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Invited review

Reactivity of the metal–silicon bond in organometallic chemistry ☆

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Abstract

The reactivity of molecules containing a metal–silicon bond is currently attracting considerable attention owing to its relevance to a number of important stoichiometric and catalytic transformations. The focus of this review concerns those stoichiometric reactions involving the metal–silicon bond which result in isolable Si-containing metal complex(es). Catalytic reactions are therefore only considered when strong evidence for M–Si intermediate complexes is provided. Reactions in which the silicon atom leaves the metal complex are not examined. For convenience, the reactions will be classified into insertion and migration reactions, although this terminology does not necessarily have a mechanistic implication and is somewhat arbitrary since many reaction products could belong to one or the other section.

Keywords: Silicon; Metal–Silicon bonds; Insertion reactions; Migration reactions

1. Introduction

Organosilicon compounds attract increasing interest owing to their synthetic applications and physico-chemical properties [1–3]. In order to develop new metal catalysts for the synthesis of such compounds a good understanding of the reactivity of metal–silicon bonds is needed [1,4–8]. The synthesis and structures of complexes containing a M–Si bond have been investigated for many years. At least two major objectives of such studies can be identified: (i) to allow a comparison with related systems containing a M–C bond; (ii) to provide a better understanding and insight into the elementary steps that may take place in very important metal-catalyzed industrial reactions, such as hydrosilylation [6,9–11] and the dehydrogenative coupling of primary or secondary silanes [10,12–25], also in the new reactions that are being rapidly developed for organic synthesis, such as silylformylation [9,26,27] and double silylation (see below).

This review is focused on those stoichiometric reactions involving the M–Si bond which result in isolable Si-containing metal complex(es). Catalytic reactions are only considered when strong evidence for M–Si intermediate complexes is available. Reactions in which the Si atom leaves the metal complex will not be examined. Although compounds which contain a M(H–SiR$_3$) moiety and display agostic interactions may be formally viewed as resulting from protonation of the M–Si bond, they will not be examined here [4c–e]. Other aspects of the chemistry of metal–silicon compounds have been reviewed recently [5,7].

The reactions are classified for convenience into insertion and migration reactions, although this division does not necessarily have a mechanistic implication and is somewhat arbitrary since many reaction products could belong to either of the two sections.

2. Insertion reactions

Insertion of a molecule A–B into the metal–silicon bond(s) of a metal complex will generally occur as shown in Scheme 1.

As in the case of corresponding reactions involving a metal–carbon bond, this process leads to the formation of two new bonds; either M–A and Si–A bonds or M–A and Si–B bonds. We will consider the various reactions according to the nature of the newly formed bonds, with a subdivision depending on the nature of the AB molecule.

2.1. Formation of a Si–C bond

These reactions have been intensively studied because of their considerable synthetic potential and cen-

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☆ Dédié au profeseur Jean Dehand à l'occasion de son départ à la retraite, en témoignage d'amitié et d'estime.

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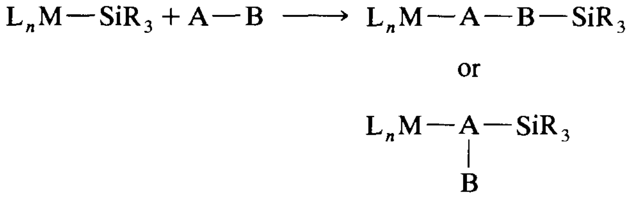
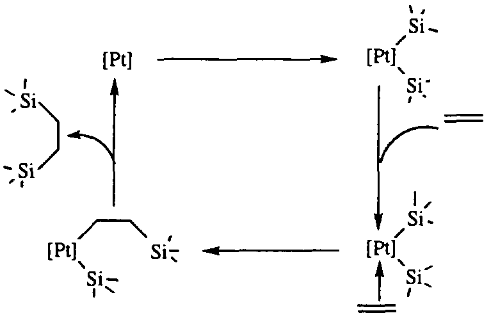


$$L_nM{-}SiR_3 + A{-}B \longrightarrow L_nM{-}A{-}B{-}SiR_3 \quad \text{or} \quad L_nM{-}\underset{\displaystyle B}{\underset{|}{A}}{-}SiR_3$$

Scheme 1.

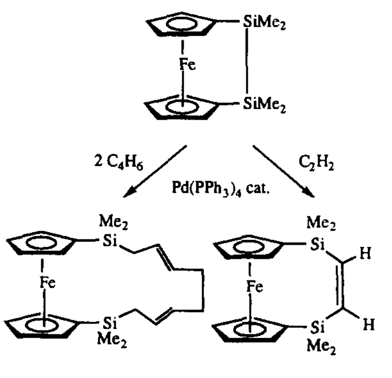
tral role in a number of metal-catalyzed transformations, including the formation of polymers by insertion of organic unsaturated compounds into an Si–H or Si-Si bond [1,28,29].

The bis-silylation (or double-silylation) reaction was pioneered by Kumada and co-workers [30] and is particularly attractive in that two Si–C bonds are created by addition of Si–Si bonds to unsaturated organic substrates, such as alkynes [31–39], alkenes [40–44] and 1,3-dienes [30,38,45–51]. Nickel, palladium and platinum are the metals most often used in the catalysts for this transformation, See Scheme 2.



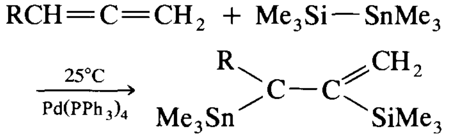
Scheme 2.

A representative recent example from Manners' group [38] is the formation of the structurally characterised ferrocenophanes $Cp_2Fe(SiMe_2)_2$ (CH=CH) or *trans, trans*-$Cp_2Fe(SiMe_2)_2(CH_2CH{=}CHCH_2)_2$, obtained by insertion of acetylene or butadiene, respectively, into the Si–Si bond of the ferrocenyldisilane $Cp_2Fe(SiMe_2)_2$ (Eq. (1)).



(1)

Related to the bis-silylation is the palladium-catalyzed activation of silylstannanes in the presence of unsaturated organic compounds. It should be noted however, that an insertion of the substrate into the Pd–Si or into the Pd–Sn bond of an intermediate is conceivable [52,53] (Eq. (2)).



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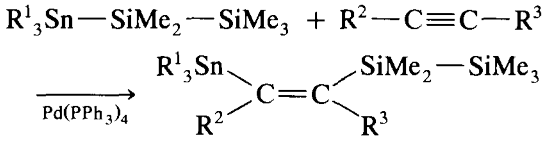
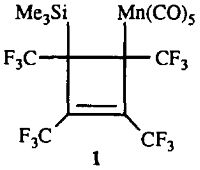


(2b)

2.1.1. *Insertion of alkynes*

2.1.1.1. Into a Ti–Si bond. An intermediate containing a Ti(III)–Si bond, $[Cp_2Ti{-}SiMe_2Ph]$, was suggested to be the active species in the *syn*-silyltitanation of alkynes (and 1,3-dienes, see below) [54].

2.1.1.2. Into a Mn–Si bond. Clark and Hauw reported in 1972 that under UV irradiation the reaction of $Me_3SiMn(CO)_5$ with $F_3CC{\equiv}CCF_3$ afforded as the main product compound **1**, which contains two perfluorobutyne units; some of the mono-insertion product **2** was also formed [55].



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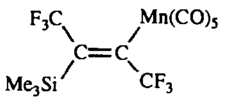

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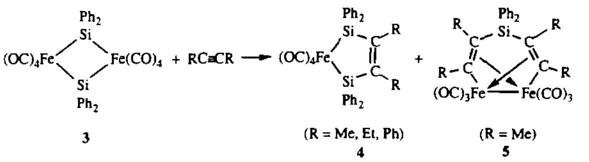
2.1.1.3. Into a Fe–Si bond. The same group observed that under UV irradiation the reaction of $Me_3SiFe(CO)_2Cp$ with $F_3CC{\equiv}CCF_3$ or $F_3CC{\equiv}CH$ involves *cis*-addition [56]. The Fe–Si bonds of the μ-diphenylsilanediyl iron carbonyl complex **3** were shown to readily react with alkynes; *cis*-silylation gave the structurally characterized disilaferracyclopentene complex **4** and diferrasilacycloheptadiene complex **5** (Eq. (3)) [57,58].

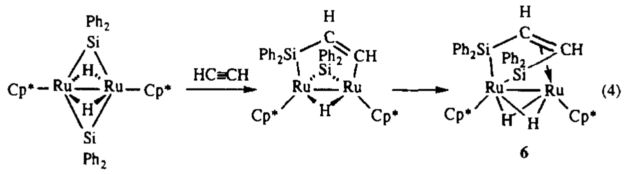


3 4 5

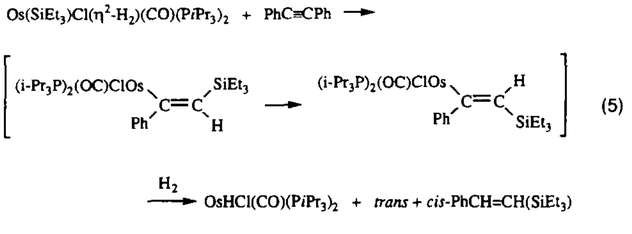
(3)

Insertion of coordinated $CH_2=SiMe_2$ into the Fe–Si bond of an intermediate was suggested by Pannell and co-workers to be responsible for the photochemically-induced rearrangement of $CpFe(CO)_2CH_2SiMe_2SiMe_3$ into $CpFe(CO)_2SiMe_2CH_2SiMe_3$. This was also observed in the case of the tungsten complex $CpW(CO)_3CH_2SiMe_2SiMe_3$ in the presence of PPh_3. The structure of the rearranged product $CpW(CO)_2(PPh_3)SiMe_2CH_2SiMe_3$ was established by X-ray diffraction [59].

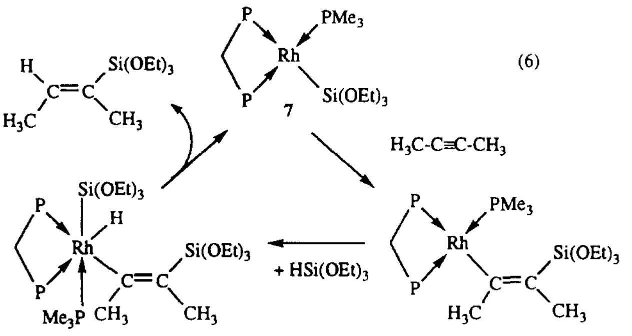
2.1.1.4. Into a Ru–Si bond. The reaction of the diruthenium complex $[(\eta\text{-}C_5Me_5)Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)]_2$ with an excess of acetylene was found to occur by selective insertion into the Ru–Si bond, the Ru–H bonds remaining intact (Eq. (4)). Reductive coupling between two bridging ligands then gave the 2,5-disilaruthenacyclopentene complex **6**, which was characterized by X-ray diffraction [60].



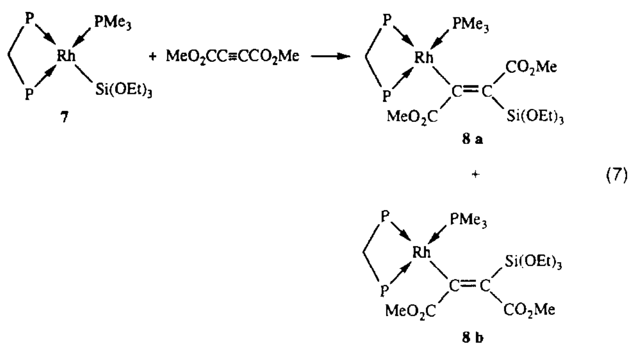
2.1.1.5. Into a Os–Si bond. The osmium complex $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$, which was the first example of a silyl dihydrogen metal complex, was shown to be an intermediate in the hydrosilylation of phenylacetylene with $HSiEt_3$ catalyzed by $Os(H)Cl(CO)(PiPr_3)_2$ (Eq. (5)) [61].



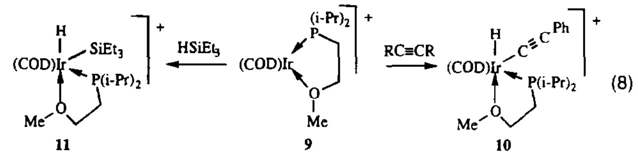
2.1.1.6. Into a Rh–Si bond. In order to account for the formation of a mixture of *cis*-1-(triethylsilyl)-1-hexene, *trans*-1-(triethylsilyl)-1-hexene (as a minor product) and the α-isomer in the Rh-catalyzed ($Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $RhCl(PPh_3)_3$) hydrosilylation of 1-hexyne with $HSiEt_3$, Ojima et al. proposed a mechanism involving an initial insertion of the alkyne into a Rh–Si bond and subsequent generation of a carbene-type zwitterionic rhodium complex as the key intermediate [62]. The structurally characterized complex $Rh[(t\text{-}Bu)_2PCH_2P(t\text{-}Bu)_2](PMe_3)Si(OEt)_3$ **7** efficiently catalyzes the hydrosilylation of but-2-yne in (*E*)-2-triethoxysilylbut-2-ene. This reaction involves insertion of the alkyne into the Rh–Si bond, as in the following cycle proposed by Hofmann et al. [63].



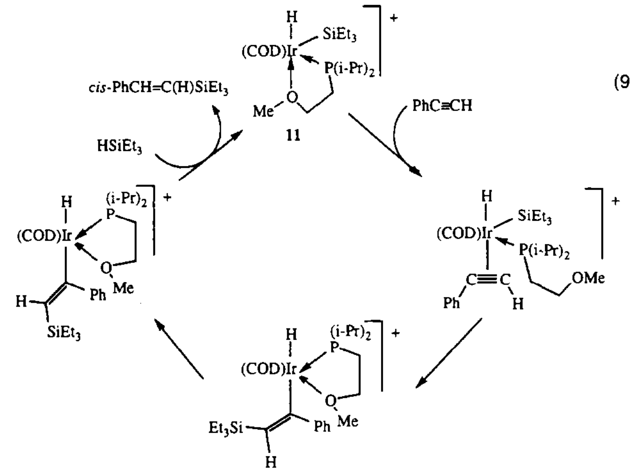
The insertion product **8** could be isolated when DMAD was used, and was shown to consist of two isomers differing in the vinyl stereochemistry (Eq. (7))



2.1.1.7. Into a Ir–Si bond. Insertion of PhC≡CH into the Ir–Si bond of Ir(III) and Ir(V) complexes accounts for their catalytic activity in the hydrosilylation of PhC≡CH with $HSiEt_3$. Interestingly, the thermodynamically less-stable *cis*-vinylsilane, formed by a net *anti*-addition of SiH to C≡C bond, was obtained with 99.2% selectivity [64]. More recently, the cationic Ir(I) complex **9**, containing a hemilabile phosphino ether ligand, was found to lead to Ir(III) complexes **10** and **11** in the presence of PhC≡CH and $HSiEt_3$ (Eq. (8)). These are key intermediates in the formation of $PhC{\equiv}CSiEt_3$ and *cis*-$PhCH=CH(SiEt_3)$ [65].

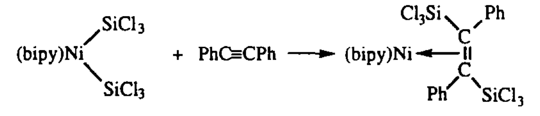


The following catalytic cycle was suggested to account for the formation of *cis*-PhCH=CH(SiEt$_3$).



(9)

2.1.1.8. *Into a Ni–Si bond.* The bis(trichlorosilyl)nickel(II) complex Ni(SiCl$_3$)$_2$(bipy) was found to react very readily with PhC≡CPh at room temperature in toluene to give the violet insertion product **12** (Eq. (10)) [66].



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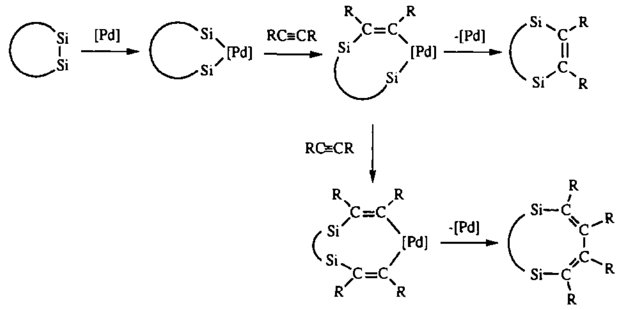
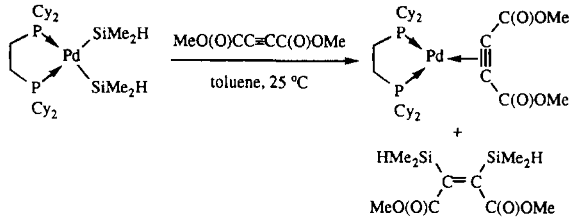
(10)

2.1.1.9. *Into a Pd–Si bond.* Silylpalladium complexes are believed to be key intermediates in a number of Pd-catalyzed transformation of organosilanes, such as hydrosilylation and bis-silylation (see above) of organic substrates, or the synthesis of enynes by the coupling of Me$_3$SiI, acetylenes, and acetylenic tin reagents [67]. For insertion of unsaturated hydrocarbons such as alkynes into Si–Si bonds, which is catalyzed by transition metals such as palladium, the proposed mechanism involves oxidative addition of the Si–Si bond to the palladium centre to give an intermediate with two Pd–Si bonds in which the alkyne could insert. Subsequent reductive elimination would yield the insertion product(s) (Scheme 3) [29,31,34,35,38,41,45,68].

Only few stable complexes containing a Pd–Si bond have been isolated, particularly in the case of non-chelating systems [28,43,69–72]. Their limited stability and high reactivity is of course responsible for their catalytic activity. The involvement of bis(silyl)palladium complexes in the above reactions is substantiated by recent studies which led to the preparation and first structural characterization of the stable complexes Pd(dcpe)(SiHRMe)$_2$ (R = H, Me) [72]. This allowed an investigation of their reactivity with alkynes (Eqs. (11) and (12)) [28,72].



Scheme 3.



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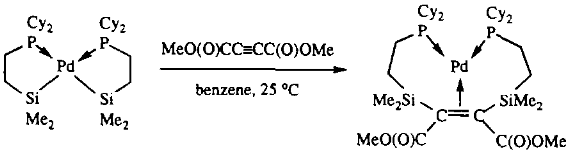

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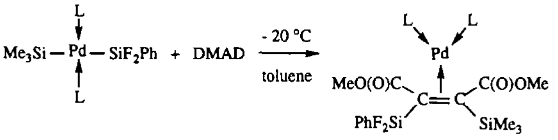
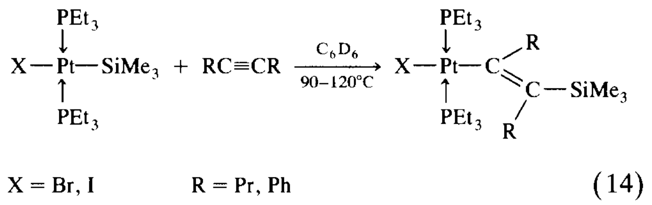


(13)

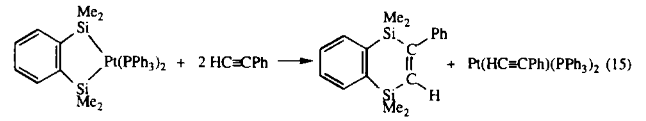
The complexes *trans*-[Pd(SiF$_2$Ph)$_2$L$_2$] are inactive towards bis-silylation, apparently owing to the strength of the Pd–SiF$_2$Ph bond. However, the bis(silyl) complex [Pd(SiF$_2$Ph)(SiMe$_3$)(PMe$_2$Ph)$_2$] was shown to react at −20 °C with PhC≡CPh to give the bis-silylation product in 82% yield. With the PMe$_3$ analog, reaction of DMAD afforded the structurally characterized Pd(0) complex of the bis-silylated olefin (Eq. (13)) [43]. These results strongly support the role of Pd–Si bonds in the catalytic bis-silylation of alkynes (and also olefins, see below). Insertion of alkynes into the Pd–Si bond of a Si–Pd–I unit was also recently suggested to be involved in a catalytic reaction [67].

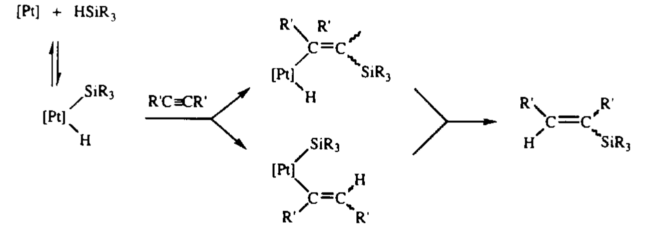
2.1.1.10. *Into a Pt–Si bond.* One of the first (if not the first) insertion reactions into a metal–silicon bond was reported by Chatt et al. in 1970 [73]; this work reported that that phenylacetylene inserts into the Pt–Si bond of *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$] in boiling benzene to give *trans*-[PtCl{$C_2HPh(SiPh_3)$}$(PMe_2Ph)_2$]. Although the exact structure of this substituted-vinyl complex was not established, that of the related *trans*-[PtBr{(E)-C(Ph)=C(Ph)$SiMe_3$}$(PEt_3)_2$] was recently determined by X-ray diffraction [74] (Eq. (14)).



(14)

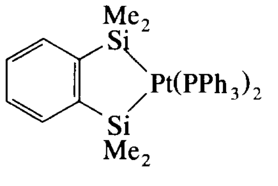
The C=C double bond and the $BrCPtP_2$ mean plane make a dihedral angle of 85.6°, and the bulky $SiMe_3$ group preferentially occupies a position opposite to the sterically demanding platinum moiety, accounting for the predominance of the (*E*) over the (*Z*) isomer. The greater reactivity of the iodo complex than of the bromo analog was attributed to the stronger *trans* influence of the iodide ligand. It was also found that the Pt–Si bond of *trans*-[PtBr($SiMe_3$)$(PEt_3)_2$] was much more reactive than the Pt–H bond of the related complex *trans*-[Pt(H)Br$(PEt_3)_2$] [74]. This suggests that the hydrosilylation of alkynes catalyzed by platinum complexes may proceed under certain conditions via insertion of the alkyne into the Pt–Si bond rather than the Pt–H bond (Scheme 4). Other studies have been reported on the reactivity of alkynes toward Si–Pt bonds [51,75–80].





Scheme 4.

Eaborn's bis (silyl) platinum complex **13** was shown to catalyze the dehydrogenative double silylation of PhC≡CH with *o*-bis(dimethylsilyl)benzene, the reaction proceeding by alkkyne insertion into a Pt–Si bond followed by reductive elimination [51,80,81].



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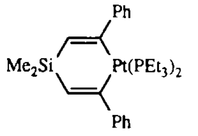
Similar reactions of palladium complexes have been examined recently (see Section 2.1.1.). On the other hand, reaction of the bis(silyl)complex *cis*-[Pt $(SiHMe_2)_2(PEt_3)_2$] with C_2Ph_2 (3 equiv., toluene, 60°C, 0.5 h) afforded the structurally characterized 4,4-dimethyl-2,6-diphenyl-1-platina-4-sila-2,5-cyclohexadiene complex **14**.



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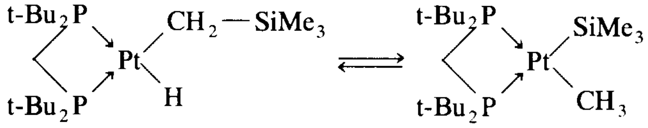
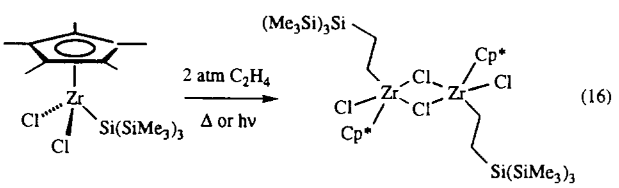
One of mechanisms discussed involved the (silylene) platinum species [$(Et_3P)_2Pt=SiMe_2$] [75].

Detailed mechanistic investigations have been carried out on reactions involving Pt compounds that are capable of activating C–Si bonds under mild conditions [82,83].



2.1.2. Insertion of alkenes

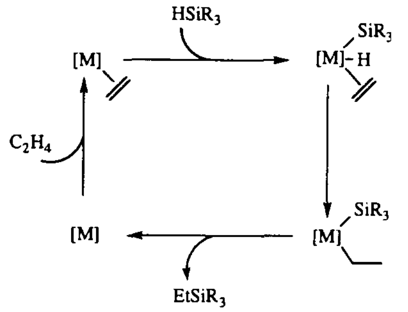
2.1.2.1. Insertion of monoenes. The silyl derivatives [(η-C_5Me_5)MCl_2{Si$(SiMe_3)_3$}] and [Cp(η-C_5Me_5)ZrCl{Si$(SiMe_3)_3$}] (M = Zr, Hf) undergo photochemically and thermally induced insertion reactions of C_2H_4 into the M–Si bond to give the corresponding β-silylalkyl complexes (Eq. (16)) [84].



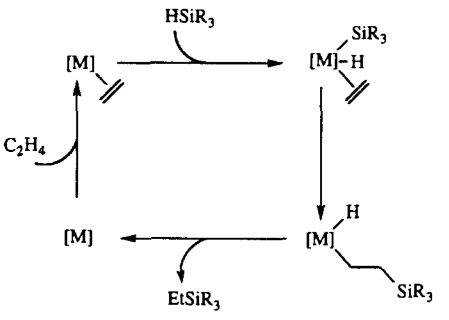
The hafnium derivative was found to react more sluggishly than its zirconium analog, to give the mononuclear [$Cp^*Cl_2HfCH_2CH_2Si(SiMe_3)_3$].

The insertion of alkenes into a metal-silicon bond represents a key step in the hydrosilylation of alkenes catalyzed by transition metals [6,9,10]. Although the Chalk-Harrod's mechanism for this reaction has been widely accepted [11,85] (Scheme 5) the fact that it does not account for the formation of alkenylsilanes, which are often observed as by-products [86–95], led to proposals of alternative mechanisms.

Insertion of the alkene into the metal–Si bond rather than the metal–hydrogen bond was suggested to take place [86,96] (Scheme 6).



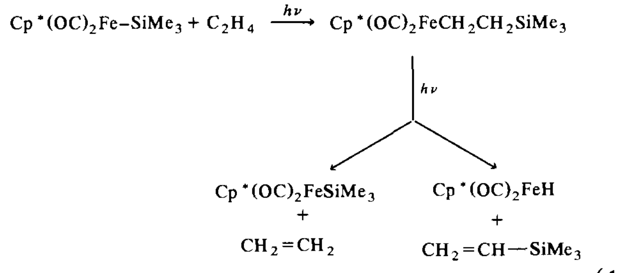
Scheme 5. Chalk-Harrod Mechanism of Alkene Hydrosilylation.



Scheme 6. Variant on Chalk-Harrod Mechanism for Hydrosilylation.

The β-silylalkyl complexes have been isolated (Eqs. (17), (18)) [55,97], providing good evidence for silyl migratory insertion reactions.

$$(OC)_5Mn{-}SiMe_3 + C_2F_4 \xrightarrow{h\nu} (OC)_5MnCF_2CF_2SiMe_3 \quad (17)$$

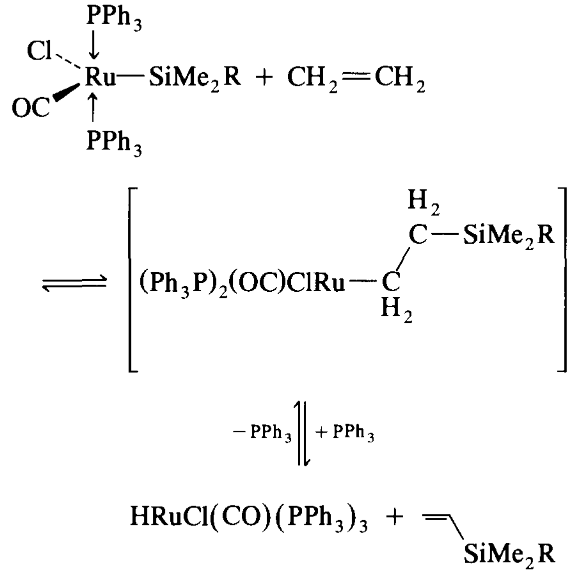


$$Cp^*(OC)_2Fe{-}SiMe_3 + C_2H_4 \xrightarrow{h\nu} Cp^*(OC)_2FeCH_2CH_2SiMe_3 \xrightarrow{h\nu} Cp^*(OC)_2FeSiMe_3 + CH_2{=}CH_2 \;\;/\;\; Cp^*(OC)_2FeH + CH_2{=}CH{-}SiMe_3$$

(18)

The reaction shown in Eq. (18) represented the first example of insertion of an unactivated olefin into a metal–silicon bond. Photolysis of the product resulted in β-elimination and β-$SiMe_3$ transfer, to yield vinylsilane and ethylene in a 2:1 ratio [97].

The Ru complex $RuCl(CO)(PPh_3)_2(SiMe_2R)$ (R = Me, OEt) reacts reversibly with ethylene to give the intermediate $RuCl(CO)(PPh_3)_2(CH_2CH_2SiMe_2R)$, which loses vinylsilane in the presence of PPh_3 [98].



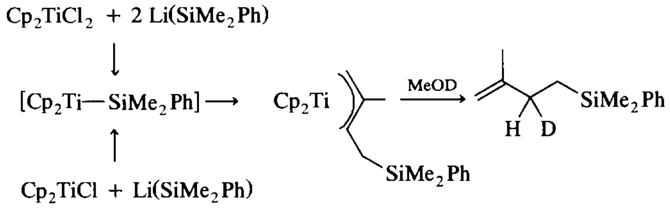
(19)

In subsequent studies with $Co(SiEt_3)(CO)_4$, which is an effective hydrosilylation catalyst, Wrighton concluded that ethylene insertion into the Co–Si bond was the rate determining step in a cycle that did not involve the formation of a metal olefin silyl hydride. This represented the first example of insertion of a non-actived olefin into the metal–Si bond of a catalytically active complex [96]. Further evidence has been obtained that insertion of alkenes into M–Si bonds can occur and be involved in hydrosilylation pathways (eg. Co [99], Rh [100] and Ir [64]).

Thorn and Harlow reported that ethylene inserts into the Rh–Si bond of $Rh(PMe_3)_3SiPh_3$ to give triphenylvinylsilane and unidentified rhodium compounds [101]. The complex $CpRh(C_2H_4)(SiR_3)H$ (R = Me, Et) reacted very slowly with ethylene to give $CpRh(C_2H_4)_2$ and $CpRh(C_2H_4)(CH_2{=}CHSiR_3)$ in a ratio of 2.5:1 [100,102].

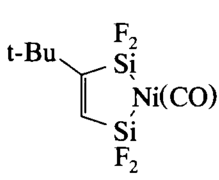
A new Si–C bond forming process was invoked for the transfer dehydrogenative coupling of $HSiEt_3$ catalyzed by complexes $(\eta^6\text{-arene})Ru(H)_2(SiEt_3)_2$ and $Cp^*Rh(H)_2(SiEt_3)_2$. Formation of the carbosilane dimer $H(Et)_2Si\text{-}CH(Me)\text{-}SiEt_3$ was attributed to a β-H elimination reaction to give a η^2-silene intermediate $Cp^*Rh(H)(SiEt_3)[\eta^2\text{-}Et_2Si{=}CH(Me)]$, followed by regioselective migration of another silyl ligand to the silene carbon [103].

2.1.2.2. *Reactions with polyenes.* Silylated π-allyltitanium intermediates were suggested to result from the insertion of 1,3-dienes into Ti(III)–Si species (Eq. (20)) [54].



(20)

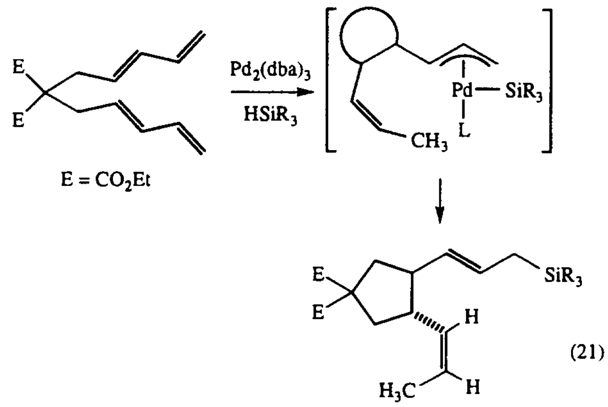
The disilametallacycle **15** obtained from $[Ni(CO)_4]$ and 3-*tert*-butyl-1,1,2,2 tetrafluoro-1,2-disilacyclobutene



15

was found to react with various conjugate dienes to give primarily products of 1,4-addition. Although these dienes would also react with the disilacyclobutene, the Ni mediation enhances the yield and selectivity under much milder conditions and the reaction procedes much faster than when mediated by $Fe(CO)_5$ or Group 6 metal carbonyls [104]. Similar reactions have also been mediated by Pd or Pt complexes, and again involve olefin insertion into metal–silicon bonds [38,45,46].

A nickel- or palladium-catalyzed carbocyclization of a tetraene substrate was reported which involved Si–C bond formation before product formation (Eq. (21)) [105].

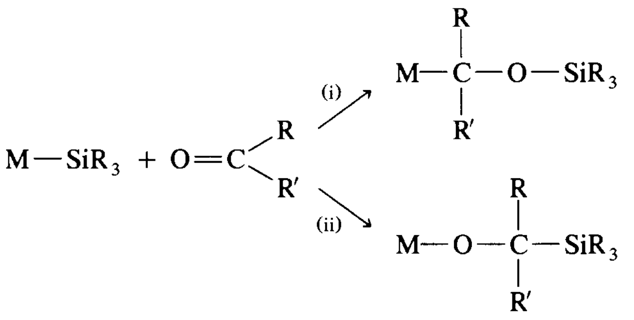


(21)

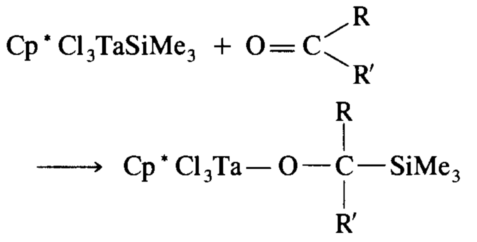
The 1,4-disilylation of 1,3-dienes by organodisilanes is catalyzed by platinum complexes. The intermediacy of species containing at least one Pt–Si bond is strongly suggested, although no stable complex could be isolated [49].

2.1.3. Insertion of organic carbonyl compounds

Reactions of aldehydes and ketones with metal silyl complexes $L_nM\text{-}SiR_3$ have led to a number of interesting transformations that are related to the hydrosilylation of carbonyl groups [106]. Although most reactions involve formation of a strong silicon–oxygen single bond (106–127 kcal mol^{-1}) [107,108] (path (i) in Scheme 7), and will therefore be considered in Section 2.3, examples of formation of a silicon–carbon bond have been discovered in the case of reaction involving complexes of tantalum, which is more oxophilic than silicon (path (ii) in Scheme 7) [109a]. The nucleophilic transfer of a silyl group from the metal to the carbonyl function observed in the insertion reaction of Eq. (22), was attributed to the $M^{\delta+}\text{–}Si^{\delta-}$ polarity of the d^0 transition metal–silicon bond.



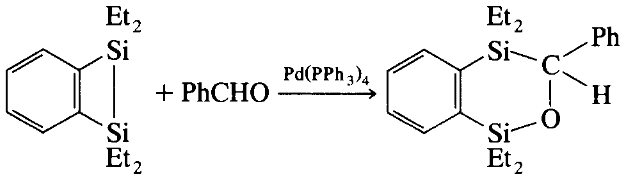
Scheme 7.



$$Cp^*Cl_3TaSiMe_3 + O{=}C(R)(R') \longrightarrow Cp^*Cl_3Ta{-}O{-}C(R)(R'){-}SiMe_3 \qquad (22)$$

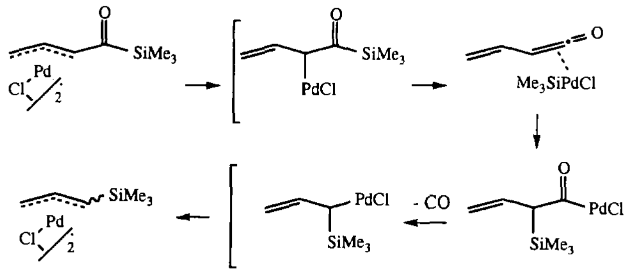
The Mg–Si bond of silicon analogues of Grignard compounds also react with ketones and enones with formation of an Si–C bond [109b].

Catalytic activation of disilanes has also been applied to bis-silylation of organic carbonyl compounds, as exemplified in Eq. 23 [42,110].



(23)

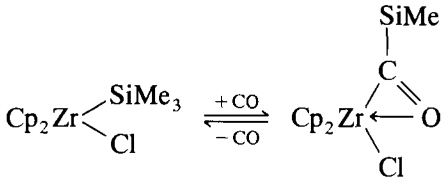
The decarbonylation of [(silylcarbonyl)allyl]palladium chlorides was suggested to involve ketene insertion into a Pd–Si bond (Scheme 8) [111].



Scheme 8.

2.1.4. Insertion of other molecules

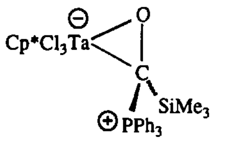
2.1.4.1. Insertion of CO. The first, reversible CO insertion into a M–Si bond was observed by Tilley for $Cp_2ZrCl(SiMe_3)$, which afforded the corresponding silaacyl complex [112].



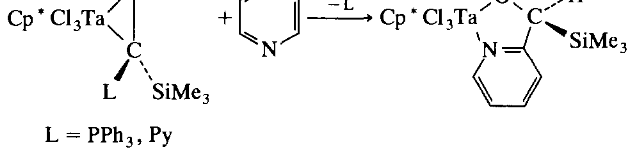
(24)

16

A crystal structure study of the silaacyl complex **16** confirmed the η^2-bonding mode of the carbonyl moiety. This resembles the situation found in the acyl derivatives. The corresponding $SiPh_3$ derivative was found to be indefinitely stable under an inert atmosphere [113]. Insertion of CO into the metal–silicon bond of the tantalum, zirconium and hafnium silyls $Cp^*Cl_3Ta\text{-}SiR_3$ and $Cp^*Cl_2M\text{-}SiR_3$ (M = Zr, Hf) gave unstable η^2-silaacyl derivatives which were characterized by low-temperature NMR studies (M = Zr, Hf) [114] or in the form of Lewis-base adducts, such as **17**.

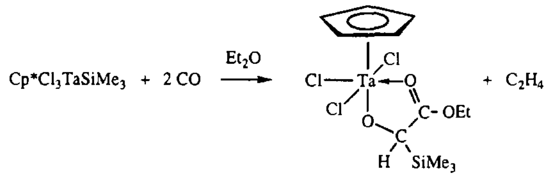


This indicates the strong electrophilic character of silaacyl carbonyl groups [115]. Insertion of the silaacyl carbon of the Ta and Hf complexes into an ortho C–H bond of pyridine has been observed to be a very facile process; an example is shown in Eq. (25) [114].



(25)

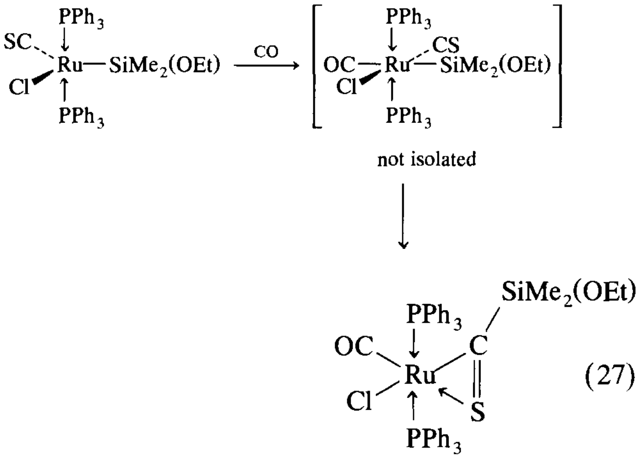
When the silaacyl tantalum complex was not stabilized by the added donor ligand L a complex reaction, involving a solvent molecule occurred to give **18** [116].



(26)

Use of ^{13}CO established that the chelate ring carbon atoms are derived from carbon monoxide.

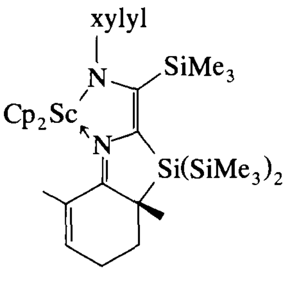
2.1.4.2. Insertion of CS. An instantaneous migratory insertion involving the silyl and thiocarbonyl ligands of $M[SiMe_2(OEt)]Cl(CS)(PPh_3)_2$ (M = Ru, Os) was observed upon addition of CO to these complexes [117]. This resulted in η^2-silathioacyl complexes, such as the structurally characterized **19**.



(27)

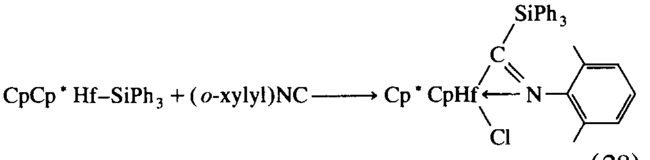
19

2.1.4.3. Insertion of CNR. Reaction of $Cp_2Sc[Si(SiMe_3)_3](THF)$ with CN(xylyl) led to insertion of the latter into the Sc–Si bond. The η^2-iminosilaacyl complex was isolated, and found to react further to give complex **20**, perhaps via a silene intermediate [118].



20

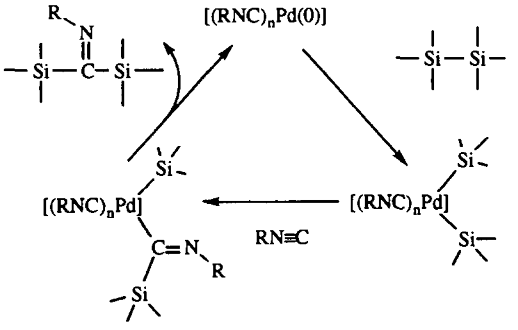
Complexes of Zr and Hf containing a η^2-iminosilaacyl ligand have also been obtained by insertion of *o*-xylylisonitrile into d^0 Zr–Si and Hf–Si bonds [113].



(28)

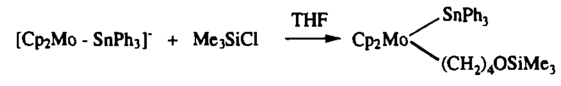
Related η^2-iminosilaacyl zirconium complexes, prepared in situ by reaction of the Zr–silyl complex $Cp_2ZrCl[Si(t\text{-}Bu)Ph_2]$ with arylisonitriles, were shown to give an azazirconacyclopentene upon treatment with a metal hydride followed by addition of an alkyne [113b].

The palladium-catalyzed insertion of aromatic isonitriles into the silicon–silicon linkages of oligosilanes to yield oligo(silylimines) (Scheme 9) is suggested to involve an insertion step of RNC into the Pd–Si bond of an intermediate [119]. A similar catalytic cycle was proposed for the Pd(0)-mediated insertion of isonitriles into the silicon–tin bond of organosilylstannanes, which affords organosilyl(*N*-substituted imino)stannanes [120].



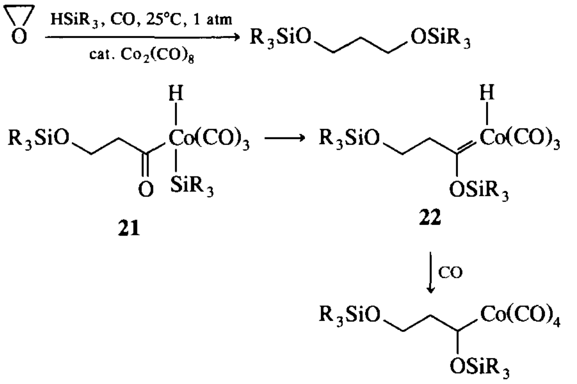
Scheme 9.

2.1.4.4. Insertion of cyclic ethers. Complexes of the type $Me_3Si\text{-}Mn(CO)_5$ react with epoxides and cyclic ethers in a regioselective manner to give (siloxy)alkylmanganese pentacarbonyl complexes. They can undergo subsequent insertion reactions with alkenes or alkynes to afford manganacycles, which can be demetalated photochemically [121]. Tetrahydrofuran may undergo ring opening and insert into a silicon transition-metal bond. This leads to the formation of siloxy derivatives, and is one of the reasons why Et_2O is often a preferred solvent in this chemistry. A recent such example [122] is shown in Eq. (29):



$$[Cp_2Mo\text{-}SnPh_3]^- + Me_3SiCl \xrightarrow{THF} Cp_2Mo\begin{matrix} SnPh_3 \\ (CH_2)_4OSiMe_3 \end{matrix} \qquad (29)$$

More recently, it has been found that $Co_2(CO)_8$ catalyzes the reaction of cyclic ethers with hydrosilanes and CO [123].



(30)

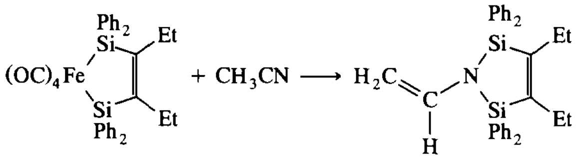
21 **22** **23**

The 1,3-migration of silicon in **21**, followed by insertion of the carbene ligand into the H–Co bond would lead to the α-siloxyalkyl cobalt complex **23**. Related silicon migration reactions will be examined below.

2.2. Formation of a Si–N bond

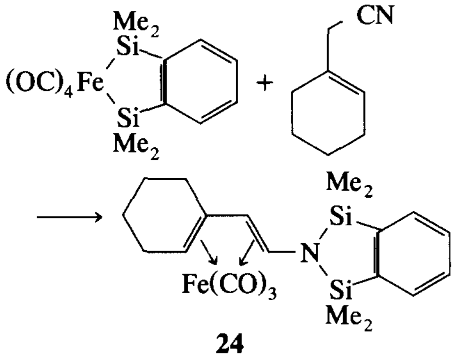
2.2.1. Insertion of organic nitriles

Disilylated iron complexes react photochemically with organic nitriles to give disilylated enamines in high yield [57,124].



(31)

In some cases, the iron carbonyl moiety is retained, as in **24** [124].

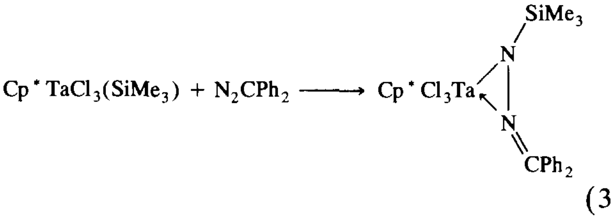


24

(32)

2.2.2. Insertion of diazo compounds

Diphenyldiazomethane inserts into the Ta–Si bond of $Cp^*TaCl_3(SiMe_3)$ (Eq. (33)) [109]:

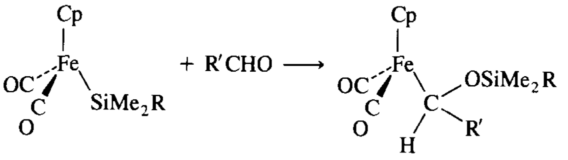


(33)

2.3. Formation of a Si–O bond

2.3.1. Insertion of organic carbonyl compounds

The photochemical reaction of iron–silyl complexes $CpFe(CO)_2(SiMe_2R)$ with aromatic aldehydes yielded α-siloxy iron complexes (Eq. (34)) [125]:



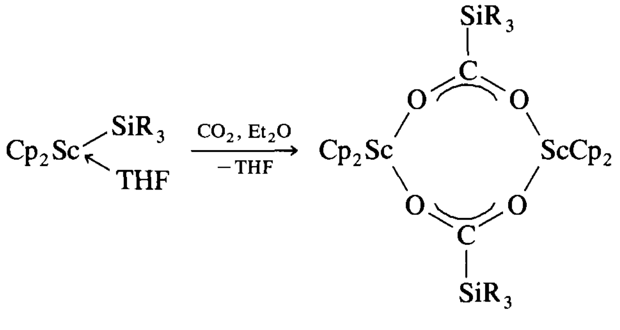
(34)

Such species are believed to be key intermediates in the photochemical hydrosilylation of aldehydes catalyzed by $CpFe(CO)_2Me$ or $CpFe(CO)_2[C(O)Me]$ [126]. The work carried out by Gladysz in this area has been reviewed previously [106].

Reaction of $HSiMe_3$ with $CpFe(CO)_2R$ was suggested to lead to a hydrido, acyl silyl intermediate which rearranged to an iron–silyl complex containing an η^2-coordinated RCHO. This was suggested to preceed the insertion into the Fe–Si bond, resulting in the formation of α-(metallooxy)alkyl) species $[CpFe(CO)_2\{CH(R)(OSiMe_3)\}]$, which then undergo elimination of the corresponding silyl enol ether [126].

2.3.2. Insertion of CO_2

Reaction of CO_2 with d^0 Sc–Si complex $Cp_2Sc(SiR_3)(THF)$ rapidly yields the dimeric silylcarboxylate insertion product **25** [127] (Eq. (35)).

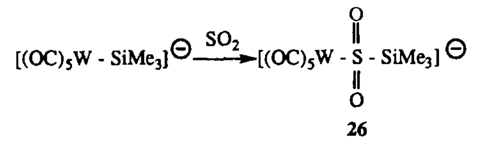


25

(35)

2.3.3. Insertion of SO_2

The first reported example of SO_2 insertion into a transition metal–silicon bond was found with $[PPN][W(CO)_5(SiMe_3)]$ (Eq. (36)). Infrared data for the product are consistent with a sulfinato-S complex **26**. Note than the less electrophilic CO_2 failed to react [128].



$$[(OC)_5W-SiMe_3]^{\ominus} \xrightarrow{SO_2} [(OC)_5W-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-SiMe_3]^{\ominus} \quad (36)$$

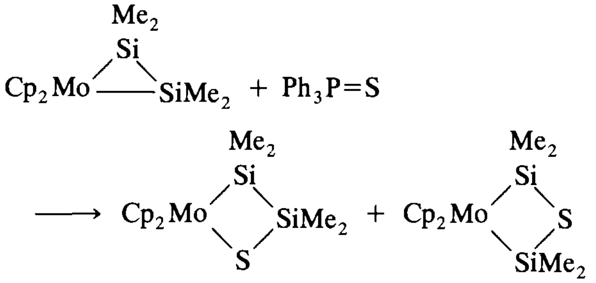
26

2.3.4. Insertion of O_2

The siloxide complex $Cp_2Zr(OSiMe_3)Cl$ resulted from the rapid, exothermic reaction of $Cp_2Zr(SiMe_3)Cl$ with dry oxygen [129].

2.4. Formation of a Si–S bond

Whereas reaction of elemental S with $Cp_2Mo(\eta^2\text{-}SiMe_2)_2$ occurs with insertion of a S atom into the Si–Si bond, that with $Ph_3P{=}S$ occurs predominantly by formal insertion of the S atom into the Mo–Si bond (Eq. (37)). The mechanism suggested involves zwitterionic intermediates [130].



(37)

3. Migration reactions

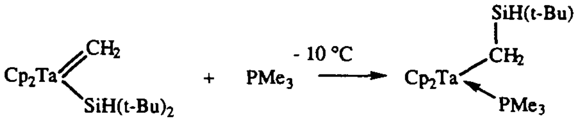
The classification into insertion and migration reactions is somewhat arbitrary and generally has no mechanistic implications. Many insertion reactions discussed above could also be viewed as resulting from the migration of a silicon-containing ligand onto a coordinated molecule. However, we have adopted the terminology generally used by the authors in refering to their reactions.

As indicated in Section 1, reactions in which the metal originally bound to Si is lost in the reaction will not be examined here in detail, although they often illustrate unique properties of the M–Si bond [131].

3.1. Formation of a Si–C bond

3.1.1. Silyl migration onto an alkylidene

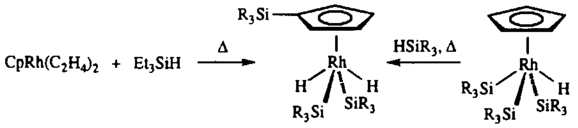
Even at −10°C, facile migration of a silyl group from tantalum to an alkylidene was observed (Eq. (38)) [132]. A comparative study showed that the order of migratory aptitude in the $Cp_2Ta({=}CHR)(X)$ system is $X = H > SiH(^tBu)_2 \gg Ph > Me$.



(38)

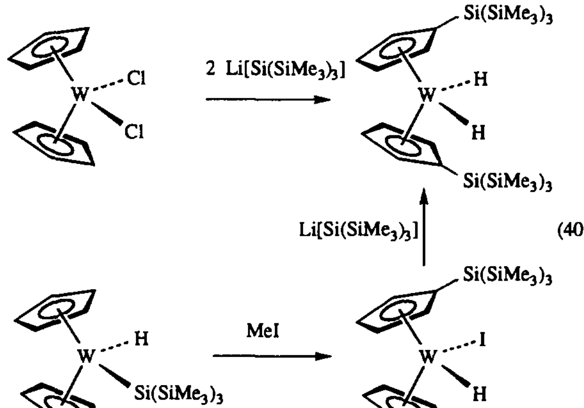
3.1.2. Silyl migration onto a Cp-type ligand

The thermal reaction of $CpRh(C_2H_4)_2$ with $HSiEt_3$ at 383 K affords $(\eta\text{-}C_5H_4SiR_3)Rh(H)_2(SiR_3)_2$ (R = Me, Et), which is also formed by thermal activation of $CpRh(H)(SiR_3)_3$ in the presence of an excess of silane [133] (Eq. (39)).



(39)

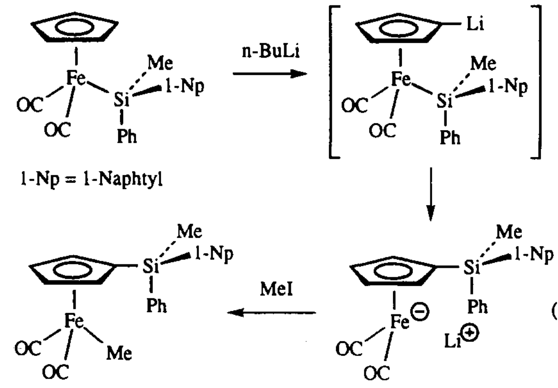
Upon treatment of Cp_2WCl_2 with $Li[Si(SiMe_3)_3]$ the structurally characterised tungstenocene dihydride $[C_5H_4Si(SiMe_3)_3]_2WH_2$ was rapidly formed (Eq. (40)). Some steps in the formation of $[C_5H_4Si(SiMe_3)_3]_2WH_2$ can be performed individually. The silyl complex $Cp_2W(H)Si(SiMe_3)_3$, which is obtained from $Cp_2W(H)Cl$ and $Li[Si(SiMe_3)_3]$, reacts with methyliodide to give the ring-substituted product $Cp[C_5H_4(SiMe_3)_3]W(H)I$. A base-induced rearrangement was excluded for this transformation [134,135].



(40)

In the examples given above, no proton-abstracting agent was required. In general, deprotonation of the Cp ring occurs first and is followed by intramolecular migration of the metal-bound silyl group.

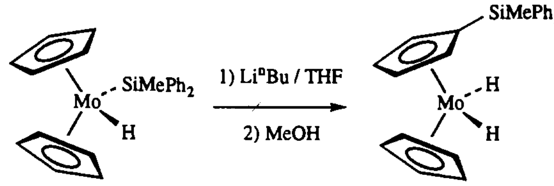
The base-induced silyl group migration in $CpFe(CO)_2SiR_3$ was shown to occur with retention of configuration at the Si atom, which emphasizes the analogy between this intramolecular organometallic [136,137] reaction and the Brook-type rearrangement (Eq. (41)).



(41)

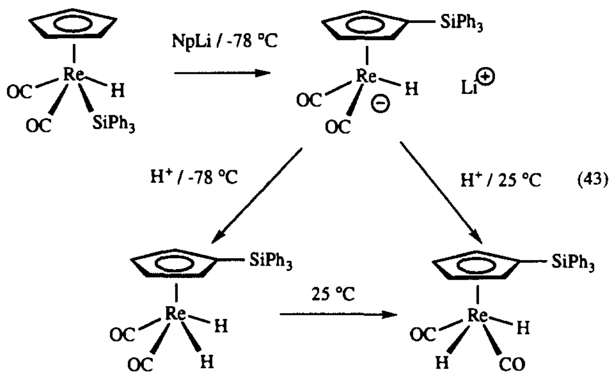
A similar migration sequence has been observed upon base-treatment of $CpRu(CO)_2SiMe_3$ [138]. An anionic shift of the aminosilyl group from iron to the η^5-Cp ring of $CpFe(CO)_2\text{-}SiMe_2NMe_2$ was observed by Malisch and co-workers [139]. Similar reactions were reported by Pannell's group with the iron complex $CpFe(CO)_2SiMe_2CH_2SiMe_3$ [59], and extended to the migration of silyl and oligosilyl ligands in η^5-indenyl iron complexes [140].

Treatment of $CpW(CO)_3CH_2SiMe_2SiMe_3$ with LDA and MeI led to $[\{\eta^5\text{-}(SiMe_3CH_2SiMe_2)C_5H_4\}W(CO)_3Me$. The silyl group migration occurs with a rearrangement that involves the cleavage of the Si–Si bond of the disilyl ligand [59]. Reaction of $Cp_2Mo(H)(SiMePh_2)$ with n-butyllithium in THF, followed by addition of methanol, afforded $[\eta\text{-}(MePh_2Si)C_5H_4]CpMo(H)_2$ as a result of silyl migration from Mo to Cp [122].



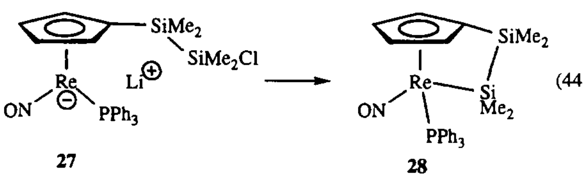
(42)

Upon addition of neopentyllithium to $CpRe(H)(CO)_2(SiPh_3)$ and subsequent acidification, either of the dihydride complexes *cis*- and *trans*-$[\eta^5\text{-}C_5H_4SiPh_3]Re(H)_2(CO)_2]$ can be obtained, depending on the reaction conditions as shown in Eq. (43) [141].



(43)

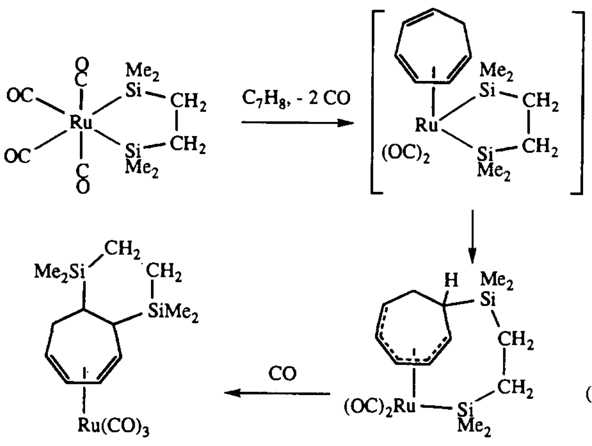
The Re disilyl complex CpRe(NO)(SiMe$_2$SiMe$_2$Cl)(PPh$_3$) was transformed into (C$_5$H$_4$Li)Re(NO)(SiMe$_2$SiMe$_2$Cl)(PPh$_3$) as a result of deprotonation with *n*-BuLi/TMEDA. After a slow silatropic shift to give **27**, a subsequent cyclization gave the final disilametallacycle **28** [142].



27 **28** (44)

3.1.3. Silyl migration onto other hydrocarbyl ligands

A number of reactions have been performed with mono- and dinuclear ruthenium carbonyl trimethylsilyl complexes containing cyclic polyolefins during which migration of the silyl ligand from the metal to this ligand was observed [143–146]. Some of the products have been structurally characterized [147].



(45)

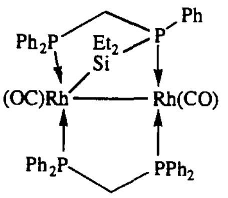
3.2. Formation of a Si–N bond

The reaction of NMe$_3$ with the silylcobalt complex (Me$_3$Si)Co(CO)$_4$ afforded the silylammonium compound [Me$_3$SiNMe$_3$]$^+$[Co(CO)$_4$]$^-$ [148].

3.3. Formation of a Si–P bond

The silylphosphonium compound [Me$_3$SiPMe$_3$]$^+$[Co(CO)$_4$]$^-$ was formed immediately by reaction of (Me$_3$Si)Co(CO)$_4$ with PMe$_3$. Similar reactions were observed with the corresponding ethyl derivatives [148], and with other phosphine ligands. However, it was noted that reaction of phosphines with silylcobalt tetracarbonyls to give silylphosphonium compounds is not a general process for all phosphines or all silyl cobalt tetracarbonyls [149].

Reaction of the dinuclear complex Rh$_2$(μ-H)$_2$(μ-dppm)$_2$(CO)$_2$ with Et$_2$SiH$_2$ led to the unusual complex **29**, which results from cleavage of one phenyl group of a dppm ligand and formation of a P–Si bond [150].



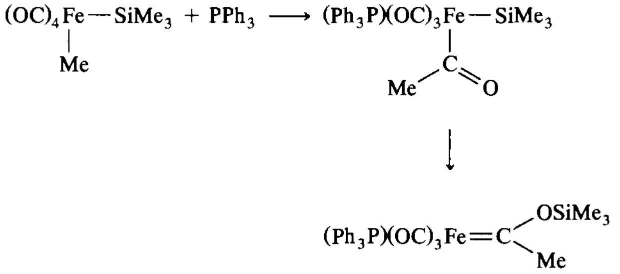
29

It appears reasonable to assume that formation of an intermediate containing a Rh-SiEt$_2$H or a Rh$_2$(μ-SiEt$_2$) moiety is formed before elimination of benzene.

3.4. Formation of a Si–O bond

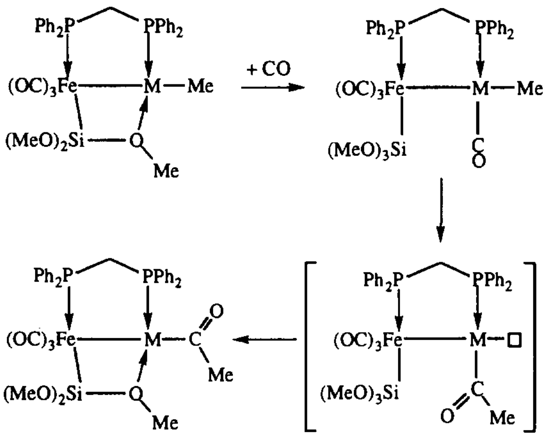
The first example of metal to oxygen migration of an SiR$_3$ group was reported in 1973 by MacDiarmid and co-workers [151]. Under thermal conditions, Me$_3$SiOCCo$_3$(CO)$_9$ and (Me$_3$SiOC)$_4$Co$_2$(CO)$_4$ were formed as a result of migration of the SiMe$_3$ group to the oxygen of a carbonyl group. Related observations have been made with chlorosilanes, although Co(SiCl$_3$)(CO)$_4$ is stable in ether solvents, in contrast to Co(SiMe$_3$)(CO)$_4$. The siloxy cluster Cl$_3$SiOCCo$_3$(CO)$_9$ therefore had to be prepared by reaction of SiCl$_4$ with [Co(CO)$_4$]$^-$ [152].

Treatment of the iron–silyl complex *cis*-[Fe(Me)(SiMe$_3$)(CO)$_4$] with PPh$_3$ afforded the (siloxy)carbene complex (Ph$_3$P)(OC)$_3$Fe=C(Me)(OSiMe$_3$). It was assumed that the reaction involved an intermediate acyl complex, which would then undergo a 1,3-silatropic shift [153].



$$(OC)_4Fe(Me)-SiMe_3 + PPh_3 \longrightarrow (Ph_3P)(OC)_3Fe(C(O)Me)-SiMe_3 \longrightarrow (Ph_3P)(OC)_3Fe{=}C(OSiMe_3)(Me) \qquad (46)$$

Siloxycarbene intermediates have been invoked for the reaction of iron [126] or cobalt [154,155] acetyl complexes with monohydrosilanes. It has also been postulated that an intermediate containing a metal–silyl bond was involved in the ruthenium-catalyzed reaction of 1,6-diynes with HSiR$_3$ and CO leading to catechol



30 M = Pd
31 M = Pt

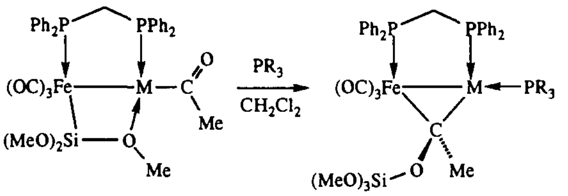
Scheme 10.

derivatives (silyl migration to a coordinated CO molecule) [156].

Bridging siloxycarbene intermediates were suggested in the hydrosilylation of organoiron acyl complexes catalyzed by Mn carbonyl complexes but they could not be isolated [157].

More recently, stable, bridging siloxycarbene complexes were isolated in the course of studies of Fe–Pd and Fe–Pt bimetallic complexes. Carbonylation of the heterobimetallic alkyl complexes $(OC)_3Fe[\mu\text{-}Si(OMe)_2(OMe)](\mu\text{-dppm})MMe$ (M = Pd, Pt) afforded the stable acyl complexes $(OC)_3Fe[\mu\text{-}Si(OMe)_2(OMe)](\mu\text{-dppm})M[C(O)Me]$ (M = Pd **30**, M = Pt **31**) in which the acyl ligand is trans to the metal–metal bond [158,159]. This was rationalized by assuming that opening of the μ–Si–O bridge liberates a vacant coordination site which is then occupied by CO to give (in the case of Pt) the spectroscopically characterized CO adduct $(OC)_3[(MeO)_3Si]Fe(\mu\text{-dppm})Pt(CO)(Me)$ (Scheme 10). Subsequent *cis*-migration of the methyl group would result in a complex with the acyl ligand trans to phosphorus. The very fast isomerization leading to **30** and **31** must be driven, at least in part, by the tendency to re-establish the μ–Si–O bridge.

Upon addition of one equivalent of PR_3 to a CH_2Cl_2 solution of $(OC)_3Fe[\mu\text{-}Si(OMe)_2(OMe)](\mu\text{-dppm})Pt[C(O)Me]$ **31** a phosphine induced silyl shift occurred, leading to the μ-siloxycarbene complexes $(OC)_3Fe[\mu\text{-}C(Me)OSi(OMe)_3](\mu\text{-dppm})Pt(PR_3)$ **32** in nearly quantitative yield (Eq. (47)) [160]. The basicity of the PR_3 ligand seems to have a more important effect than its cone angle on the rate of this transformation. IR monitoring revealed that the reaction with PEt_3 was complete within ca. 20 min, whereas in the case of $P(OMe)_3$, even in a slight excess, more than 1 h was needed. With $AsPh_3$ (in a slight excess) no reaction was observed even after 3 h. The more labile palladium derivatives **33** were obtained analogously in high yields from the reactions of **30** with PR_3 (Eq. (47)).

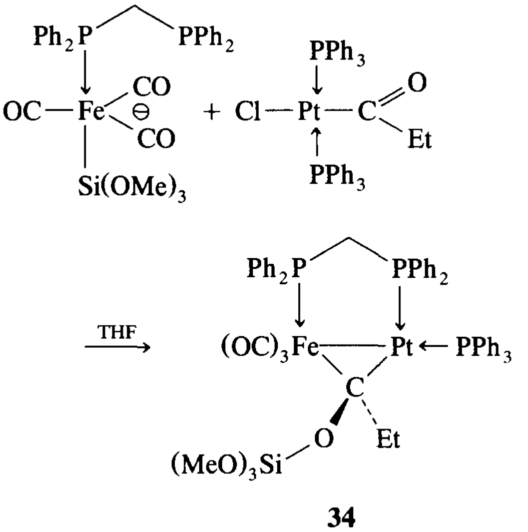


(47)

30 M = Pd
31 M = Pt

33 M = Pd
32 M = Pt

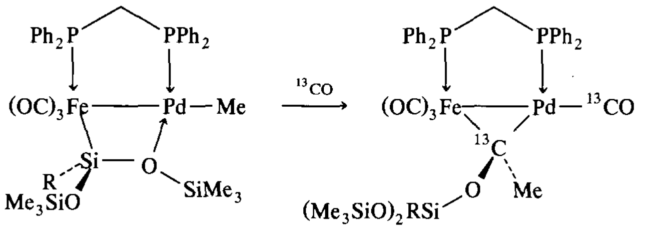
Evidence that the C–O unit found in the carbene ligand originated from the acyl group was provided by a ^{13}C labelling experiment. There are two possible roles for the phosphine ligand: (i) it may render the acyl oxygen more electron-rich, thus favouring Si-migration; (ii) it may stabilize the acyl ligand in a *cis* position with respect to the metal–metal bond long enough to allow Si-migration to occur. Conversely, the absence of Si-migration during the synthesis of **30** and **31** (Scheme 10) would be due to the preferred μ–Si–O bridge formation. This isomerization must be very rapid since it could not be observed spectroscopically. Complex **34**, which was structurally characterized, was also made by reaction of the metalate $K[Fe\{Si(OMe)_3\}(CO)_3(\eta^1\text{-dppm})]$ with *trans*-$[PtCl(COEt)(PPh_3)_2]$ (Eq. (48)) [160].



(48)

34

Unexpectedly, the outcome of the carbonylation of the siloxyl complexes **35**, prepared from their chloro precursors differed markedly from that of the $Si(OMe)_3$-derivative. After a solution of **35** had been purged for 5 min with CO, the heterobimetallic siloxycarbene-bridged complex $(OC)_3Fe(\mu\text{-}C[OSi(OSiMe_3)_3]Me)(\mu\text{-dppm})Pd(CO)$ **36** was formed in quantitative yield (Eq. (49)) [161]. Again, labelling studies shared that the carbene carbon came from a CO molecule.



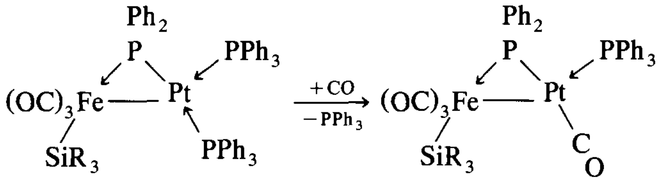
35a, R = OSiMe$_3$ **36a**, R = OSiMe$_3$

35b, R = Me **36b**, R = Me

(49)

3.5. Formation of a Si–Metal bond

Intermolecular transfer of a silyl ligand from one metal to another provides a well-known method for the synthesis of transition metal silyl complexes by use of reagents like Hg(SiMe$_3$)$_2$ or Cd(SiF$_3$)$_2$ [71,162,163]. However, the first, fully characterized intramolecular migration reaction of a silyl ligand from one metal to another was reported in 1992 in the course of studies of reaction of iron–platinum complexes containing a three electron donor μ_2-diaryl(or dialkyl)phosphido bridging ligand. When CO was bubbled through a solution of a complex **37**, selective substitution of the PPh$_3$ ligand trans to the phosphido-bridge occurred, leading to **38**. This was followed by an unexpected, quantitative rearrangement in solution to the isomeric **39**, in which the Si atom is now bonded to Pt, the Pt-bound CO ligand having migrated to the Fe centre (Eq. (50)) [164].

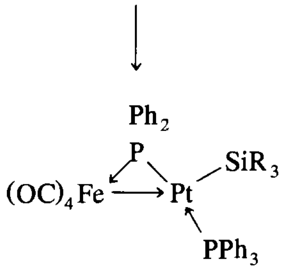


37a, R = OMe **38a**, R = OMe

37b, R$_3$ = Me$_2$Ph **38b**, R$_3$ = Me$_2$Ph

37c, R$_3$ = MePh$_2$ **38c**, R$_3$ = MePh$_2$

37d, R = Ph$_3$ **38d**, R = Ph$_3$



39a, R = OMe

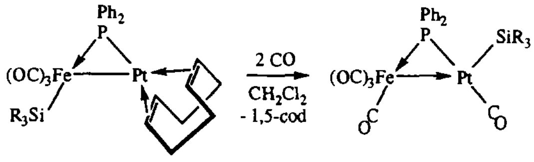
39b, R$_3$ = Me$_2$Ph

39c, R$_3$ = MePh$_2$

(50)

The result of this dyotropic-type rearrangement was established by the X-ray structure analysis of **39a**. 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, the migration is complete within ca. 1 h, whereas for the SiMe$_2$Ph group ca. 5 h are required, and for the even bulkier SiMePh$_2$ group more than 1 day was needed. The SiPh$_3$ derivative **38d**, which was also structurally characterized, did not rearrange [165a].

However, carbonylation of the more reactive 1,5-cod complexes [(OC)$_3$(R$_3$Si)Fe(μ-PPh$_2$)Pt (1,5-cod)] **40** [165b] yielded the isomeric complexes (OC)$_4$Fe(μ-PPh$_2$)Pt(CO)(SiR$_3$) **41** within minutes, irrespective of the nature of the SiR$_3$ ligand: even SiPh$_3$ was found to migrate from iron to platinum (Eq. (51)).

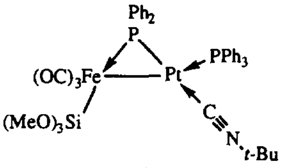


40a, R = OMe **41a**, R = OMe

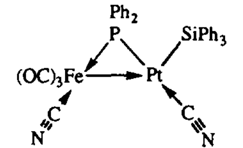
40d, R = Ph **41d**, R = Ph

(51)

The possibility of inducing silyl migration in the phosphido-bridged complexes **37** by use of isonitriles instead of CO was examined, but no evidence for it was found, irrespective of the nature of the SiR$_3$ group and of the stoichiometry or steric and electronic nature of the various isonitriles used. Instead, stereoselective phosphine substitution occurred, to give **42**. However, the enhanced reactivity of the 1,5-cod complexes **40** allowed the silyl transfer of a Fe-bound SiR$_3$ group to the adjacent platinum center to take place under mild conditions: addition of two equivalents of t-BuNC afforded (OC)$_3$(t-BuNC)Fe(μ-PPh$_2$)Pt(CN-t-Bu)(SiR$_3$) (**43**) [166].

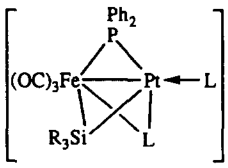


42



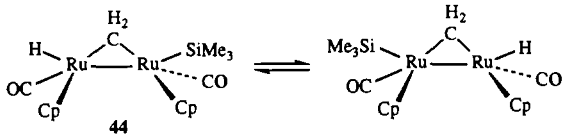
43

The study of the CO-induced silyl migration reaction in a 1:1 mixture of complexes **40a** and (OC)$_3$(Ph$_3$Si)-Fe(μ-PCy$_2$)Pt(1,5-cod) revealed that only **41a** and (OC)$_4$Fe(μ-PCy$_2$)Pt(SiPh$_3$)(CO) were formed. This indicates that the silyl transfer reaction occurs in an intramolecular manner. An intermediate (or transition state) possessing a bridging μ-SiR$_3$ group could account for this mutual ligand exchange.



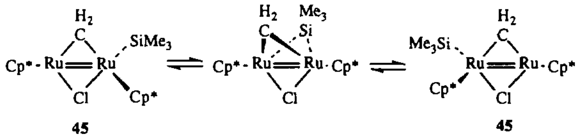
Unusual bridging bonding modes for an SiR_3 group have already been structurally established for a pentaborane [167] and more recently for the polynuclear copper complex $[Li(THF)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2$ [168].

Interestingly, in recent studies by Akita et al. and Girolami and co-workers [169,170] on dinuclear $SiMe_3$-substituted Ru–Ru complexes **44** and **45**, it was concluded that the silyl ligand could reversibly flip from one metal centre to another via a μ_2-SiR_3 intermediate.

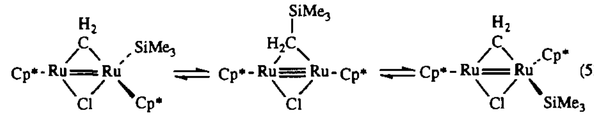


(52)

Girolami's diruthenium complex **45** shows dynamic behaviour that involves reversible migration of the silyl group between the two Ru centers at low temperatures (Eq. (53a)) and reversible migration to the bridging methylene group in the high-temperature dynamic process (Eq. (53b)) [170].

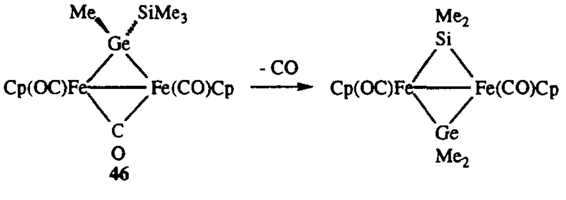


(53a)



(53b)

The germylene-bridged complex $[CpFe(CO)]_2(\mu$-$CO)[\mu$-$Ge(Me)SiMe_3]$ **46** undergoes slow transformation to a mixture of the *cis* and *trans* isomers of the doubly bridged germylene silylene complex $[CpFe(CO)]_2(\mu$-$SiMe_2)(\mu$-$GeMe_2)$ (Eq. (54)). This transformation involves rupture of the Si–Ge bond and formation of a Fe–Si bond [171].



(54)

Acknowledgements

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