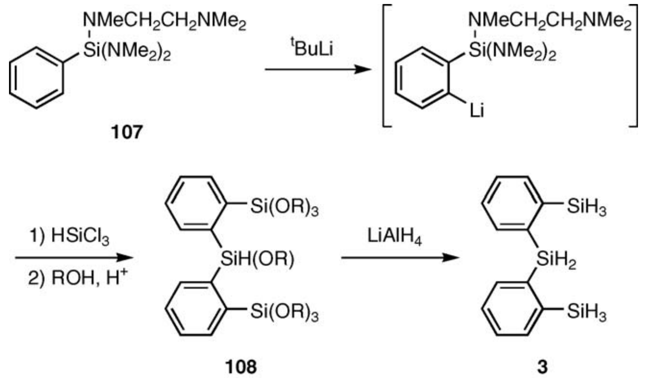


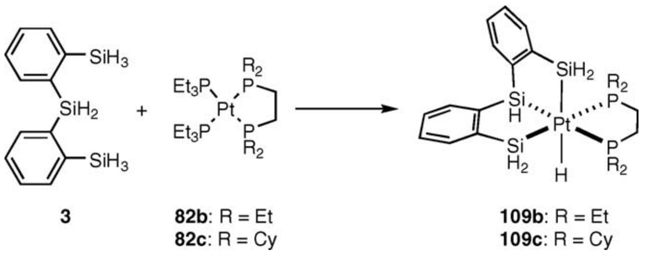
106

Hydrosilane **3** can be prepared by using Tamao's *ortho*-lithiation of (aminosilyl)benzene **107** [51] as a key reaction similarly to the synthesis of hydrosilanes **1** and **2** (Scheme 26) [76].

The reaction of hydrosilane **3** with platinum complexes **82b** and **82c** proceeds cleanly to form expected tris(silyl)(hydrido)platinum(IV) complexes **109b** and **109c**, respectively (Scheme 27) [77]. The complexes are highly thermally stable; for example, complex **109b** does not show any sign of noticeable decomposition even after heating in toluene-d_8 up to 170 °C.



Scheme 26.

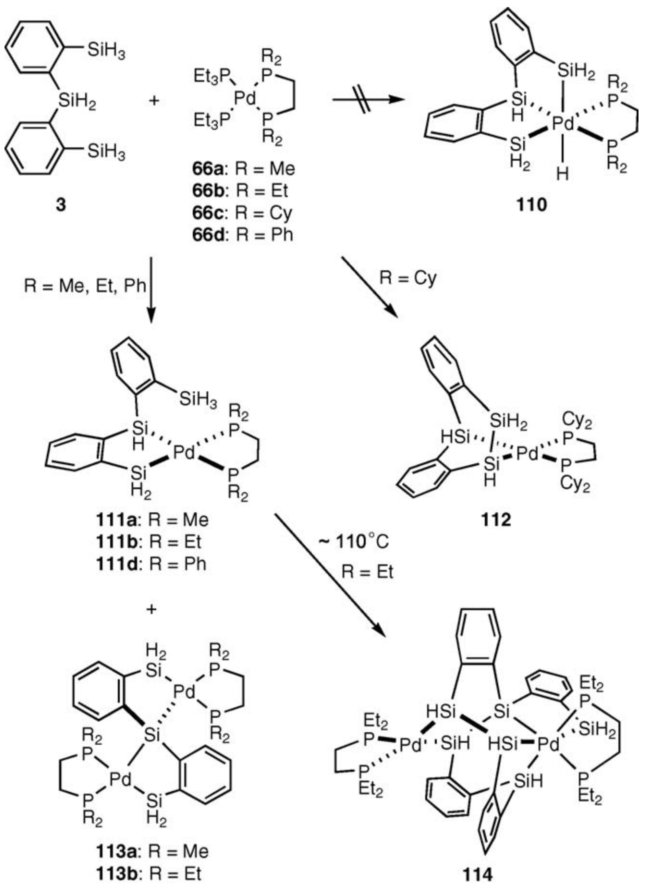


Scheme 27.

5.2. Reaction with palladium complexes

The reaction of hydrosilane **3** with palladium(0) complexes **66a–d** affords two different types of bis(silyl)palladium(II) complexes depending on the phosphine ligands (Scheme 28).

The reaction of complexes **66a**, **66b** and **66d** with 1 equiv of **3**, respectively, forms simple bis(silyl)palladium complexes **111a**, **111b** and **111d**, but not tris(silyl)(hydrido)palladium(IV) complexes **110** similar to the platinum complexes **109b** and **109c** [77]. Dinuclear complexes **113a** and **113b** are also formed as



Scheme 28.

minor products in the reaction of **66a** and **66b**, respectively [76]. As anticipated, complexes **113a** and **113b** can be prepared as major products when the reaction is conducted with a 1:2 ratio of **3** to **66a** or **66b**. The solid-state structure of **111b** confirmed by X-ray diffraction shows that a free SiH_3 group is remaining unreacted. ^1H NMR spectroscopy of **111b** at room temperature, however, does not display a signal corresponding to the free SiH_3 group but instead exhibited only one broad signal for six hydrogens bound to Si atoms, suggesting the exchange of these hydrogens at this temperature. This dynamic behavior does not freeze completely even at −90 °C. Complexes **111a** and **111d** show a similar dynamic behavior in NMR spectroscopy.

Interestingly, dcpe complex **66c** affords another type of bis(silyl)palladium(II) complex, **112**, whose structure was confirmed by X-ray diffraction (Fig. 6) [76]. Complex **112** has a new Si–Si bond and its formation mechanism may be similar to that for complex **95** from hydrosilane **2**. Scheme 29 shows two plausible pathways to the formation of complex **112**, both of which assume the intermediacy of tris(silyl)(hydrido)palladium(IV) **110**. One proceeds through Si–Si reductive elimination from **110** generating **115**, subsequent oxidative addition of a Si–H bond and H–H reductive elimination from **116**. The other is a concerted mechanism that involves simultaneous elimination of H_2 and Si migration from Pd to another Si via transition state **117**.

Thermolysis of depe complex **111b** up to 110 °C in toluene affords new dinuclear complex **114** as a major product [77]. During the heating reaction, several intermediates are observed by NMR spectroscopy although their structures have not been established. Complex **114** has a bis(silyl)palladium(II) and a tetrakis(silyl)palladium(IV) centers tethered by two disilanylene bridges.

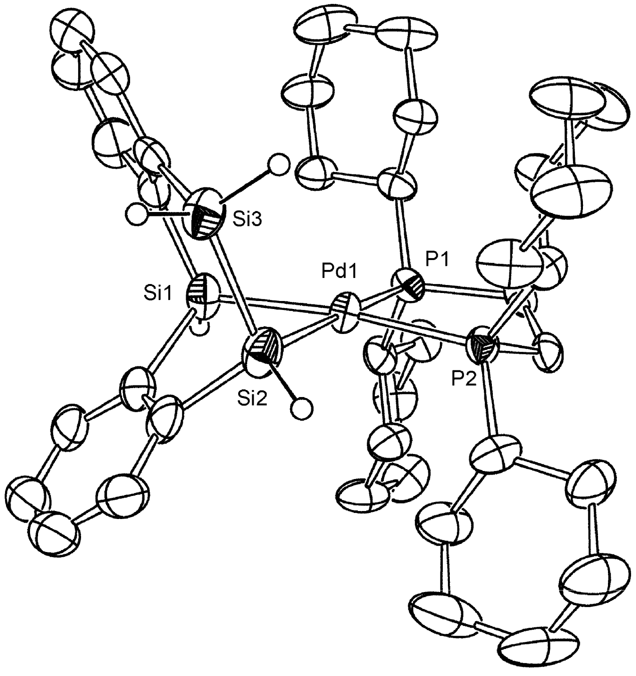
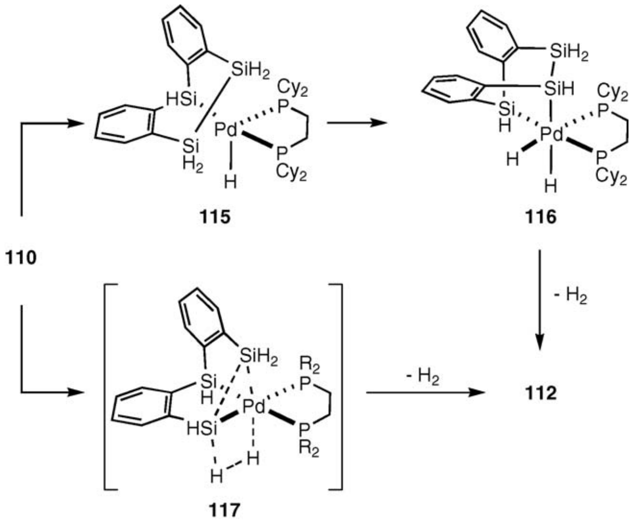


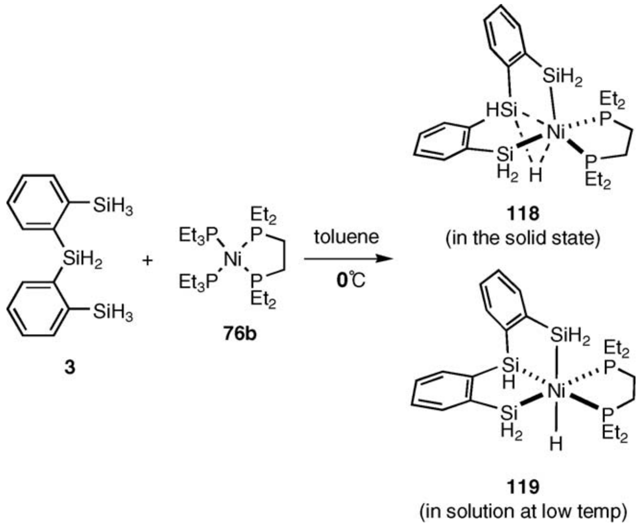
Fig. 6. Molecular structure of complex **112** (50% probability level). Hydrogen atoms bound to carbon atoms are omitted for clarity.



Scheme 29. Plausible mechanisms for the formation of complex **112**.

5.3. *Reaction with nickel complexes*

Hydrosilane **3** reacts with 1 equiv of complex **76b** at 0 °C to form a nickel complex having a unique behavior. In the solid state the complex is a bis(silyl)[η^2-(Si–H)]nickel complex **118** as characterized by X-ray diffraction (Scheme 30) [78]. In solution, the complex displays a dynamic behavior as observed by variable-temperature multinuclear NMR spectroscopy and has proved to be tris(silyl)(hydrido)nickel(IV) complex, respectively **119** at low temperature, which agrees with the results of theoretical calculations (vide infra). Complexes **118** and **119** are the first examples of η^2-(Si–H)nickel and (hydrido)nickel(IV) complexes. The structure determined by X-ray diffraction is



Scheme 30.

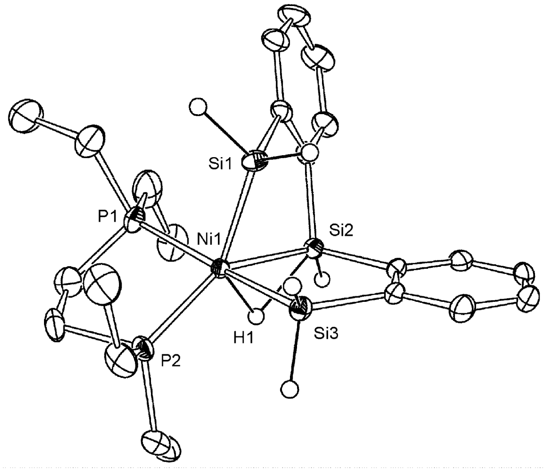


Fig. 7. Molecular structure of complex **118** (50% probability level). Hydrogen atoms bound to carbon atoms are omitted for clarity.

shown in Fig. 7. The coordination geometry of the nickel atom in **118** can be described to be distorted-trigonal-bipyramidal (DTBP) with Si1, η^2-(Si2–H) and P2 ligands at equatorial positions (the atomic numbering refers to that in Fig. 7). The Ni–Si2 distance (2.3480(8) Å) is considerably longer than the known Ni–Si bonds (2.11–2.30 Å)

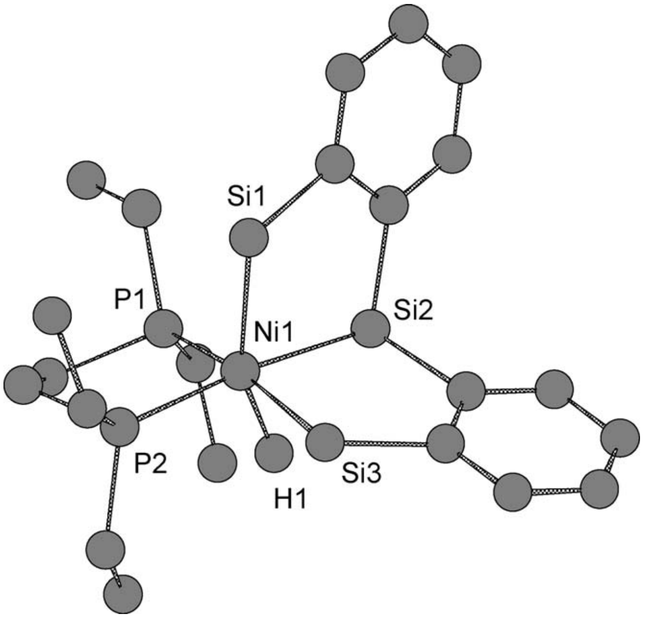


Fig. 8. Molecular structure of **118** optimized with B3LYP/6-31G* (Ni, Si and P atoms), cc-pVDZ (H1 atom) and 3-21G* (C and other H atoms). Only H atom bound to Ni is shown for clarity.

Table 1
$^{29}Si\{^1H\}$ NMR data for (silyl)platinum complexes

Complex	Solvent	Chemical shift, δ (ppm) (multiplicity)	Coupling constants (Hz)			Ref.
			^1J(Pt–Si)	^2J(P–Si)	^4J(Pt–Si)	
55	$CDCl_3$	27.36 (t)	1197	59		[52]
56	$C_6D_5CD_3$	−13.18 (dd)	626	21, 135		[52]
		−13.00 (t)	635	13		
58a	C_6D_6	−60.47 (s)				[52]
		−51.15 (dd)	625	12, 17		
		−32.67 (t)	599	13		
		−26.75 (dd)	626	10, 139		
59	C_6D_6	−27.36 (t)	617	14		[52]
		−12.89 (dd)	596	21, 136		
60	C_6D_6	−54.94 (ddd)	362, 771	8, 99, 104		[52]
		−26.86 (t)	733	17		
85a	Solid state (CP/MAS)	−94 (quasi septet)	(125)			[71]
		0.7	757			
85b	Solid state (CP/MAS)	−94.5 (m)				[71]
		−3.1	767			
89	C_6D_6	−48.8 (dd)	685	12, 18		[71]
		−34.8 (t)	592	13		
		−19.2 (s)			6	
		8.2 (dd)	641	7, 138		
90	C_6D_6	−37.5 (dd)	746	15, 155		[71]
		−25.4 (dd)	643	10, 12		
		−19.0 (s)			7	
		6.5 (dd)	671	10. 141		
91	$C_6D_5CD_3$	−26.6 (t)	657	15		[71]
		6.9 (dd)	668	12, 133		

[48d,50,67,70,79] and reflects the η^2-(Si–H)Ni character. The IR spectrum of the crystal showed a broad absorption around 1600 cm^{-1} that is assignable to Ni···H···Si moiety.

Fig. 8 is the fully optimized structure of **118** with density functional theory (DFT). It is envisioned to represent the most stable structure of **118** in solution. The Si2···H1 distance is now 2.362 Å and showing no bonding. The Ni–Si2 distance (2.266 Å) is within the range of the known Ni–Si bond distances. The structure of the complex has changed from DTBP in the solid state (X-ray) structure to distorted-octahedral and a schematic drawing **119** is more appropriate to represent its structure.

Thermal stability of complex **118** in solution is very low as compared with the corresponding platinum complex **109b**; even at room temperature in toluene, it gradually decomposes to a mixture of unidentified compounds.

6. Tables of NMR and X-ray data

See Tables 1–8.

7. Conclusions

The chemistry of group 10 metal complexes with metal–silicon bonds has made great progress during the last decade. Such complexes have been prepared by a number of methods, among which the reaction of hydrosilanes with group 10 metal complexes is used most widely. 1,2-Disilylbenzene **1**, 1-dimethylsilyl-2-silylbenzene **2** and bis(2-silylphenyl)silane **3**, precursors of chelating silyl ligands with less steric congestion, have proved to be quite useful to stabilize a number of formally high valent silyl group 10 metal species as well as di- and trinuclear complexes. By

Table 2
^{29}Si{^{1}H} NMR data for (silyl)palladium and (silyl)nickel complexes

Complex	Solvent	Chemical shift, δ (ppm) (multiplicity)	Coupling constants (Hz)		Ref.
			^2J(P–Si)	^1J(H–Si)[a]	
(Silyl)palladium complexes					
64	C_6D_6	−8.31 (t)	17		[56]
		−6.58 (dd)	17, 162		
65	THF-d_8	−18.5 (br)			[56]
67a	THF-d_8	−17.9 (s)		160	[57]
67b	C_6D_6	−18.0 (d)	143	160	[57]
69b	$C_6D_5CD_3$	−12.9 (dd, SiH)	22, 124	182	[57]
		−11.3 (s, SiH_2)		184	
		20.0 (ddd, SiH)	5, 23, 111	187	
112	C_6D_6	−61.8 (s, *Si*H_2)		174	[76]
		−31.4 (dd, Pd*Si*HSiH_2)	13. 142	141	
		23.8 (dd, C*Si*HC)	13, 143	143	
113a	THF-d_8	−23.8 (tt)	11, 79	152	[76]
		79.8 (tt)	11, 128		
113b	$C_6D_5CD_3$	−22.8 (tt)	10, 76	154	[76]
		82.4 (tt)	11, 125		
(Silyl)nickel complexes					
78	C_6D_6	−7.7 (t)	35		[67]
80a	C_6D_6	−0.35 (dd)	20, 116		[67]
		4.62 (t)	18		
80b	$C_6D_5CD_3$	−2.11 (dd)	20, 101		[70]
		3.03 (t)	16	164	
81b	Solid state (CP/MAS)	−48.5 (br, s)			[70]
		79.9 (br, s)			
118/119	$C_6D_5CD_3$[b]	−2.3 (t)	22	80	[78]
		34.4 (t)	40	173	
	$C_6D_5CD_3$[c]	0.0 (t)	19	173	
		39.23 (t)	44	170	

[a] ^1J(H–Si) values were obtained by ^{1}H-coupled ^{29}Si NMR spectra.

[b] At 20 °C.

[c] At −80 °C.

Table 3
^{31}P NMR data for (silyl)platinum complexes

Complex	Solvent	Chemical shift, δ (ppm) (multiplicity)	Coupling constants (Hz)			Ref.
			^1J(Pt–P)	^2J(P–P)	^3J(Pt–P)	
55	$CDCl_3$	32.55 (s)	1706			[52]
56	$C_6D_5CD_3$	−16.2 (s)	1188			[52]
57	CD_2Cl_2 (−20 °C)	14.01 (s)	1776			[52]
58a	$C_6D_5CD_3$	−40.78 (d)	1624	23		[52]
		−34.15 (d)	1220	23		
58b	$C_6D_5CD_3$	−29.76 (d)	1273	31		[52]
		−25.76 (d)	1283	31		
59	C_6D_6	−44.1 (s)	1316			[52]
60	C_6D_6	−46.18 (t)	1078	17	299	[52]
		16.54 (t)	2013	17	173	
84a	THF-d_8	39.5 (d)	1623	13		[71]
		40.0 (d)	1337	13		
84b	THF-d_8	65.5 (d)	1682	13		[71]
		66.5 (d)	1372	13		
85a	THF-d_8	−10.3 (s)	1102		239	[71]
		−5.9 (s)	971		201	
85b	$C_6D_5CD_3$	13.0 (s)	923		194	[71]
		18.0 (s)	1065		224	
89	C_6D_6	−19.77 (d)	999	8		[71]
		−15.61(d)	1428	8		
90	C_6D_6	−12.83(d)	1023	17		[71]
		−11.43 (d)	1159	17		
91	$C_6D_5CD_3$	−20.69 (s)	1037			[71]
92	$C_6D_5CD_3$	−20.69 (s, AA′X pattern)	945, 1283	16		[71]

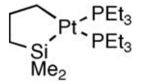
Table 4
^{31}P NMR data for (silyl)palladium and (silyl)nickel complexes

Complex	Solvent	Chemical shift, δ (ppm) (multiplicity)	^2J(P–P) (Hz)	Ref.
(Silyl)palladium complexes				
63	C_6D_6	−2.38 (s)		[55]
64	C_6D_6	15.87 (s)		[56]
65	THF-d_8	2.68 (br)		[56]
67a	THF-d_8	17.1 (s)		[57]
67b	C_6D_6	44.4 (s)		[57]
69a	C_6D_6	21.1 (d)	24	[57]
		21.4 (d)	24	
69b	$C_6D_5CD_3$	48.5 (d)	24	[57]
		48.8 (d)	24	
112	C_6D_6	60.3 (d)	22	[76]
		61.2 (d)	22	
113a	THF-d_8	11.4 (br)		[76]
		15.2 (br)		
113b	$C_6D_5CD_3$	35.5 (dd)	25, 36	[76]
		38.2 (dd)	25, 36	
(Silyl)nickel complexes				
78	C_6D_6	−20.48 (s)		[67]
		35.82 (s)		
80a	C_6D_6	39.27 (s)		[67]
81b	Solid state (CP/MAS)	48.6 (br, s)		[70]
		52.0 (br, s)		
118/119	$C_6D_5CD_3$	61.7 (s)		[78]

Table 5
^{195}Pt NMR data for (silyl)platinum complexes

Complex	Solvent (temperature)	Chemical shift, δ (ppm)[a]	Ref.
(Silyl)platinum(IV) complexes			
16a	$CDCl_3$	−6863	[27]
16b	$CDCl_3$	−6863	[27]
16c	$CDCl_3$	−7160	[27]
16d	$CDCl_3$	−6860	[27]
56	$C_6D_5CD_3$	−6568	[52]
58a	$C_6D_5CD_3$	−6566	[52]
58b	$C_6D_5CD_3$	−6704	[52]
59	$CDCl_3$	−6844	[52]
60 (Pt^{IV} nucleus)	C_6D_6	−6176	[52]
109c	C_6D_6	−6837	[77]
(Silyl)platinum(II) complexes			
20 (L = PPr_3, SiR_2 = $SiH(n\text{-}C_6H_{13})$, *trans*-isomer	C_6D_6	−4777	[30b]
23 (R_2 = Me_2)	CD_2Cl_2	−5293	[33]
55	$CDCl_3$	−5020	[52]
			[52]
57	CD_2Cl_2 (−20 °C)	−5240	[52]
60 (Pt^{II} nucleus)	C_6D_6	−4599	[52]
trans-$Pt(SiMe_3)Cl(PEt_3)_2$	C_6D_6	−4985	[80]
trans-$Pt(SiMe_3)Br(PEt_3)_2$	C_6D_6	−5015	[80]
trans-$Pt(SiMe_3)I(PEt_3)_2$	C_6D_6	−5039	[80]
120[b]	$C_6D_5CD_3$	−4980	[81]
cis-$Pt(SiPh_3)(CH{=}CH_2)(PMe_2Ph)_2$	CD_2Cl_2 (−30 °C)	−4821	[82]

[a] Relative to $PtCl_6^{2-}$.

[b] 

120 .

using these hydrosilanes, hitherto unknown types of silyl group 10 metal complexes, including (silyl)palladium(IV), (silyl)nickel(IV), tetrakis(silyl)platinum(IV), (η^2-Si–H)nickel and formal hexa(silyl)palladium complexes, have been isolated and structurally characterized. In addition, the reaction of **1**–**3** with group 10 metal complexes showed unique metal-dependent diversity reflecting the character of each metal. Thus, hydrosilanes **1**–**3** have proved to be rich sources of chemistry that cannot be seen by other hydrosilanes and provide unique opportunities to look into mechanistic aspects of catalysis involving hydrosilanes.

Table 6
Selected bond distances (Å) for (silyl)platinum complexes

Complex	M–Si	M–P	Si···Si or Si–Si	Pt···Pt or Pt–Pt	Ref.
59	*trans* to Si: 2.428(2), 2.430(2), *trans* to P: 2.383(1), 2.376(2)	2.398(1), 2.418(2)			[52]
60	Pt^{IV}–Si: 2.415(9), 2.44(1), 2.40(1), 2.41(1) Pt^{II}–Si: 2.39(1), 2.352(9)	Pt^{IV}–P: 2.43(1), 2.392(9) Pt^{II}–P: 2.31(1), 2.32(1)	2.72(1)	3.93(1)	[52]
85a	2.3888(9), 2.3862(9), 2.4124(9)	2.3300(9), 2.327(1)	2.832(1)	3.8444(2)	[71]
85b	2.394(1), 2.391(1), 2.433(1)	2.359(1), 2.370(1)	2.792(2)	3.8863(2)	[71]
86	2.350(5), 2.387(5)	Equatorial: 2.309(5), 2.310(5) Axial: 2.394(5)			[71]
90	2.388(1), 2.393(1), 2.371(1)	2.346(1), 2.334(1)			[71]
91	2.400(2), 2.403(2), 2.406(1), 2.398(2)	2.359(2), 2.358(2)			[71]
92	2.413(1), 2.404(1), 2.368(1), 2.451(1)	2.344(1), 2.347(1)			[71]

Table 7
Selected bond distances (Å) for (silyl)palladium complexes

Complex	M–Si	M–P	Si···Si or Si–Si	Pd···Pd or Pd–Pd	Ref.
64	2.345(2), 2.394(4)	2.337(2)			[56]
69a[a]	Pd1–SiH_2: 2.348(3), 2.353(3) Pd1–SiH: 2.437(3)–2.562(3) Pd2–Si or Pd3–Si: 2.373(3)–2.414(3)	2.299(3)–2.322(3)	2.488(4), 2.589(4)	2.891(2), 2.912(2)	[57]
69b[a]	Pd1–SiH_2: 2.348(3)–2.364(2) Pd1–SiH: 2.420(3)–2.521(2) Pd2–Si or Pd3–Si: 2.371(2)–2.409(3)	2.301(3)–2.345(8)	2.514(3)–2.579(3)	2.9036(8)–2.9231(8)	[57]
112	2.348(3), 2.356(3)	2.333(2), 2.315(2)	2.333(4)		[76]
113a	2.3818(8), 2.334(1)	2.3354(9), 2.3375(9)			[76]

[a] The atomic numbering refers to that in Fig. 2.

Table 8
Selected bond distances (Å) for (silyl)nickel complexes

Complex	M–Si	M–P	Si···Si or Si–Si	Ni–Ni	Ref.
78	2.247(3), 2.255(3)	Equatorial: 2.163(3), 2.163(3) Axial: 2.248(2)			[67]
80a	2.2900(9), 2.2522(7)	2.1973(7)			[67]
81a	2.210(1)–2.304(1)	2.144(1)–2.186(1)	Si···Si: 2.693(2), 2.685(1)	2.6658(7)	[70]
81b	2.2098(6)–2.2976(6)	2.1568(6), 2.2042(6)	Si···Si: 2.7049(9)	2.7201(7)	[70]
99	2.257(2), 2.263(2)	Equatorial: 2.160(2), 2.182(2), Axial: 2.237(2)	Si–Si: 2.357(2), 2.361(2)		[70]
118	2.2445(6), 2.2552(6), 2.3480(8)	2.1978(6), 2.2156(6)			[78]

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