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Versatile Silylphosphine Ligands for Transition Metal Complexation

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<http://dx.doi.org/10.5772/intechopen.73502>

Abstract

In this chapter, a review throughout the literature on the chemistry of multidentate silylphosphines is presented. The incorporation of P and Si functionalities in cooperation in a single ligand backbone is exceptionally versatile, and examples of this rich chemistry stemming from the works of many research groups around the world are herein provided. The ligand systems can be flexible or rigid and incorporate varying numbers of P, Si and even other atoms. Exceptional ligand-metal systems are discussed in terms of their structure, reactivity and, in some cases, catalytic activity.

Keywords: silicon, phosphorous, silylphosphines, transition metals, multidentate ligands

1. Introduction

In modern Coordination and Organometallic Chemistry, ligand design is recognised as crucial for the development of efficient and selective complexes for important transformations including medicinal chemistry, material science and catalysis. Polydentate-rigid or semi-rigid ligands constrain the geometry at the metal centre providing inherently well-defined coordination geometries for potential incoming substrates. Indeed, a good number of these metal-ligand systems are capable of performing selectively difficult activations and many research groups around the world have directed their endeavours to the study of their chemical properties.

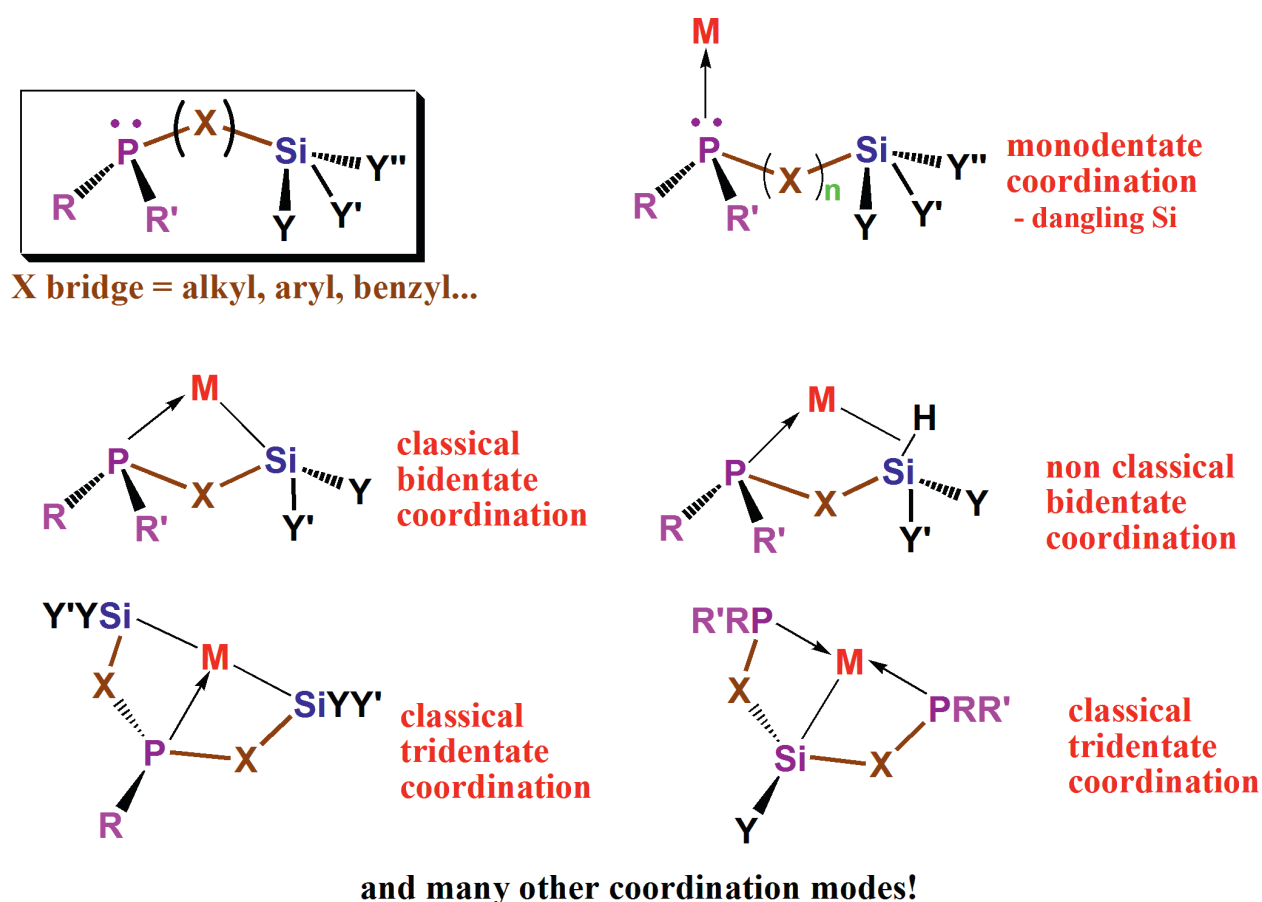
The incorporation of dual functionalities in a single ligand backbone has also been shown to modify the properties of the compounds making them especially prone to undergo selective

transformations resulting from differing reactivity of the coordinating atoms in the ligand. A wide variety of combinations of donor atoms have been employed to date, including for example, soft and hard donor atoms in what is known as hemilabile ligands.

In this chapter, the chemistry related to silylphosphine ligands which include in their structure both a basic P as well as a Si is reviewed. Si derivatives are exceptionally good sigma donors and exert a considerably high *trans*-influence/effect, thus their coordination generates electron rich metal centres in turn capable of activating otherwise inert substrates. Phosphines have long been preferred ligands due to their ability to tune their steric and electronic properties depending on the substituents on P. The incorporation of P and Si in a ligand framework also allows for the employment of NMR spectroscopic tools deriving from ^{31}P and ^{29}Si nuclei.

2. Silylphosphine ligands: definition, general structure and bonding

Silylphosphines can be described as bi- or polydentate ligands bearing at least one basic phosphorous (III) atom, usually a phosphine PR_3 or phosphite $\text{P}(\text{OR})_3$, and at least one silicon-substituted



Scheme 1. General structure of silylphosphine ligands and examples of main coordination modes.

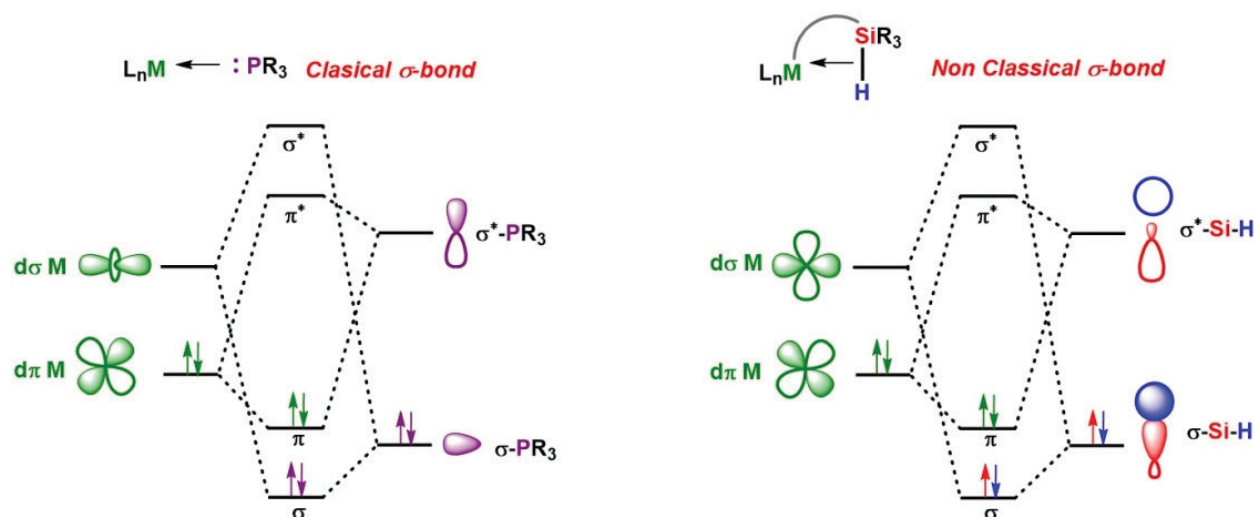


Figure 1. Molecular orbital diagrams of the phosphine and non-classical Si–H sigma moieties.

moiety. The P (III) group is able to form a coordination bond to the transition metal, while the silyl moiety is potentially prone to bind by means of loss of H_2 , alkane or arene molecules. Between the P and Si atoms, there are generally a number of carbon atoms in the form of an alkyl or aryl bridges (**Scheme 1**). Else a direct P–Si bond can be established. Silylphosphines are potentially bi-, tri- or polydentate ligands, the coordination number depending on the number of P or Si moieties present in the ligand backbone.

Therefore, the molecular orbitals can be described as those of the phosphine and silicon donor moieties. For example, for the non-classical bidentate coordination mode, the frontier orbitals are shown schematically in **Figure 1**. A bidentate *P*, *Si* ligand can readily coordinate to the metal centre both through the phosphorous atom via the donation of the electron lone pair on P to an empty d-orbital on the metal and through the σ -Si–H electron pair donated to a suitable empty d-orbital on the metal generating a 3c-2e non-classical bond. In both bonds, the stabilisation is given by the retro-donation of electron density of a filled d-orbital to an anti-bonding orbital. In the full oxidative addition process of the Si–H bond to the metal, due to the strong retro-donation of the d-orbital $\rightarrow \sigma^*(Si-H)$, the final product results in the formation of two 2c-2e bonds: M–H, M–Si. As expected, depending on the substituents on both the P and Si atoms, the molecular orbital diagrams and the energy of the HOMO and LUMO will vary. In general, it could be said according to **Figure 1**, the HOMO generally possess a higher ligand character, while the LUMO is more metal centred.

3. Silylphosphine ligands throughout the chemical literature: a review

Stobart and co-workers pioneered the systematic study of transition metals bound to silylphosphine ligands. As early as in 1983, they reported the synthesis and full characteri-

sation of an extensive family of silanes modified with a phosphorous fragment connected to the silicon atom by a polymethylene chain, of general formula $(XYZ)Si(CH_2)_nPR_2$ (where X, Y, Z = Me, Ph, Cl or H; $n = 1-3$; R = Me or Ph;) (**Figure 2**, compounds **1-33**) [1]. The reactivity of Vaska's complex $trans-[Ir(PPh_3)_2(CO)(Cl)]$ towards $Ph_2P(CH_2)_2SiRR'H$ (compounds: **12**, **14**, **16**, **18**, **20**) was also investigated. The reaction results in the formation of air stable six-coordinated Ir(III) compounds, resulting from coordination of the ligands through the P atom and of the oxidative addition of the Si-H bond (compounds: **34-38**) (**Figure 3**). Furthermore, the reactions of $Ph_2P(CH_2)_2SiMe_2H$ towards the dimers $[M(\mu-Cl)(COD)]_2$ ($M = Rh, Ir$; COD = 1, 5-cyclooctadiene), also afford the M(III) complexes $[MCl\{Ph_2P(CH_2)_2SiMe_2\}_2]$ ($M = Rh$ **39**; Ir **40**) which are quiral with the two phosphorous atoms in *trans* disposition while the two Si dispose in a *cis* fashion (**Figure 3**) [2]. The fact that the reactivity of complexes **39** and **40** was remarkably constrained due to the *trans*-labilising effect of the silyl groups, was exploited in their use as catalysts for transformations of organic substrates [3]. Several works reported in the literature have argued on the high extent of *trans*-influence silyl groups exercise on a transition metal centre. There are various reasons for this behaviour including an excellent sigma orbital overlap as well as a favourable electronic release of the Si [4, 5]. This is in agreement with only a few compounds exhibiting a *trans* coordination of the Si atoms in many cases as kinetic products in equilibria with their *cis* isomers [6, 7] even when employing chelating silylphosphines (*vide supra*) [8-11] (Section 8).

It was found that the ligands with two or three phosphorous atoms and a Si-H bond (compounds **41-52**, **Figure 4**) coordinate via oxidative addition to the metal centre (i.e. rhodium, iridium, ruthenium and platinum) and impose steric constraints on the coordination sphere in turn restraining substrate entry to sites which could suffer the strongly labilising *trans* effect of the silyl group, increasing the complexes' capabilities as catalysts [12] (**Figure 4**).

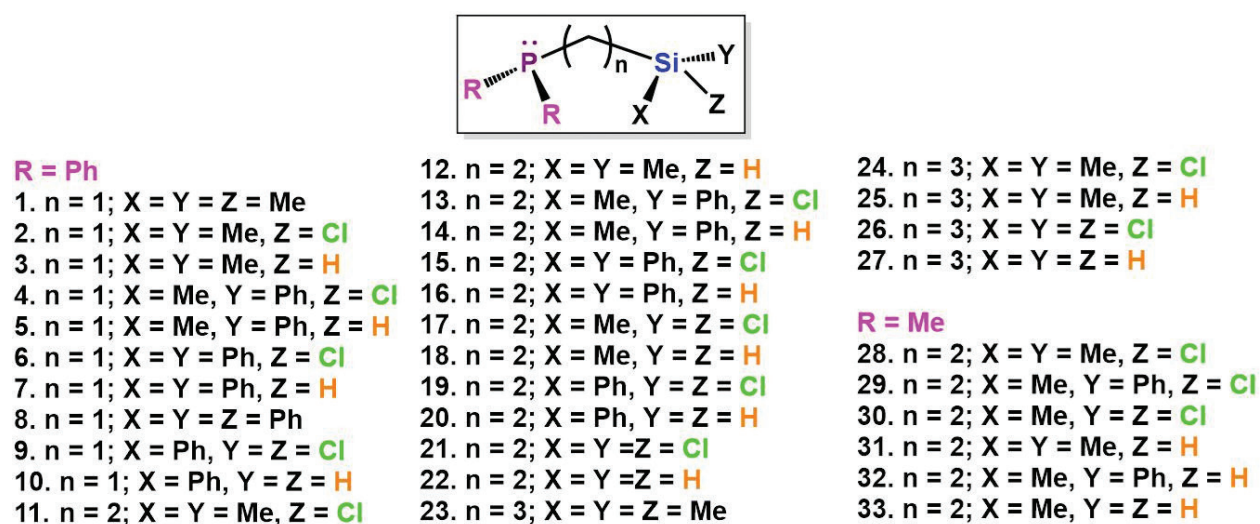


Figure 2. The silylphosphine ligands bearing alkyl bridges reported in Ref. [1].

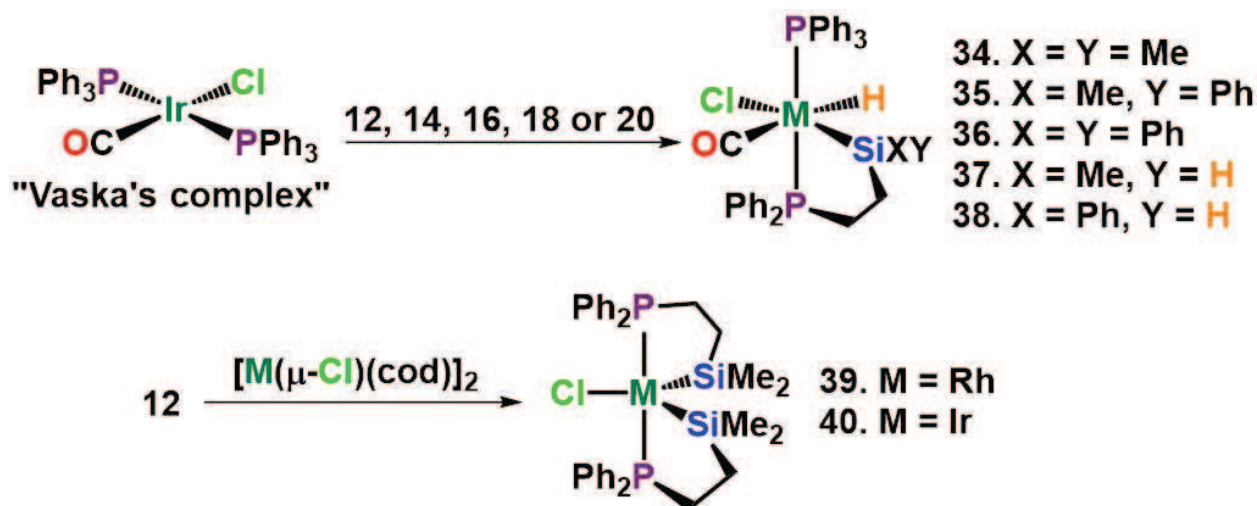


Figure 3. The reactivity of group 9 metals as reported in Ref. [2].

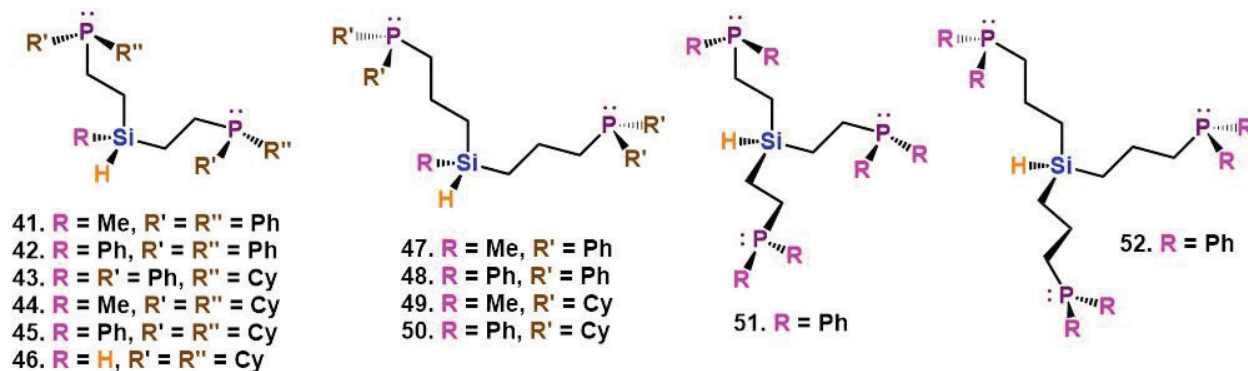


Figure 4. Design of poly(phosphino)-silane ligands reported in Ref. [12].

4. Silylphosphines complexation in tetra-coordinated systems

4.1. Square-planar geometry

Turculet and co-workers have further made significant contributions in the field of silylphosphine chemistry. They introduced a *PSiP*-type ligand $[(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}_2]$ (**53**) and explored its reactivity with transition metal precursors. The complexes $[\text{MCl}\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}]$ (M = Ni or Pd) (**64**, **65**) were treated with alkyl lithium or Grignard reagents. In the case of **65** treatment with stoichiometric amounts of MeLi led to the formation of $[\text{Pd}(\text{Me})\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}]$ (**61**) which regenerates complex **65**, upon reaction with Ph_2SiClH while renders $[\text{Pd}\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}(\text{SiHPh}_2)]$ (**66**) from reaction with Ph_2SiH_2 . The direct reaction of **53** and $[\text{Pd}_2(\text{dba})_3]$ provides complex $[\text{Pd}\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}_2\}(o\text{-C}_6\text{H}_4\text{-PCy}_2)]$ (**63**) derived from Si-C(sp²) bond activation. Treatment of complex **64** with MeMgBr led to $[\text{Ni}(\text{Me})\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}]$ (**60**) and complex $[\text{Ni}\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}_2\}(o\text{-C}_6\text{H}_4\text{-PCy}_2)]$ (**62**) resulting from

ligand rearrangement. Complexes **62** (Ni) and **63** (Pd) constitute rare examples of reversible Si-C(sp²) and Si-C(sp³) bond cleavage (**Figure 5**) [13, 14].

Moreover, the reactivity of **54** towards [PtCl₂(SEt₂)₂] leads to the generation of [PtCl{(o-C₆H₄-PPh₂)₂SiMe}] (**67**) where the ligand coordination results in adoption of a distorted square planar geometry around Pt with a persistent Cl atom bonded *trans* to the silyl group (**Figure 5**) [9].

Iwasawa and collaborators reported an interesting system for the catalytic hydrocarboxylation of allenes using the Pd(II) hydride complex [PdH{(o-C₆H₄-PPh₂)₂SiMe}] (**68**) as the active catalyst. Their methodology also served for the synthesis of β,γ-unsaturated carboxylic acids. In general, complex [Pd(OTf){(o-C₆H₄-PPh₂)₂SiMe}] (**69**) in catalytic ratios 1.0 mol% or 2.5 mol % was used in soft conditions of CO₂ pressure (1 atm) with 150 mol% of AlEt₃ or ZnEt₂ for carboxylation of 1,1-disubstituted, monosubstituted or disubstituted allenes to the respective carboxylic acid or ester [15]. In addition, the chemical properties of complex **69** were described as well. To mention some, **69** undergoes transmetalation with AlEt₃ followed by β-hydride elimination to generate the proposed complex **68**. Complex **69** reacted with an excess of B₂pin₂ at room temperature leading to HBpin and the monoborylpalladium complex [Pd(Bpin){(o-C₆H₄-PPh₂)₂SiMe}] (**70**) which promotes the product of borylation of styrene as well as other alkenes (**Figure 5**) [16–18].

Milstein and co-workers described the design and synthesis of the first pincer-type silanol-Pt(II) compound by using a *PSiP* ligand. The ligand {(o-C₆H₄-PiPr₂)₂SiH₂} (**58**) was obtained in moderate yields from the *o*-bromophosphine. It readily reacts with [(Me₂S)₂Pt(Me)Cl] at room temperature to give the bicyclic complex [PtCl{(o-C₆H₄-PiPr₂)₂SiH}] (**72**), which then undergoes autoxidation yielding the silanol complex [PtCl{(o-C₆H₄-PiPr₂)₂Si(OH)}] (**73**) in moderate yields (65%) (**Figure 5**) [19].

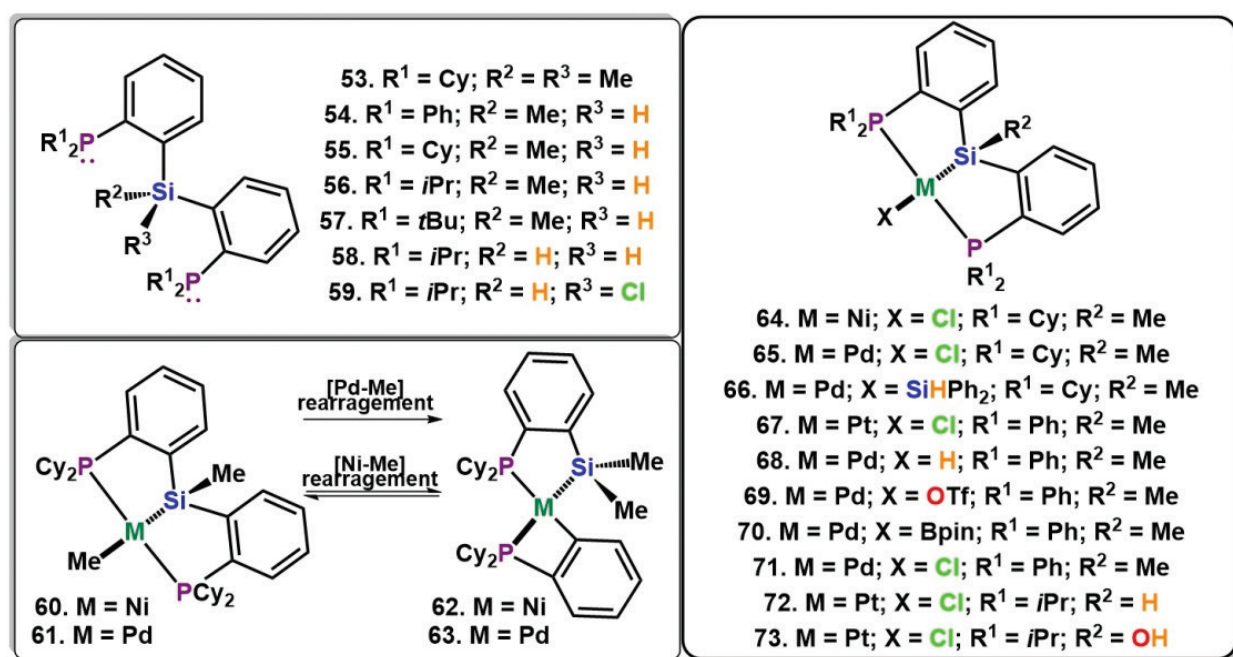


Figure 5. [PSiP] ligands and their square planar group 10 metal complexes [13-19, 26, 59].

4.2. Tetrahedral and trigonal pyramidal geometries

hand, the mixture of **54** with $[\text{Pt}(\text{PPh}_3)_4]$ is discussed in Section 5.2 [22].

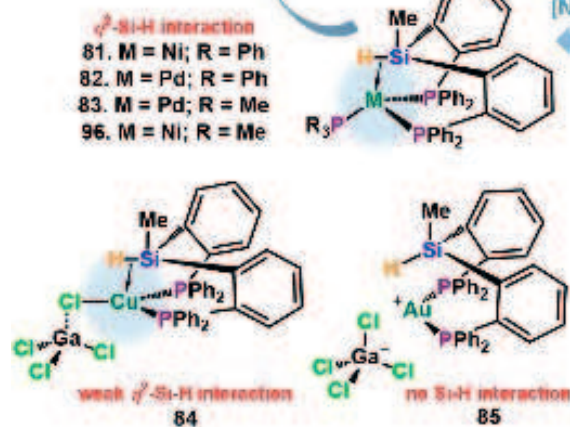


Figure 6. Reactivity of **54**. Tetra-coordination is highlighted in blue and penta-coordinated in purple [21-23, 26-29].

Bourissou and co-workers reported the reactivity of the *PSiP* ligand **54** towards CuCl and $\text{AuCl}(\text{SMe}_2)$, which was subsequently followed by a stoichiometric addition of GaCl_3 (complexes **84**, **85**). The addition of the gallium halide was envisioned to increase the electrophilicity of the central metal and thus to escalate the strength of non-classical $\sigma\text{-SiH}$ bond interaction at the metal. In complex **84**, the coordination of the ligand occurs through the two phosphorous atoms and a weak sigma interaction $\text{Si-H}\cdots\text{Cu}$. The spectroscopic evidence as well as computational analyses (geometry optimisations and NBO analyses) are in agreement with weak donation $\sigma\text{-SiH} \rightarrow \text{Cu}$ in combination with a negligible $\text{Cu} \rightarrow \sigma^*\text{SiH}$ back-donation in **84**. Meanwhile in the cationic gold complex **85**, the coordination of **54** took place only through the two phosphorous atoms as any non-classical Si-H bond interaction to the metal was strongly disfavoured as it was found to be by computational means 15.9 kcal/mol (**Figure 6**) [23].

Extraordinarily, **86** (described in more detail in Section 5.2) demonstrated to be a suitable precursor for the synthesis of stable 14-electron $[\text{Ru}(\text{X})\{(\text{o-C}_6\text{H}_4\text{-Cy}_2)_2\text{SiMe}\}]$ ($\text{X} = \text{O}^t\text{Bu}$ (**87**), $\text{N}(\text{SiMe}_3)_2$ (**88**); NHPh (**89**); $\text{NH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (**90**)) complexes, donning unusual trigonal pyramidal coordination geometries explained once again by the presence of the strongly σ -donating silyl group in the apical site with the contribution of steric effects of the phosphino substituents in the equatorial plane (**Figure 7**) [24].

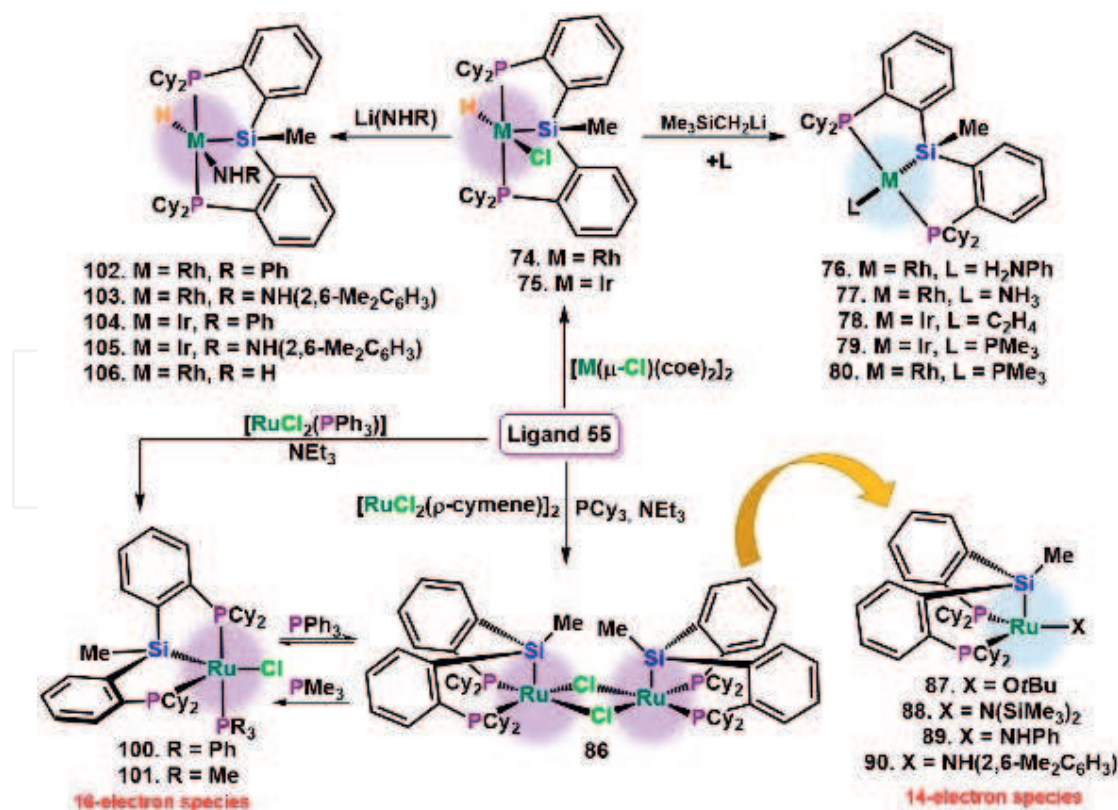


Figure 7. Reactivity of ligand **55**. Tetra-coordination is highlighted in blue and penta-coordination in purple [20, 24-25, 36].

5. Silylphosphines complexation in penta-coordinated systems

5.1. Square pyramidal geometry

The reactivity of **55** with $[\text{RuCl}_2(p\text{-cymene})]_2$ was carried out in the presence of PCy_3 and Et_3N rendering a binuclear complex that preserves bridging chloride ligands $[\text{Ru}(\mu\text{-Cl})\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}]_2$ (**86**), which was exhaustively characterised spectroscopically (**Figure 7**). The ligand coordinates each Ru atom through two P, one Si and two Cl atoms in a distorted square pyramidal geometry, in which the silyl group occupies the apical coordination site. This Ru(II)-ligand system brings about stability and selectivity in catalytic transformations including the transfer hydrogenation of ketones. In this case, Li *et al* observed high conversion of the corresponding secondary alcohols for numerous dialkyl, diaryl, and alkyl/aryl ketones, employing 0.2 mol% of **86** with 5 mol% of KO^tBu at 80°C [25].

The activation of Si-H bonds in ligands of general formula $(o\text{-C}_6\text{H}_4\text{-PR}_2)_2\text{SiHMe}$ (R = Ph or Cy; **54** and **55**) was also observed in monomeric Ru systems. Compound **54** reacted with $[\text{RuCl}_2(\text{PPh}_3)_3]$ in the presence of triethylamine as a base affording complex $[\text{RuCl}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{SiMe}\}(\text{PPh}_3)]$ (**91**). The X-ray diffraction study confirms the coordination of the ligand through the two phosphorous and the silicon atom adopting a facial arrangement with the silyl group occupying the basal position of a distorted square pyramidal geometry around Ru. The Cl atom disposes *trans* to the silyl group, and the remaining site was occupied by a PPh_3 . Complex **91** reacted with LiEt_3BH to form octahedral-Ru hydride complex **92** in moderate yield (**Figures 6**) [26].

5.2. Trigonal bipyramidal geometry

The mixture of **54** with $[\text{Pt}(\text{PPh}_3)_4]$ at room temperature led to the generation of five-coordinated Pt(II) complex $[\text{PtH}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{SiMe}\}(\text{PPh}_3)]$ (**93**). In contrast with the derivatives of Ni(0) **81** and Pd(0) **82** (**Figure 6**), where the Si-H bond is only slightly activated, the Pt(II)-hydride complex **93** derives from the complete oxidative addition of the Si-H bond. The crystalline structure displays a trigonal bipyramidal geometry with the silyl group in the apical position in the metal centre. The opposed apical site was taken by the hydride ligand which in the ^1H NMR spectrum revealed a quartet at δ -7.92 ppm ($^2J_{\text{PH}} = 18.9$ Hz) with ^{195}Pt satellites exhibiting a measured coupling constant $^{195}\text{Pt}\text{-}^1\text{H}$ of 650 Hz, which is considerably small compared with some *cis*-H-Pt(II)-Si species previously reported ($^1J_{\text{PtH}} = 890\text{--}1010$ Hz); supporting the proposal that the hydride is located *trans* to Si atom (**Figure 6**) [22].

A study of the reaction of complex **82** and its related analogue $[\text{Pd}\{\eta^2\text{-(}o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{SiHMe}\}(\text{PMe}_3)]$ (**83**) towards B_2pin_2 was made, since it could provide a means of accessing Pd(II) hydrides via oxidative addition of the Si-H bond. Two isomers: *cis* and *trans* were proposed. Depending on the phosphine choice, the isolation of one isomer was possible through a reversible σ -bond metathesis pathway. In the case of the PMe_3 ligated complex, the kinetic product *cis*- $[\text{Pd}(\text{Bpin})\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{SiMe}\}(\text{PMe}_3)]$ (**94**) showed a slow reverse reaction and was obtained predominantly. In contrast, for the PPh_3 derivative, the equilibrium favoured the thermodynamic isomer *trans*- $[\text{Pd}(\text{Bpin})\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{SiMe}\}(\text{PPh}_3)]$ (**95**) as a major product (**Figure 6**) [27, 28]. In relation

to unusual bonding modes, Sun and collaborators reported the systematic reactivity of the tridentate ligand **54** towards the low-valent nickel compound $[\text{Ni}(\text{PMe}_3)_4]$ which induced the formation of Ni(0) complexes $[\text{Ni}\{\eta^2-(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{MeSi-H}\}(\text{PMe}_3)]$ (**96**, **Figure 6**). Complex **96** did not undergo the oxidative addition process of a Si–H bond even in the presence of independent silanes (Et_3SiH , Ph_2MeSiH). However, the reactivity with chlorosilanes Me_3SiCl or MeHSiCl_2 led to the formation of Ni(II) complex $[\text{NiCl}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{MeSi}\}]$ (**97**). The halogenated products $[\text{NiX}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{SiMe}\}(\text{PMe}_3)]$ ($\text{X} = \text{Br}$ (**98**); I (**99**)) were easily obtained from reaction with EtBr or MeI of complex **96** (**Figure 6**) [29].

The versatility of ligand **55** was also probed in the coordination towards Ru. With the aim of preparing highly valuable 16-electron complexes, complex **86** was reacted with monodentate phosphines. The reaction with PPh_3 results in small conversion to the five-coordinated compound $[\text{Ru}(\text{Cl})\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}(\text{PPh}_3)]$ (**100**) in equilibrium with **86**. Interestingly, this latter compounds are also formed from the reaction of ligand **55** and $[\text{RuCl}_2(\text{PPh}_3)_3]$ in the presence of NEt_3 albeit in low yields. However, the production of the isolable penta-coordinate complex $[\text{Ru}(\text{Cl})\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}(\text{PMe}_3)]$ (**101**) was possible in quantitative yields when employing **86** in solution and the smaller, more σ -electron-donating PMe_3 (**Figure 7**) [30].

In complexes **74** and **75** (**Figure 7**), the ligand coordinates in a tridentate fashion through the phosphorous atoms which dispose in *trans* and the Si which sits in the equatorial plane of a trigonal bipyramidal geometry. The remaining sites were taken by the hydride derived from the ligand and a Cl atom. Remarkably, besides the intermolecular C–H activation ability imposed by the coordination of ligand **55** to Ir, complex **75** also exhibits facile N–H bond activation of ammonia and anilines while its Rh analogues undergo mainly adduct formation. Likewise, the starting complexes **74** and **75** react with lithium anilides $[\text{Li}(\text{NHR})]$ generating isolable anilido hydride complexes $[\text{MH}(\text{NHR})\{(o\text{-C}_6\text{H}_4\text{-PCy}_2)_2\text{SiMe}\}]$ ($\text{M} = \text{Rh}$, $\text{R} = \text{Ph}$ (**102**); $\text{M} = \text{Rh}$, $\text{R} = \{2, 6\text{-Me}_2\text{C}_6\text{H}_3\}$ (**103**); $\text{M} = \text{Ir}$, $\text{R} = \text{Ph}$ (**104**); $\text{M} = \text{Ir}$, $\text{R} = \{2, 6\text{-Me}_2\text{C}_6\text{H}_3\}$ (**105**); $\text{M} = \text{Ir}$, $\text{R} = \text{H}$ (**106**)) upon mixing. The new compounds were described as being very resistant to N–H bond reductive elimination even in the presence of alkyl or aryl substrates (**Figure 7**) [20].

The ligand $(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si-H}$ (**107**) reacts with $[\text{Ni}(\text{PPh}_3)_4]$ to yield the complex $[\text{Ni}\{\eta^2-(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{Si-H}(o\text{-C}_6\text{H}_4\text{-PPh}_2)\}(\text{PMe}_3)]$ (**109**) bearing non-classical $\sigma\text{-Si-H}$ bonds. On the other hand, complex **109** undergoes thermal oxidative addition at the Ni centre and loss of PMe_3 to allow the coordination of the previously uncoordinated phosphorous, thus rendering a compound of formula $[\text{NiH}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ (**110**). In a subsequent step, HCl was added to afford the formation of $[\text{NiCl}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ (**111**), which was also obtained when compound **109** was combined with one equivalent of MeHSiCl_2 . Compounds $[\text{NiX}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ ($\text{X} = \text{Br}$, **112**; I , **113**) were obtained from the reaction of **110** with either EtBr or MeI (**Figure 8**).

Peters and co-workers have also reported the synthesis and reactivity of silanes functionalised with phosphines and/or sulphur derivatives. In particular, the ligand **107** reacts with $[\text{Fe}_2\text{Mes}_4]$ leading to the formation of $[\text{Fe}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}\text{Mes}]$ (**114**), which was characterised structurally by single crystal X-ray diffraction. The analysis discloses a distorted octahedral geometry around the Fe atom in which the ligand has taken four out of the six coordination positions, a mesityl group occupies one more and the sixth site (*trans* to silyl group) is occupied by an agostic interaction ($\text{C-H}\cdots\text{Fe}$) from a methyl group in *ortho* position of the mesityl bonded to

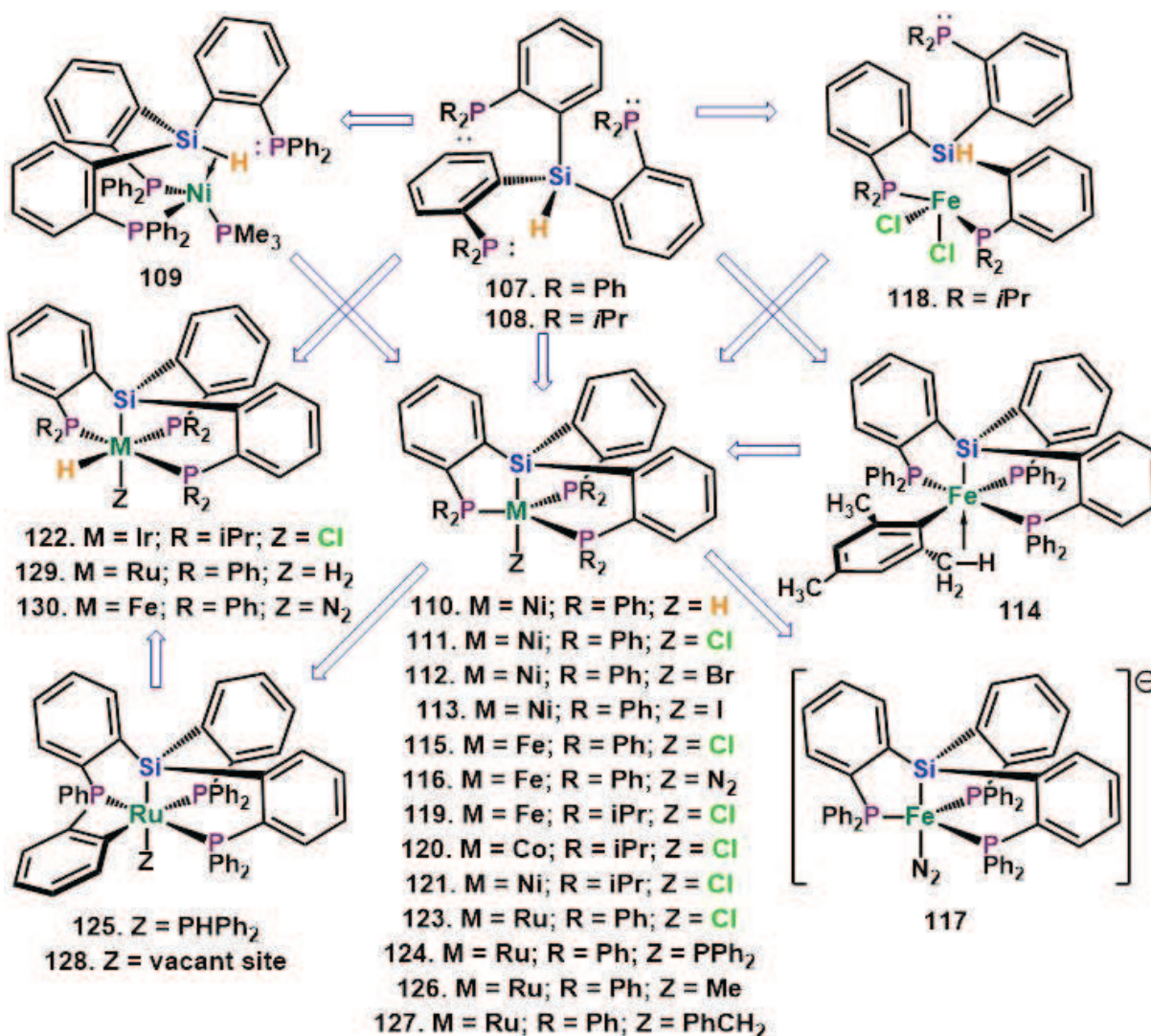


Figure 8. The chemistry of P_3Si systems [31-34].

the metal. The reaction of this agostic complex with HCl leads to the formation of complex $[FeCl\{(o-C_6H_4-PPh_2)_3Si\}]$ (**115**). Subsequent reduction with Na/Hg amalgam under a N₂ atmosphere led to the Fe(I) complex $[Fe(N_2)\{(o-C_6H_4-PPh_2)_3Si\}]$ (**116**), which was again subjected to reduction with an additional equivalent of Na/Hg in the presence of [12]crown-4 to render dark purple ionic pair $[Na([12]crown-4)_2]^+[Fe(N_2)\{(o-C_6H_4-PPh_2)_3Si\}]^-$ (**117**) in which Fe is in a zero oxidation state and the dinitrogen ligand is less labile than in **116** because of stronger π backdonation from the more reduced metal [32]. Once again the nature of the substituents on the P atom is determinant. Indeed, ligand $(o-C_6H_4-P^iPr_2)_3SiH$ (**108**) reacts with FeCl₂ at room temperature producing a species with one uncoordinated phosphorous atom and the Si–H bond intact $[FeCl_2\{(o-C_6H_4-P^iPr_2)_2SiH(o-C_6H_4-P^iPr_2)\}]$ (**118**); however, if the reaction was made in the presence of MeMgCl at $-78^\circ C$, the desired complex $[FeCl\{(o-C_6H_4-P^iPr_2)_3Si\}]$ (**119**) was isolated. The reactivity of **108** with metallic precursors CoCl₂, NiCl₂ and $[Ir(\mu-Cl)(COD)]_2$ was found to yield the tripodal species $[CoCl\{(o-C_6H_4-P^iPr_2)_3Si\}]$ (**120**), $[NiCl\{(o-C_6H_4-P^iPr_2)_3Si\}]$ (**121**) and $[IrHCl\{(o-C_6H_4-P^iPr_2)_3Si\}]$ (**122**), respectively (Figure 8) [33].

Another example of the importance of the *trans*-influence of the silyl groups on the metal coordination sphere is given by the chemical properties of $[\text{RuCl}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ (**123**). The exchange reaction with LiPPh_2 (also with LiP^iPr_2) led to expected phosphide complex $[\text{Ru}(\text{PPh}_2)\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ (**124**), which decays at room temperature to the cyclometalated $[\text{Ru}(\text{PPh}_2)\{\text{Si}(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2(o\text{-C}_6\text{H}_4)\text{P}(o\text{-C}_6\text{H}_4)\text{Ph}\}]$ (**125**). The reaction of **123** with stoichiometric amounts of MeLi or PhCH_2MgCl leads to $[\text{Ru}(\text{Z})\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ ($\text{Z} = \text{Me}$ (**126**); PhCH_2 (**127**)). Successive loss of methane or toluene renders the formation of the unsaturated square pyramidal species $[\text{Ru}\{\text{Si}(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2(o\text{-C}_6\text{H}_4)\text{P}(o\text{-C}_6\text{H}_4)\text{Ph}\}]$ (**128**), which in turns affords under H_2 or N_2 atmospheres compounds $[\text{Ru}(\text{H}_2)\text{H}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ (**129**) and $[\text{Ru}(\text{N}_2)\text{H}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}]$ (**130**) in subsequent reactions steps (Figure 8) [34].

6. Silylphosphines complexation in hexa-coordinated systems: octahedral geometry

Shimada and collaborators reported on the reactivity of ligands $(o\text{-C}_6\text{H}_4\text{-PR}_2)_2\text{SiHMe}$ ($\text{R} = \text{Cy}$ (**55**), $i\text{Pr}$ (**56**), $t\text{Bu}$ (**57**); Figure 5) towards $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$. The complexes $[\text{IrClH}\{(o\text{-C}_6\text{H}_4\text{-PR}_2)_2\text{SiMe}\}]$ ($\text{R} = \text{Cy}$, **75**, $i\text{Pr}$, **131**, $t\text{Bu}$, **132**) (Figure 7 and 9) reacted with reducing agent $\text{Me}_4\text{N}\cdot\text{BH}_4$ under argon to produce the tetrahydride complexes $[\text{IrH}_4\{(o\text{-C}_6\text{H}_4\text{-PR}_2)_2\text{SiMe}\}]$ ($\text{R} = \text{Cy}$ (**133**), $i\text{Pr}$ (**134**), $t\text{Bu}$ (**135**)) or under dinitrogen gas to produce rare stable Ir(III) dihydride-dinitrogen complexes of formula $[\text{IrH}_2(\text{N}_2)\{(o\text{-C}_6\text{H}_4\text{-PR}_2)_2\text{SiMe}\}]$ ($\text{R} = \text{Cy}$ (**136**), $i\text{Pr}$ (**137**)). For the last two complexes, NMR spectroscopy reveals the presence of the *fac/mer* isomers; the meridional and facial disposition of the *PSiP* ligand was supported by single crystal X-ray diffraction (Figure 9) [35].

The complex $[\text{FeH}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_2\text{SiMe}\}(\text{PMe}_3)_2]$ (**138**) was synthesised from $[\text{Fe}(\text{PMe}_3)_4]$, its $\nu(\text{Fe-H})$ stretching band was found at 1870 cm^{-1} in the IR spectrum, while a triplet of doublets (td),

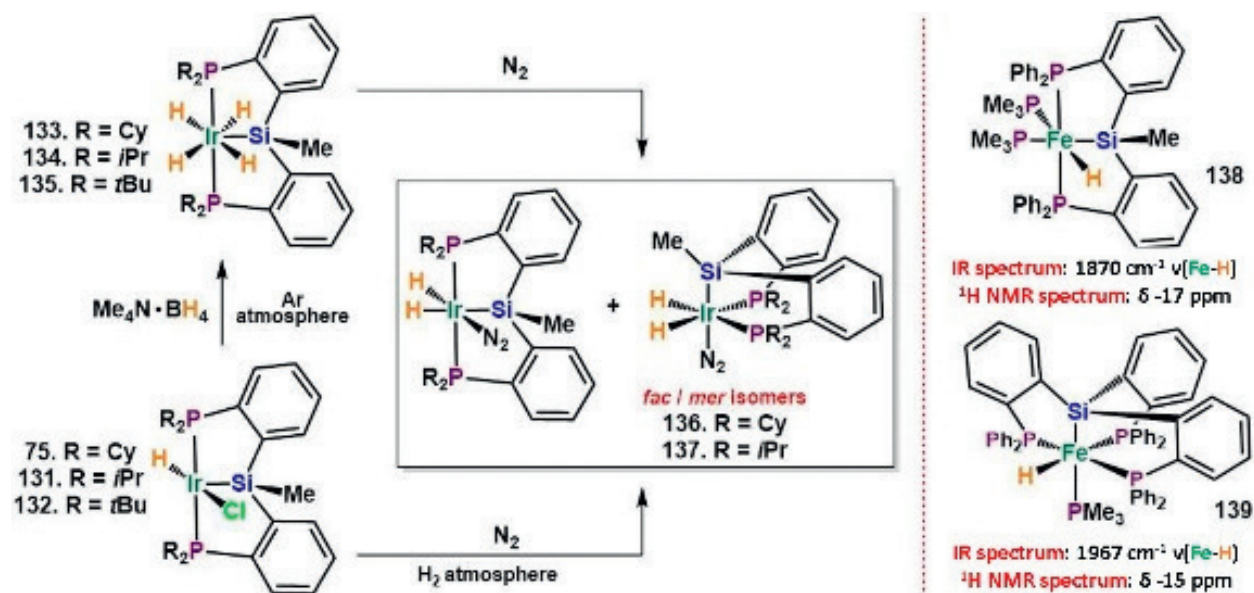


Figure 9. (Left) Chemistry of *PSiP* complexes of group 9. (Right) Related Fe octahedral complexes [35].

signal was found at $\delta -17.09$ ($J_{\text{PH}} = 71.4, 18.1$ Hz) in the ^1H NMR spectrum. By comparison, complex $[\text{FeH}\{(o\text{-C}_6\text{H}_4\text{-PPh}_2)_3\text{Si}\}(\text{PMe}_3)]$ (**139**) was characterised by a $\nu(\text{Fe-H})$ band at 1967 cm^{-1} and a signal in ^1H NMR spectrum at $\delta -15.00$ of a triplet of doublets of doublets (tdd) multiplicity with $J_{\text{PH}} = 79.4, 78.8$ and 10.8 Hz (**Figure 9**) [31].

7. Hybrid silylphosphines complexation

PSiN-ligated complexes have also been attractive synthetic targets due to the hemilability property the presence of soft P, Si and hard N atoms could impose. The synthetic strategy for the preparation of *PSiN*-type ligands involved the synthesis of $\{(o\text{-C}_6\text{H}_4)\text{-NMe}_2\}\text{SiHMeCl}$ and its reactivity towards organolithium $\{(o\text{-C}_6\text{H}_4\text{Li})\text{-PtBu}_2\}$. In this manner, the mixed-donor ligand $\{(o\text{-C}_6\text{H}_4)\text{-PtBu}_2\}\{(o\text{-C}_6\text{H}_4)\text{-NMe}_2\}\text{SiHMe}$ (**140**) was synthesised. This new-fangled ligand reacted with group 10 precursors PdBr_2 or $[\text{PtCl}_2(\text{cod})]$ to give the complexes $[\text{M}(\text{X})\{(o\text{-C}_6\text{H}_4)\text{-PtBu}_2\}\{(o\text{-C}_6\text{H}_4)\text{-NMe}_2\}\text{SiHMe}]$ ($\text{M} = \text{Pd}$, $\text{X} = \text{Br}$ (**144**); $\text{M} = \text{Pt}$, $\text{X} = \text{Cl}$ (**145**)), respectively. Treatment of the latter complexes with OTf- led to the formation of compounds $[\text{M}(\text{OTf})\{(o\text{-C}_6\text{H}_4)\text{-PtBu}_2\}\{(o\text{-C}_6\text{H}_4)\text{-NMe}_2\}\text{SiHMe}]$ ($\text{M} = \text{Pd}$ (**146**); Pt (**147**)) showing in the X-ray diffraction molecular structure a distance Pd-O of $2.3518(11)\text{ \AA}$ in **146**, which once again highlights the strong *trans*-influence of the silyl donor. The selective reversible de-coordination of the amine arm in **144** and **145** was observed upon the use of PMe_3 which yields compounds $[\text{M}(\text{X})\{(o\text{-C}_6\text{H}_4)\text{-PtBu}_2\}\text{SiHMe}\text{-}(o\text{-C}_6\text{H}_4)\text{-NMe}_2](\text{PMe}_3)]$ ($\text{M} = \text{Pd}$, $\text{X} = \text{Br}$ (**148**); $\text{M} = \text{Pt}$, $\text{X} = \text{Cl}$ (**149**)). The coordination of the *PSiN* ligand towards group 9 (Rh, Ir) and 8 (Ru) has also been studied. The complex $[\text{Ru}\{(o\text{-C}_6\text{H}_4)\text{-PtBu}_2\}\{(o\text{-C}_6\text{H}_4)\text{-CHNMe-SiMe}\}(\eta^3\text{-cyclooctene})]$ (**150**) was achieved upon thermal reaction of the *PSiN* ligand with one equivalent of $[\text{Ru}(2\text{-methylallyl})_2(\text{cod})]$. The complex resulted from the coordination of the P and Si atoms of the ligand as well as a C-H bond activation of the methyl group (NMe) with a hydrogenated cyclooctene, remaining on the coordination sphere of the metal. Overall, a square planar geometry around Ru centre is structurally proposed (**Figure 10**) [36].

Another example of an elegant catalytic application of systems derived of *PSiN* pincer-like ligands is that comprising the ligands of general formula $\{(o\text{-C}_6\text{H}_4)\text{-PR}_2\}\{(o\text{-C}_6\text{H}_4)\text{-NMe}_2\}\text{SiHMe}$

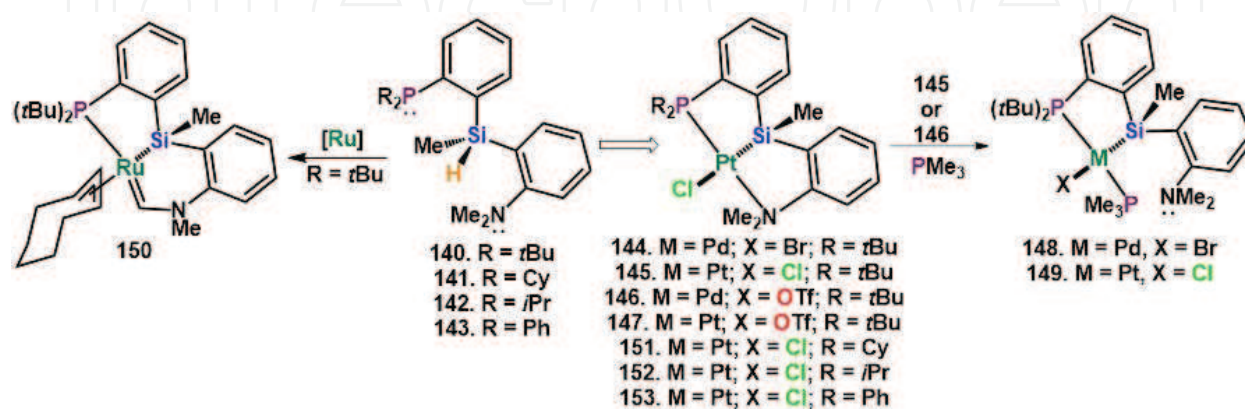


Figure 10. The chemistry of mixed *PSiN* ligands [36-37].

(R = *t*Bu (**140**); Cy (**141**); *i*Pr (**142**); Ph (**143**)) [36]. The complexes [PtCl{(*o*-C₆H₄)-PR₂(*o*-C₆H₄)-NMe₂-SiMe}] (R = *t*Bu (**145**); Cy (**151**); *i*Pr (**152**); Ph (**153**)) were synthesised by the reaction with [PtCl₂η²-(C₂H₄)₂] in the presence of Et₃N. In particular, the *PSiN*-platinum complex **151** successfully catalysed C–H borylation not only of highly electron deficient perfluoroarenes but also of the monofluorinated arenes, chloroarenes and benzoate (**Figure 10**) [37].

Regarding [M(P₃Si)] tripodal systems, an extended series of organometallic species of general formulae [M(X){(*o*-C₆H₄-PR₂)₃Si}] or [M(L){(*o*-C₆H₄-PR₂)₃Si}] (R = Ph, *i*Pr; X = Me, Cl; L = H₂, N₂, CO, NH₃, N₃R', PMe₃) has been disclosed with a variety of metals including, Fe [38–44], Co [45, 46], Ni [47], Ru [48], Os [48], Rh [45] and Ir [45], with outstanding and specific properties. Perhaps among the most novel systems, one can find the chemistry of novel hybrids (thioether/phosphine)-silane ligands (*o*-C₆H₄-PiPr₂)_{3-n}(*o*-C₆H₄-SAd)_nSiH (n = 2 (**154**); 1 (**155**)) synthesised from silyl-phosphines such as (*o*-C₆H₄-PiPr₂)₂SiHCl, **59** (**Figure 5**, section 4.1), upon lithiation of Br(*o*-C₆H₄)E (E = PiPr₂ or SAd) with varying stoichiometric amounts of Li(*o*-C₆H₄)E. The reactivity of these hybrids with FeCl₂ afforded a new class of iron complexes featuring a S–Fe–N₂ linkage (**Figure 11**) [49]. The bulky hexa-dentate ligand {(*o*-C₆H₄-PiPr₂)₂HSi-O-SiH(*o*-C₆H₄-PiPr₂)₂} (**156**) was synthesised by the controlled hydrolysis of **59** (**Figure 11**). The reactivity of **59** was also reported towards FeBr₂ and NiX₂·DME (X = Cl or Br). The complex [Fe₂(N₂)₂(μ-H)₂{((*o*-C₆H₄-PiPr₂)₂Si)₂O}] (**157**) was formed in an equilibrium mixture with [Fe₂(N₂)₂(μ-H)₂{((*o*-C₆H₄-PiPr₂)₂Si)₂O}] (**158**), which were observed at low temperature in the IR spectrum (two ν(N–N) bands at 2097 and 2060 cm^{−1}) in accordance with the determined thermodynamic parameters including a large negative entropy (−30(2) cal/mol K), consistent with the coordination of a gas molecule and a rather small enthalpy of binding (−9.0(4) kcal/mol) in line with the observation of both species at low temperature (**Figure 11**) [50]. This research is particularly relevant for the understanding of nitrogenase mimicking systems. From the reactivity of a binucleating variant of a *PSiP* ligand with NiX₂·DME (X = Cl, Br) in the presence of triethylamine, dinuclear zerovalent nickel complexes bearing both η²-(Si–H) and η²-H₂ moieties were observed by the group of Peters. Theoretical studies suggest that the Ni centre facilitates H atom exchange between the η²-(Si–H) and η²-H₂ ligands via interconversion with a higher valent Ni(II) isomer (compounds **159–161**) (**Figure 11**). This exchange has been exploited in the selective catalytic deuteration of exogenous silanes [51].



Figure 11. Chemistry of compound **59** and related reactions [49–52].

Interestingly, the synthesis of the bulkier ligand (*o*-C₆H₄-PiPr₂)₂HSi-(C₆H₃)SiPr-SiH(*o*-C₆H₄-PiPr₂)₂ (**162**) was reported very recently. The lithiation of (2,6-dibromophenyl)-isopropyl thioether with *n*BuLi in one pot followed by the stoichiometric addition of **59** affords the formation of (3-bromo-2-(isopropylthio)phenyl)(bis(2-diisopropylphenylphosphino)silane, which received the same treatment that (2,6-dibromophenyl)-isopropyl, to form the desired compound **162** (Figure 11) [52].

8. Bulky silylphosphines complexation

An example of rare kinetic stabilisation of *trans* bis(silyl) isomers was provided by the contributions of Kang, Ko and coworkers on the reaction of the bulky carborane silyl-phosphines {(R₂P)C₂B₁₀H₁₀(SiMe₂H)} (R = Me (**163**), OEt (**164**), Ph (**165**)) towards [Pt(η²-C₂H₄)(PPh₃)₃] or [Pt(COD)₂], which afforded extremely uncommon *trans*-bis(P,Si-chelates) [Pt{(R₂P)C₂B₁₀H₁₀(SiMe₂)₂}] (R = Me (**166**); OEt (**167**)) formed by “chelate-assisted” oxidative addition. However, in the presence of dimethyl acetylenedicarboxylate, the complexes endure thermally rearrangements to the thermodynamically favoured *cis* isomers **166'** and **167'**. Besides, the reaction of [Pt(η²-C₂H₄)(PPh₃)₃] towards **165** occurs via oxidative addition resulting in the mono(chelate)

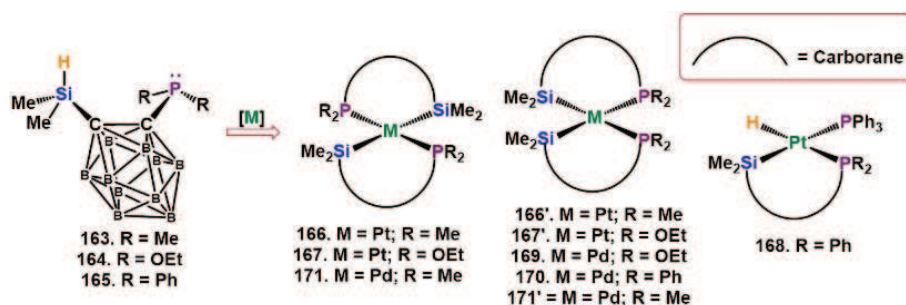


Figure 12. Bulky carborane silyl-phosphine ligands [53].

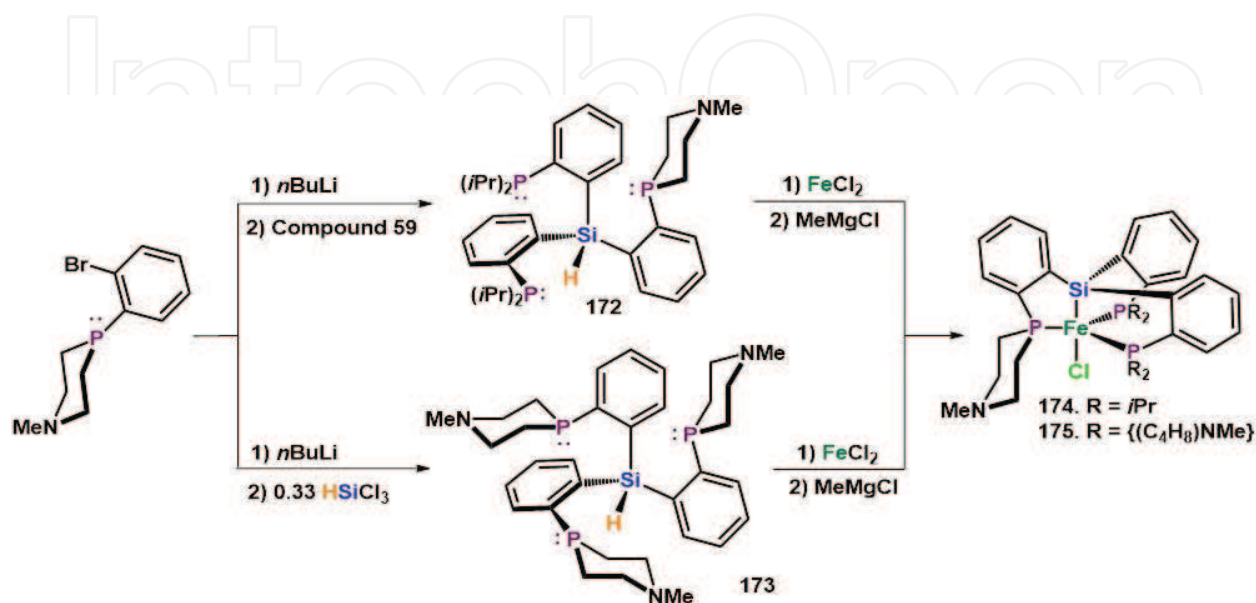


Figure 13. Syntheses of bulky cage trigonal bipyramidal iron complexes [54].

[PtH{(Ph₂P)C₂B₁₀H₁₀(SiMe₂)}(PPh₃)] (**168**). These authors also investigated the reactivity of the same bulky carborane silyl-phosphines with the palladium precursor [Pd₂(dba)₃] and observed that depending of the substituents over the phosphorous atoms, the *cis* isomer was exclusively formed [Pd{(R₂P)C₂B₁₀H₁₀(SiMe₂)}₂] (R = OEt (**169**); Ph (**170**)) or a mixture of the *trans/cis* isomers was detected when R = Me (**171/171'**) (Figure 12) [53].

Recently, the syntheses of bulky-cage trigonal bipyramidal iron complexes **174** and **175** with remote tertiary amines were reported. The synthesis of ligands **172** and **173** is shown in Figure 13. Once again, in this regard, the incorporation of secondary sphere interactions into iron-phosphine scaffolds is relevant to synthetic nitrogen fixation research [54].

9. Non-rigid and semi-rigid silylphosphines

Sola reported tridentate systems exemplified by [IrHCl{[Ph₂P(CH₂)₃]₂SiMe}] (**176**) [55] derived from the reaction of the ligand *PSiP* {[Ph₂P(CH₂)₃]₂SiHMe} (**47**, Figure 3) with the dimeric compound [Ir(μ-Cl)(cod)]₂. In solution, complex **176** displays an equilibrium between the *syn* (**176**) and *anti* (**176'**) isomers in a ratio 93:7 in C₆D₆ and C₇D₈, while in CDCl₃ or CD₂Cl₂ solutions, the ratio is *ca.* 83:17. Complex **176** (and **176'**) reacted with NaX (X = Br or I) leading to the corresponding complexes [IrHX{[Ph₂P(CH₂)₃]₂SiMe}] (X = Br (**177**); I (**178**)) also in equilibrium with their respective *syn* and *anti*-isomers (**177'**, **178'**) in similar ratios that those of **176** [56]. The mixture of isomers **176**, also reacted with Me(O₃SCF₃) to produce the isomers *syn* **179** and *anti* **179'** with general formula [IrH(O₃SCF₃){[Ph₂P(CH₂)₃]₂SiMe}]; likewise the reactivity of **176** with AgX or HX (X = PF₆) in the presence of a neutral ligand afforded the mixture of the respective *syn/anti* cationic species [IrH(L)₂{[Ph₂P(CH₂)₃]₂SiMe}]⁺[PF₆]⁻ (L = NCMe (**180/180'**), CO (**181/181'**), bipy (**182/182'**)) (Figure 14) [57].

Our research group studied the reactivity of *PSi* ligand phosphino-(benzyl)-silane Ph₂P{(o-C₆H₄)CH₂SiMe₂H} (**183**) towards the complexes [RuH₂(η²-H₂)(PCy₃)₂] (**184**) and [Ru(cod)(cot)]. Complex **185** resulted from the substitution of two molecules of dihydrogen and two of the ligands PCy₃ in **184** by two ligands **183** bonded to the ruthenium atom through the phosphorous atoms and two σ-bonds of the fragments Si—H. Following loss of H₂, complex **183** slowly transformed to the cyclometalated complex **186** and subsequently into the bis(cyclometalated) **187**. When **183** was added to [Ru(cod)(cot)], the synthetic precursor of **184**, it generated directly complex **187** in very high yield. The increase on the acidity of the methylene groups of ligand

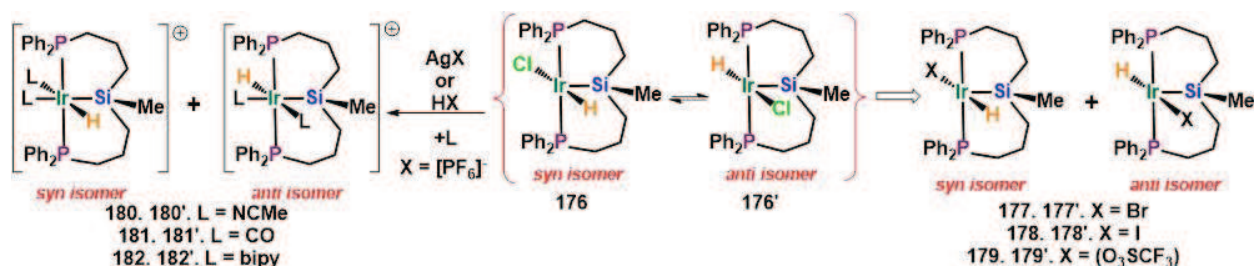


Figure 14. The chemistry of [IrP₂Si] [56, 57].

183 with respect to a non-benzilic phenylphosphine analogue, coupled with the presence of the non-classical Si—H bond interactions, which could undergo a low energy dissociation-coordination process of the Si—H bonds, was claimed to induce the gradual loss of H₂ in **185** to the final stable bis(carbometallated) complex **187**. Thus, it was reasonable to propose that the agostic interactions preceded and favoured the C—H bonds activation process [58]. Ligand *SiPSi* phosphinodibenzyl-silane PhP{(o-C₆H₄)CH₂SiMe₂H}₂ (**188**) was synthesised from PhP(*o*-tolyl)₂, it behaved as a pincer-like ligand capable of adopting different coordination modes at ruthenium through different degrees of Si—H bond activation. The reaction of **188** towards complex **184** yielded exclusively the formation of **189**, in which a Ru(II) centre is coordinated to one ligand **188**, through the P atom and two non-fully activated Si—H bonds preserving one PCy₃ and two hydride ligands of the original Ru complex. The phosphorous atoms arrange in a distorted *cis* with a P—Ru—P angle 113.32(4)° in **189** which should be compared to 107.1(4)° in bis-cyclometallated **187**. This sterically encumbered arrangement of the phosphine ligands around ruthenium has been explained due to the favourable exchange of the two formally terminal and two non-classical sigma hydrides around the metal. Certainly, the measured value of the *J*_{SiH} together with theoretical calculations and the observed chemical behaviour of **189** in solution agree with the presence of non-classical η²-Si—H character of the silyl moieties. Thus, the complex **189** was formulated as an 18-electron species stabilised by two unusual intramolecular ε-non-classical interactions. Complex **189** undergoes facile and reversible loss of dihydrogen to afford quantitatively 16-electron complex **190**, which is thought to preserve a single non-classical hydride as well as a terminal one. Moreover, NMR spectroscopic experiments on complex **189** show it to be very fluxional in the temperature range accessible, while hydride exchange in complex **190** takes place at the high-temperature regime but in the slow exchange indicates only one

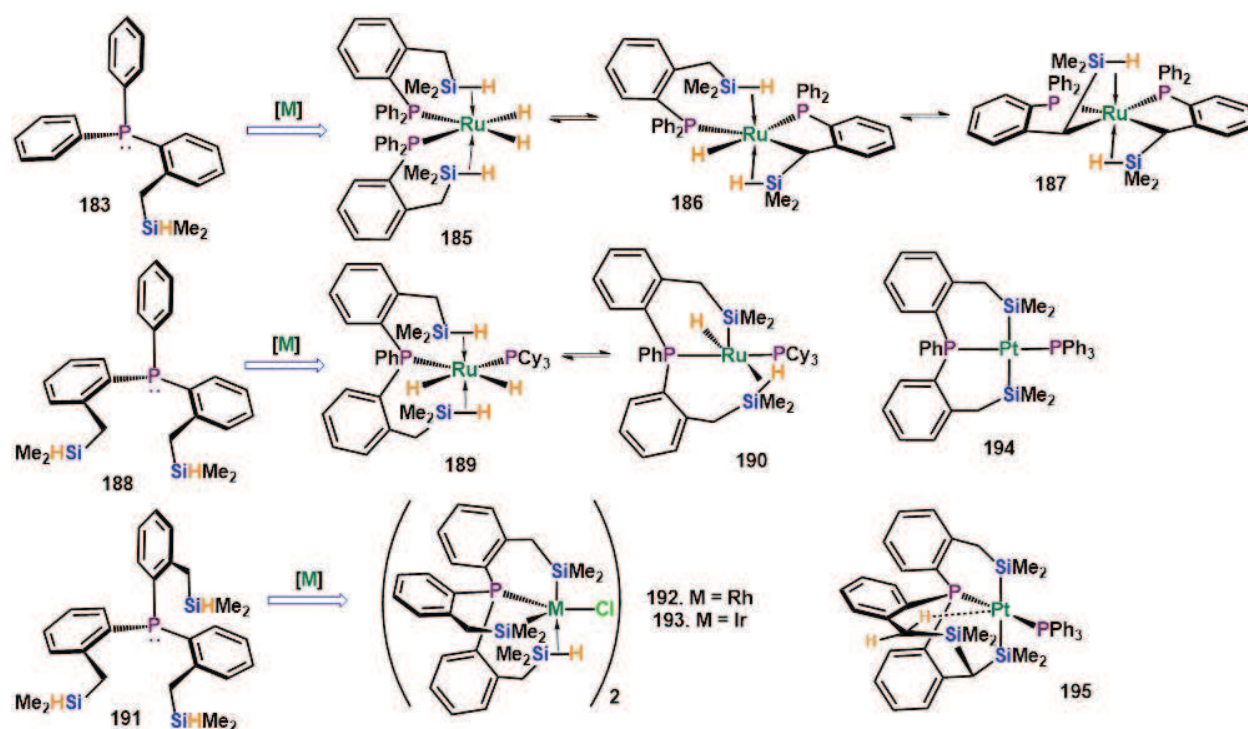


Figure 15. Chemistry of silyl-benzyl phosphines bi-, tri- and tetradentate [58-60].

hydride is bound to the two silicon atoms. In the solid-state X-ray diffraction analysis, a P-Ru-P angle of $154.37(3)^\circ$ was determined, which is significantly more obtuse than in **189** and in **187**, as expected due to the diminished hydride exchange in **190**. The free energy $\Delta_r G_{298}$ of the reaction **189** to **190** + H₂ is +16.9 kJ/mol; in line with the experimentally observed conversion at 308 K [59]. The reactivity of the ligands **183**, **188** and new *PSi*₃ ligand P{(o-C₆H₄)CH₂SiMe₂H}₃ (**191**) was also investigated with compounds [M(μ -Cl)(cod)]₂ (M = Rh, Ir) [60] and with [Pt(PPh₃)₃] [8]. Compound **191** coordinates to Rh and Ir centres as a tetradentate ligand through the phosphorus and two silyl groups, while a third Si atom engages in an agostic Si-H interaction mode [60]. Complexes **192** and **193** react with adventitious water to generate dimeric siloxane compounds. Additionally, compounds **188** and **191** react with Pt as tridentate ligands leading exclusively to compounds exhibiting a very rare *trans* silyl disposition at square planar Pt (**194**, **195**). These two complexes feature ligand (**188** and **191**) in a close to meridional disposition. Complex **195** results from ligand modification at one of the benzylic positions which undergoes formation of a new C-Si bond. Furthermore, d⁸ Pt(II) complex **195** is the first case of a silyl-platinum complex that includes a novel C-H...Pt anagostic interaction (**Figure 15**).

10. Applications of silylphosphines in the chemical industry

From the examples throughout this chapter, one can safely envisage transition metal complexes of silylphosphines as active catalysts in a variety of industrial processes. The industrial application of this type of ligand systems, nevertheless, is still at its cradle with future applications expected to materialise in the mid-term.

In principle, Si and P are capable of displaying nucleophilic behaviour and both also possess the ability to displace leaving groups such as halogens, neutral/monodentate ligands, and so on, while the factors affecting their stereochemistry may also assist the complex in the attainment of specific geometries [61]. Catalysed transfer hydrogenation has been developed mainly based on complexes derived from the platinum-metals group [62], and it is applied in industrial process and organic synthesis [63]. [PSiP-Ru] species also have shown to play an excellent role in the reduction of ketones employing ⁱPrOH as the hydrogen source. The well-known Kumada's cross-coupling reaction is an actual tool for the low-cost synthesis of styrene derivatives in the industrial scale by using Ni and Pd complexes as catalysts [64]. Some advances revealed the crucial use of phosphorous-containing compounds [65–67] and/or the very bulky donor ligands [68, 69]. Nevertheless, [PSiP-Co] systems have shown efficient conversions in relative mild reaction conditions of an aryl-Grignard reagent reaction with organic halides at 50°C for 24 h [70].

11. Conclusion and perspectives

The incorporation of dual functionalities P and Si in single ligand backbones, silylphosphines, notably modifies the properties of the complexes they form, making them especially reactive and able to undergo selective transformations resulting from differing reactivity of the coordinating atoms in the ligand in conjunction with the chelate effect.

Predictably, the observed reactivity stems from the combination of the most important qualities of the Si ligands, specifically their extremely high σ -donating character and thus their

capability of forming σ -complexes, coupled to those features of the P moieties, which can be greatly modified by the choice of substituents.

Throughout this chapter, it has been shown the study of transition metal systems bonded to silylphosphine ligands has thrived in the last decades, but the findings in the last years highlight the importance of their study. Numerous extraordinary systems displaying unusual bonding modes, structures or physicochemical properties have been reported to date and many more can be envisioned to be informed in the near future given the relatively accessible synthesis of ligands and the seemingly unlimited structural variations.

However, the catalytic and other applications of these compounds have been sparingly explored; yet the potential of many of the reported systems is foreseen. We thus expect this field of chemistry to continue growing rapidly and encourage other research groups to direct their endeavours to this fascinating area of research.

Acknowledgements

We acknowledge financial support from CONACyT-Mexico through project CB 242818 and ANR-CONACyT 274001 and a PhD grant to JZ-M

Conflict of interest

The authors declare no conflict of interest.

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