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Chapter 2

Versatile Silylphosphine Ligands for Transition Metal Complexation

Julio Zamora-Moreno and Virginia Montiel-Palma

Additional information is available at the end of the chapter

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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

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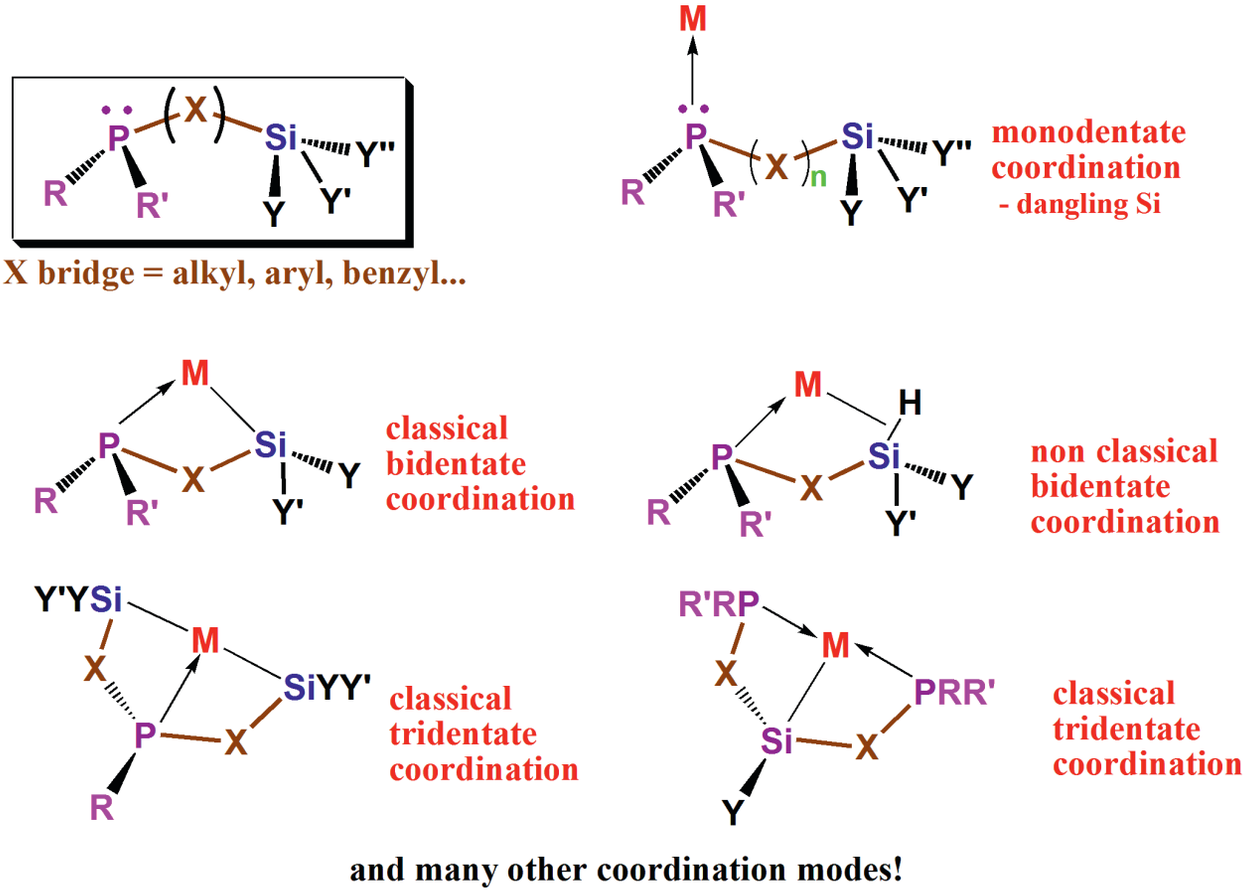
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transformations resulting from differing reactivity of the coordinating atoms in the ligand. A wide variety of combinations of donor atoms have been employed to date, including for example, soft and hard donor atoms in what is known as hemilabile ligands.

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 $P(OR)_3$, and at least one silicon-substituted



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

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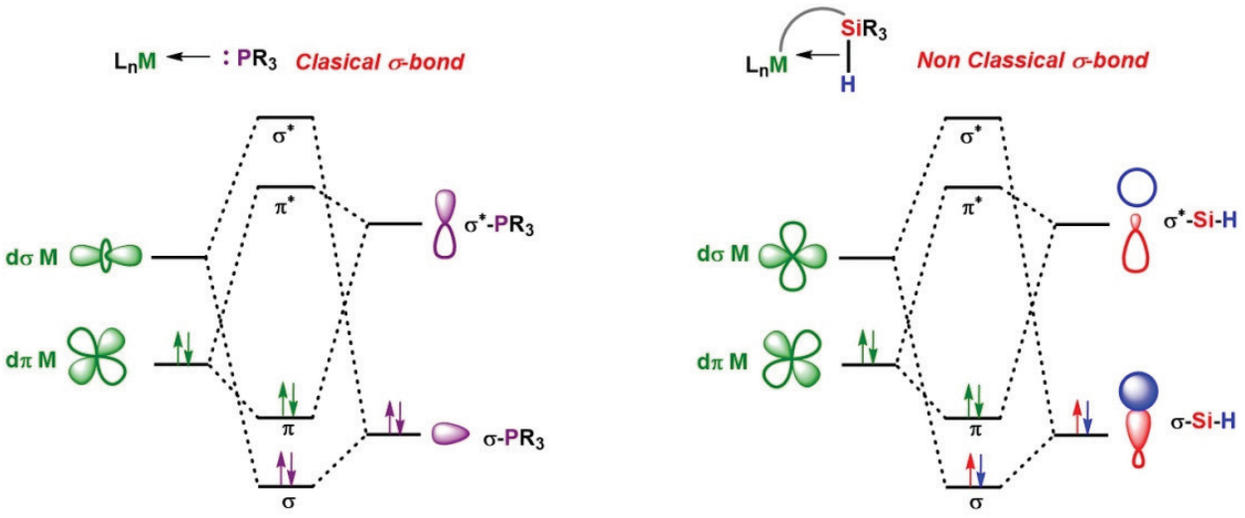


Figure 1. Molecular orbital diagrams of the phosphine and non-classical Si—H sigma moieties.

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.

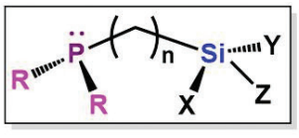
Therefore, the molecular orbitals can be described as those of the phosphine and silicon donor moieties. For example, for the non-classical bidentate coordination mode, the frontier orbitals are shown schematically in **Figure 1**. A bidentate *P*, *Si* ligand can readily coordinate to the metal centre 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 → σ*(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)_n$$PR_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(μ-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**).



R = Ph
1. n = 1; X = Y = Z = Me
2. n = 1; X = Y = Me, Z = Cl
3. n = 1; X = Y = Me, Z = H
4. n = 1; X = Me, Y = Ph, Z = Cl
5. n = 1; X = Me, Y = Ph, Z = H
6. n = 1; X = Y = Ph, Z = Cl
7. n = 1; X = Y = Ph, Z = H
8. n = 1; X = Y = Z = Ph
9. n = 1; X = Ph, Y = Z = Cl
10. n = 1; X = Ph, Y = Z = H
11. n = 2; X = Y = Me, Z = Cl
12. n = 2; X = Y = Me, Z = H
13. n = 2; X = Me, Y = Ph, Z = Cl
14. n = 2; X = Me, Y = Ph, Z = H
15. n = 2; X = Y = Ph, Z = Cl
16. n = 2; X = Y = Ph, Z = H
17. n = 2; X = Me, Y = Z = Cl
18. n = 2; X = Me, Y = Z = H
19. n = 2; X = Ph, Y = Z = Cl
20. n = 2; X = Ph, Y = Z = H
21. n = 2; X = Y =Z = Cl
22. n = 2; X = Y =Z = H
23. n = 3; X = Y = Z = Me
24. n = 3; X = Y = Me, Z = Cl
25. n = 3; X = Y = Me, Z = H
26. n = 3; X = Y = Z = Cl
27. n = 3; X = Y = Z = H

R = Me
28. n = 2; X = Y = Me, Z = Cl
29. n = 2; X = Me, Y = Ph, Z = Cl
30. n = 2; X = Me, Y = Z = Cl
31. n = 2; X = Y = Me, Z = H
32. n = 2; X = Me, Y = Ph, Z = H
33. n = 2; X = Me, Y = Z = H

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

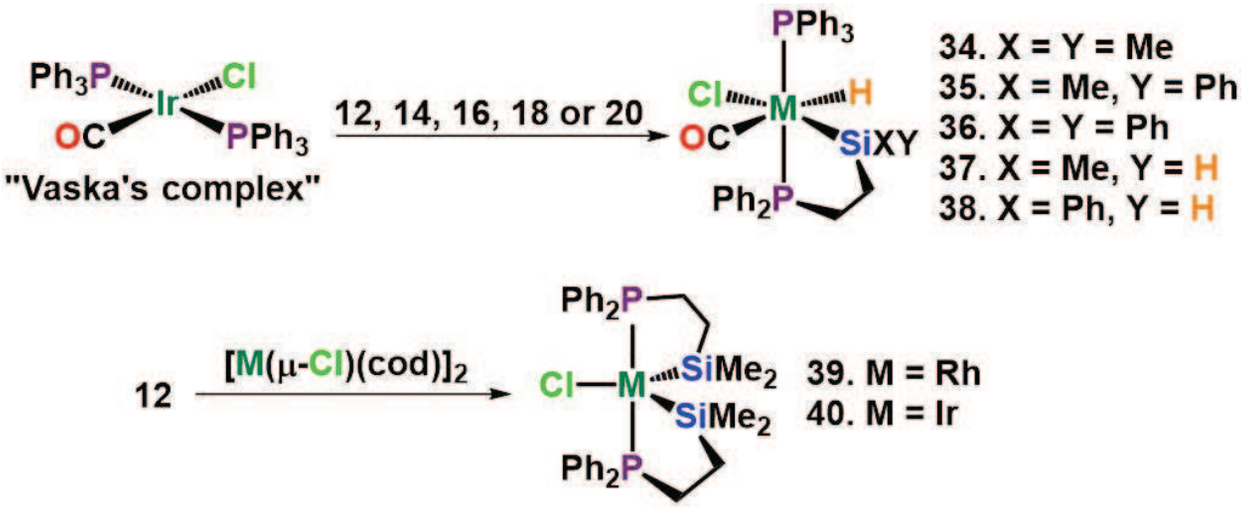


Figure 3. The reactivity of group 9 metals as reported in Ref. [2].

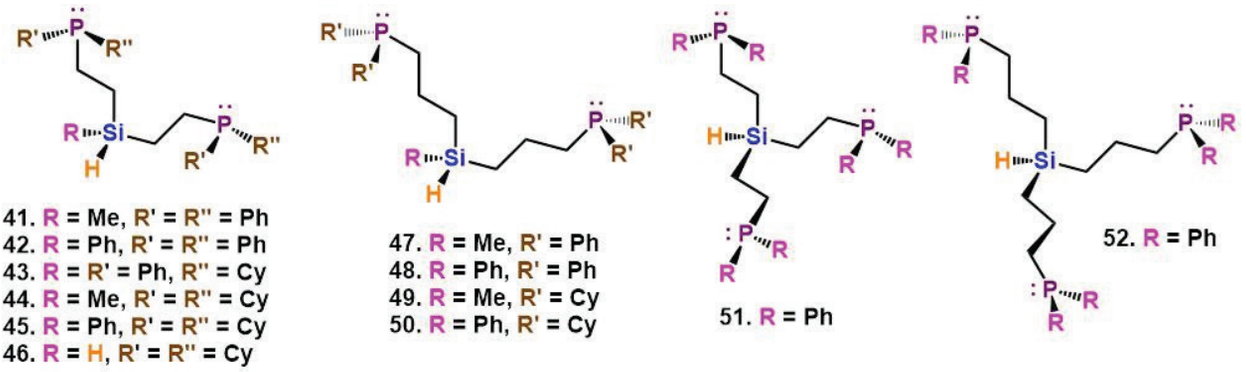


Figure 4. Design of poly(phosphino)-silane ligands reported in Ref. [12].

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*-C_6H_4-PCy_2)$_2$$SiMe_2$] (**53**) and explored its reactivity with transition metal precursors. The complexes [MCl{(*o*-C_6H_4-PCy_2)$_2$SiMe}] (M = Ni or Pd) (**64**, **65**) were treated with alkyl lithium or Grignard reagents. In the case of **65** treatment with stoichiometric amounts of MeLi led to the formation of [Pd(Me){(*o*-C_6H_4-PCy_2)$_2$SiMe}] (**61**) which regenerates complex **65**, upon reaction with Ph_2SiClH while renders [Pd{(*o*-C_6H_4-PCy_2)$_2$SiMe}($SiHPh_2$)] (**66**) from reaction with Ph_2SiH_2. The direct reaction of **53** and [$Pd_2(dba)_3$] provides complex [Pd{(*o*-C_6H_4-PCy_2)$SiMe_2$}(*o*-C_6H_4-PCy_2)] (**63**) derived from Si-C(sp^2) bond activation. Treatment of complex **64** with MeMgBr led to [Ni(Me){(*o*-C_6H_4-PCy_2)$_2$SiMe}] (**60**) and complex [Ni{(*o*-C_6H_4-PCy_2)$SiMe_2$}(*o*-C_6H_4-PCy_2)] (**62**) resulting from

ligand rearrangement. Complexes **62** (Ni) and **63** (Pd) constitute rare examples of reversible Si-C(sp^2) and Si-C(sp^3) bond cleavage (**Figure 5**) [13, 14].

Moreover, the reactivity of **54** towards $[PtCl_2(SEt_2)_2]$ leads to the generation of [PtCl{(*o*-C_6H_4-$PPh_2)_2$SiMe}] (**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*-C_6H_4-$PPh_2)_2$SiMe}] (**68**) as the active catalyst. Their methodology also served for the synthesis of β,γ-unsaturated carboxylic acids. In general, complex [Pd(OTf){(*o*-C_6H_4-$PPh_2)_2$SiMe}] (**69**) in catalytic ratios 1.0 mol% or 2.5 mol % was used in soft conditions of CO_2 pressure (1 atm) with 150 mol% of $AlEt_3$ or $ZnEt_2$ 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 $AlEt_3$ followed by β-hydride elimination to generate the proposed complex **68**. Complex **69** reacted with an excess of B_2pin_2 at room temperature leading to HBpin and the monoborylpalladium complex [Pd(Bpin){(*o*-C_6H_4-$PPh_2)_2$SiMe}] (**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*-C_6H_4-P*i*$Pr_2)_2SiH_2$} (**58**) was obtained in moderate yields from the *o*-bromophosphine. It readily reacts with $[(Me_2S)_2Pt(Me)Cl]$ at room temperature to give the bicyclic complex [PtCl{(*o*-C_6H_4-P*i*$Pr_2)_2$SiH}] (**72**), which then undergoes autoxidation yielding the silanol complex [PtCl{(*o*-C_6H_4-P*i*$Pr_2)_2$Si(OH)}] (**73**) in moderate yields (65%) (**Figure 5**) [19].

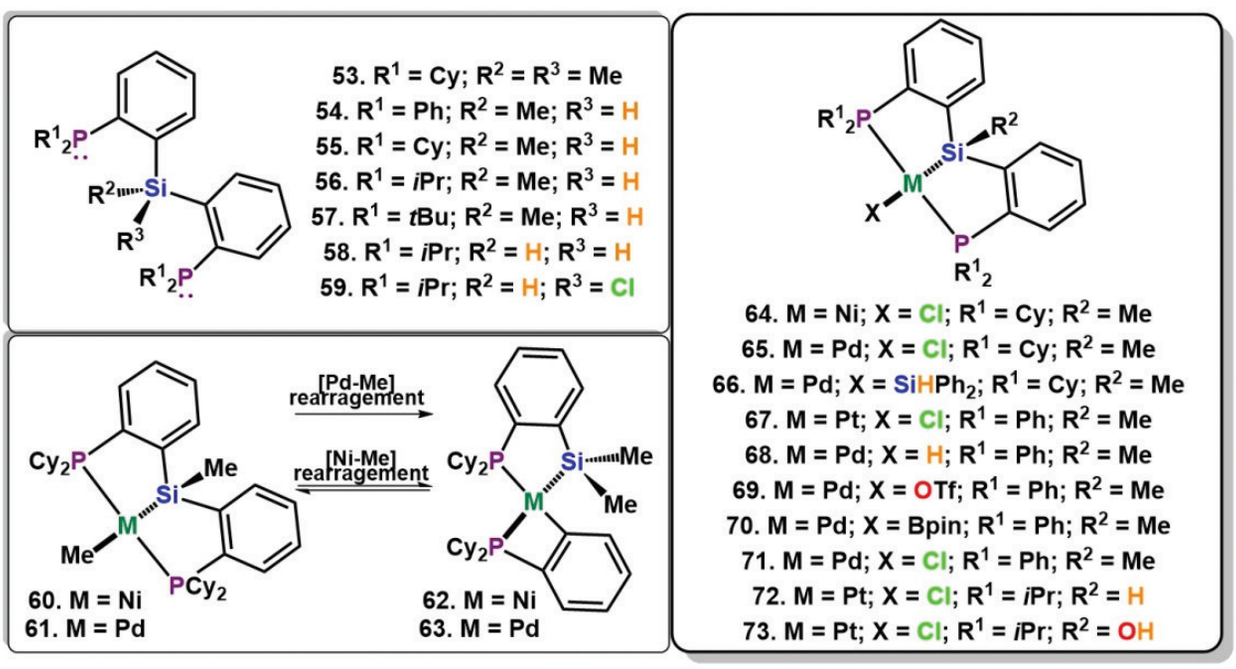


Figure 5. [PSiP] ligands and their square planar group 10 metal complexes [13-19, 26, 59].

Interestingly, changes on the identity of the substituents on the P atoms in the *PSiP* ligand backbone bring about a great strategy for the coordination of ligand **55** towards group 9 metals, in particularly rendering an Ir system able to activate intermolecular arene C—H bonds. Indeed, the reaction of **55** and $[MCl(coe)_2]_2$ (M = Rh, Ir; coe = 1-cyclooctadiene) or $[RhCl(PPh_3)_3]$ produced the monomeric complexes $[MH(Cl)\{(o\text{-}C_6H_4\text{-}PCy_2)_2SiMe\}]$ (M = Rh, **74**; Ir, **75**), which react with organolithium compound $[Me_3SiCH_2Li]$ forming neutral three-coordinate intermediate species able to subsequently coordinate neutral ligands, thus generating $[M(L)\{(o\text{-}C_6H_4\text{-}PCy_2)_2SiMe\}]$ (M = Rh, L = H_2NPh (**76**); M = Rh, L = NH_3 (**77**); M = Ir, L = C_2H_4 (**78**); M = Ir, L = PMe_3 (**79**); M = Rh, L = PMe_3 (**80**)) (**Figure 7**) [20].

4.2. Tetrahedral and trigonal pyramidal geometries

Ligand **54** (see **Figure 5**) reacted with $[Pd(PPh_3)_4]$ or $[CpPd(C_3H_5)]$ yielding complex $[Pd\{\eta^2\text{-}(o\text{-}C_6H_4\text{-}PPh_2)_2SiHMe\}(PPh_3)]$ (**82**) instead of the hypothesised hydride complex **68** which was proposed as the intermediate in the reduction of compound $[PdCl\{(o\text{-}C_6H_4\text{-}PPh_2)_2SiMe\}]$ (**71**, see **Figure 5**) with $LiHBEt_3$ in presence of PPh_3 to afford also **82** [21]. Likewise, the reaction of ligand **54** with $[Ni(PPh_3)_4]$ led to the formation of the Ni(0) complex $[Ni\{\eta^2\text{-}(o\text{-}C_6H_4\text{-}PPh_2)_2SiHMe\}(PPh_3)]$ (**81**). The Si—H, Ni—H and Ni—Si distances are 1.62(3), 1.44(2) and 2.2782(4) Å respectively, suggesting that the Si—H bond was preserved. This non-classical complexation mode is kept in solution because the observed NMR parameters such as coupling constants J_{SiH} = 89 Hz at 300 K and 77 Hz at 193 K are large ($^2J_{SiH} \leq 20$ Hz for a complete Si—H bond cleavage) and in line with the conservation of the η^2-Ni(0) structure seen in solid state (**Figure 6**). On the other hand, the mixture of **54** with $[Pt(PPh_3)_4]$ is discussed in Section 5.2 [22].

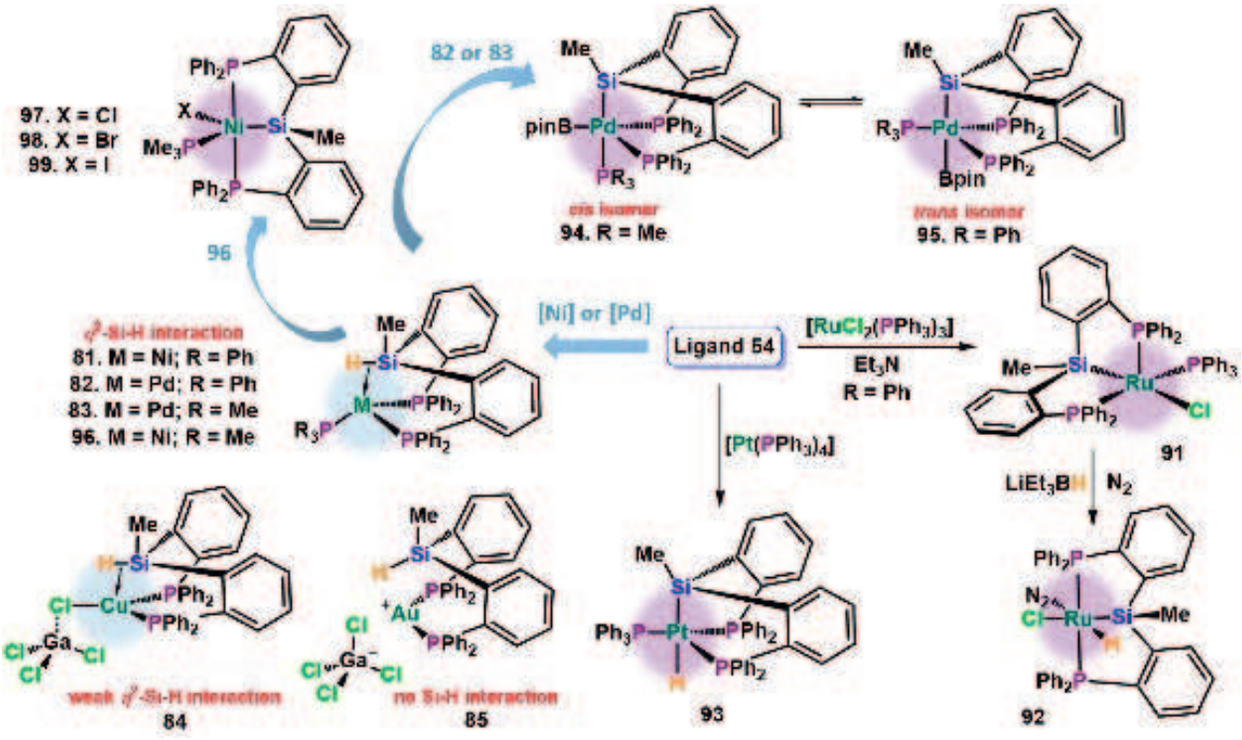


Figure 6. Reactivity of **54**. Tetra-coordination is highlighted in blue and penta-coordinated in purple [21-23, 26-29].

Bourissou and co-workers reported the reactivity of the *PSiP* ligand **54** towards CuCl and AuCl(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 σ-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 Si—H···Cu. The spectroscopic evidence as well as computational analyses (geometry optimisations and NBO analyses) are in agreement with weak donation σ-SiH → Cu in combination with a negligible Cu → σ*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 [Ru(X){(*o*-C_6H_4-Cy_2)$_2$SiMe}] (X = O^{t}Bu (**87**), N($SiMe_3$)$_2$ (**88**); NHPh (**89**); NH(2,6-$Me_2C_6H_3$) (**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].

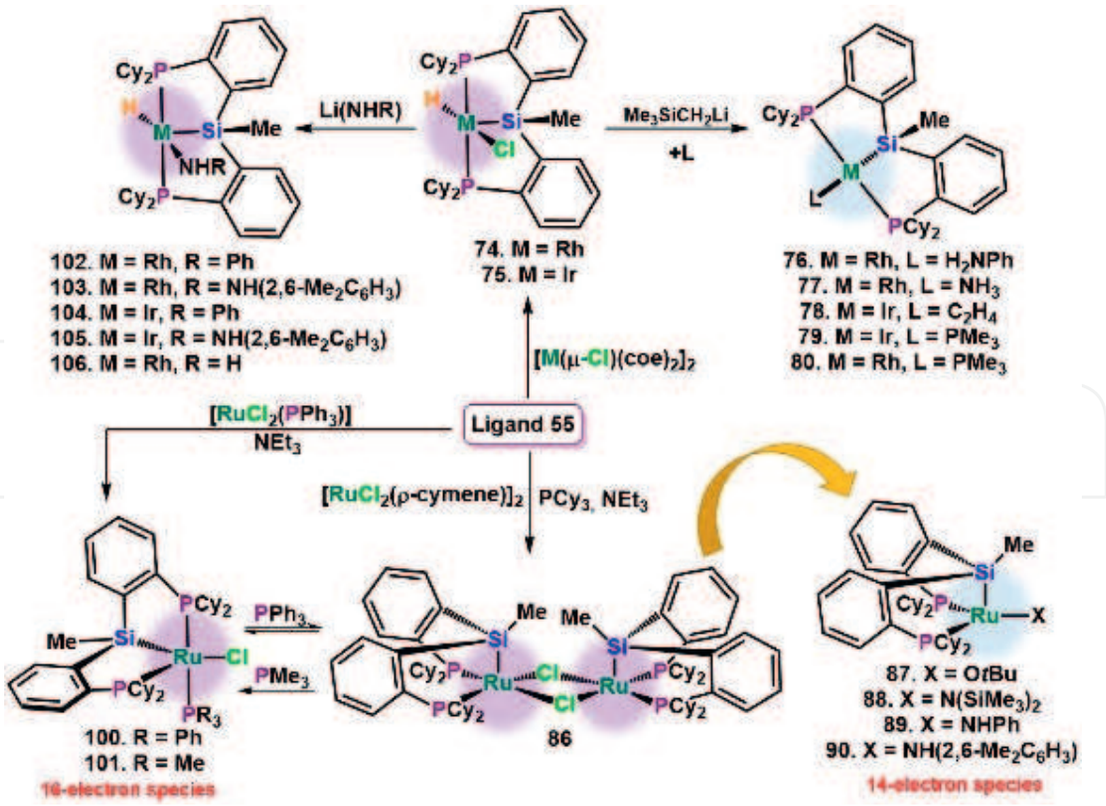


Figure 7. Reactivity of ligand **55**. Tetra-coordination is highlighted in blue and penta-coordination in purple [20, 24-25, 36].

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5. Silylphosphines complexation in penta-coordinated systems

5.1. Square pyramidal geometry

The reactivity of **55** with $[RuCl_2(p\text{-cymene})]_2$ was carried out in the presence of PCy_3 and Et_3N rendering a binuclear complex that preserves bridging chloride ligands $[Ru(\mu\text{-Cl})\{(o\text{-}C_6H_4\text{-}PCy_2)_2SiMe\}]_2$ (**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 $(o\text{-}C_6H_4\text{-}PR_2)_2SiHMe$ (R = Ph or Cy; **54** and **55**) was also observed in monomeric Ru systems. Compound **54** reacted with $[RuCl_2(PPh_3)_3]$ in the presence of triethylamine as a base affording complex $[RuCl\{(o\text{-}C_6H_4\text{-}PPh_2)_2SiMe\}(PPh_3)]$ (**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 $[Pt(PPh_3)_4]$ at room temperature led to the generation of five-coordinated Pt(II) complex $[PtH\{(o\text{-}C_6H_4\text{-}PPh_2)_2SiMe\}(PPh_3)]$ (**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 ($^2J_{PH}$ = 18.9 Hz) with ^{195}Pt satellites exhibiting a measured coupling constant $^{195}Pt\text{-}^1H$ of 650 Hz, which is considerably small compared with some *cis*-H-Pt(II)-Si species previously reported ($^1J_{PtH}$ = 890–1010 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 $[Pd\{\eta^2\text{-}(o\text{-}C_6H_4\text{-}PPh_2)_2SiHMe\}(PMe_3)]$ (**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*-$[Pd(Bpin)\{(o\text{-}C_6H_4\text{-}PPh_2)_2SiMe\}(PMe_3)]$ (**94**) showed a slow reverse reaction and was obtained predominantly. In contrast, for the PPh_3 derivative, the equilibrium favoured the thermodynamic isomer *trans*-$[Pd(Bpin)\{(o\text{-}C_6H_4\text{-}PPh_2)_2SiMe\}(PPh_3)]$ (**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 [Ni(PMe_3)$_4$] which induced the formation of Ni(0) complexes [Ni{η^2-(*o*-C_6H_4-PPh_2)$_2$MeSi-H}(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 [NiCl{(*o*-C_6H_4-PPh_2)$_2$MeSi}] (**97**). The halogenated products [NiX{(*o*-C_6H_4-PPh_2)$_2$SiMe}(PMe_3)] (X = 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 [Ru(Cl){(*o*-C_6H_4-PCy_2)$_2$SiMe}(PPh_3)] (**100**) in equilibrium with **86**. Interestingly, this latter compounds are also formed from the reaction of ligand **55** and [$RuCl_2(PPh_3)_3$] in the presence of NEt_3 albeit in low yields. However, the production of the isolable penta-coordinate complex [Ru(Cl){(*o*-C_6H_4-PCy_2)$_2$SiMe}(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 [Li(NHR)] generating isolable anilido hydride complexes [MH(NHR){(*o*-C_6H_4-PCy_2)$_2$SiMe}] (M = Rh, R = Ph (**102**); M = Rh, R = {2, 6-$Me_2C_6H_3$} (**103**); M = Ir, R = Ph (**104**); M = Ir, R = {2, 6-$Me_2C_6H_3$} (**105**); M = Ir, R = 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*-C_6H_4-PPh_2)$_3$Si-H (**107**) reacts with [Ni(PPh_3)$_4$] to yield the complex [Ni{η_2-(*o*-C_6H_4-PPh_2)$_2$Si-H(*o*-C_6H_4-PPh_2)}(PMe_3)] (**109**) bearing non-classical σ-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 [NiH{(*o*-C_6H_4-PPh_2)$_3$Si)}] (**110**). In a subsequent step, HCl was added to afford the formation of [NiCl{(*o*-C_6H_4-PPh_2)$_3$Si)}] (**111**), which was also obtained when compound **109** was combined with one equivalent of $MeHSiCl_2$. Compounds [NiX{(*o*-C_6H_4-PPh_2)$_3$Si}] (X = 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 [Fe_2Mes_4] leading to the formation of [Fe{(*o*-C_6H_4-PPh_2)$_3$Si}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 (C—H···Fe) from a methyl group in *ortho* position of the mesityl bonded to

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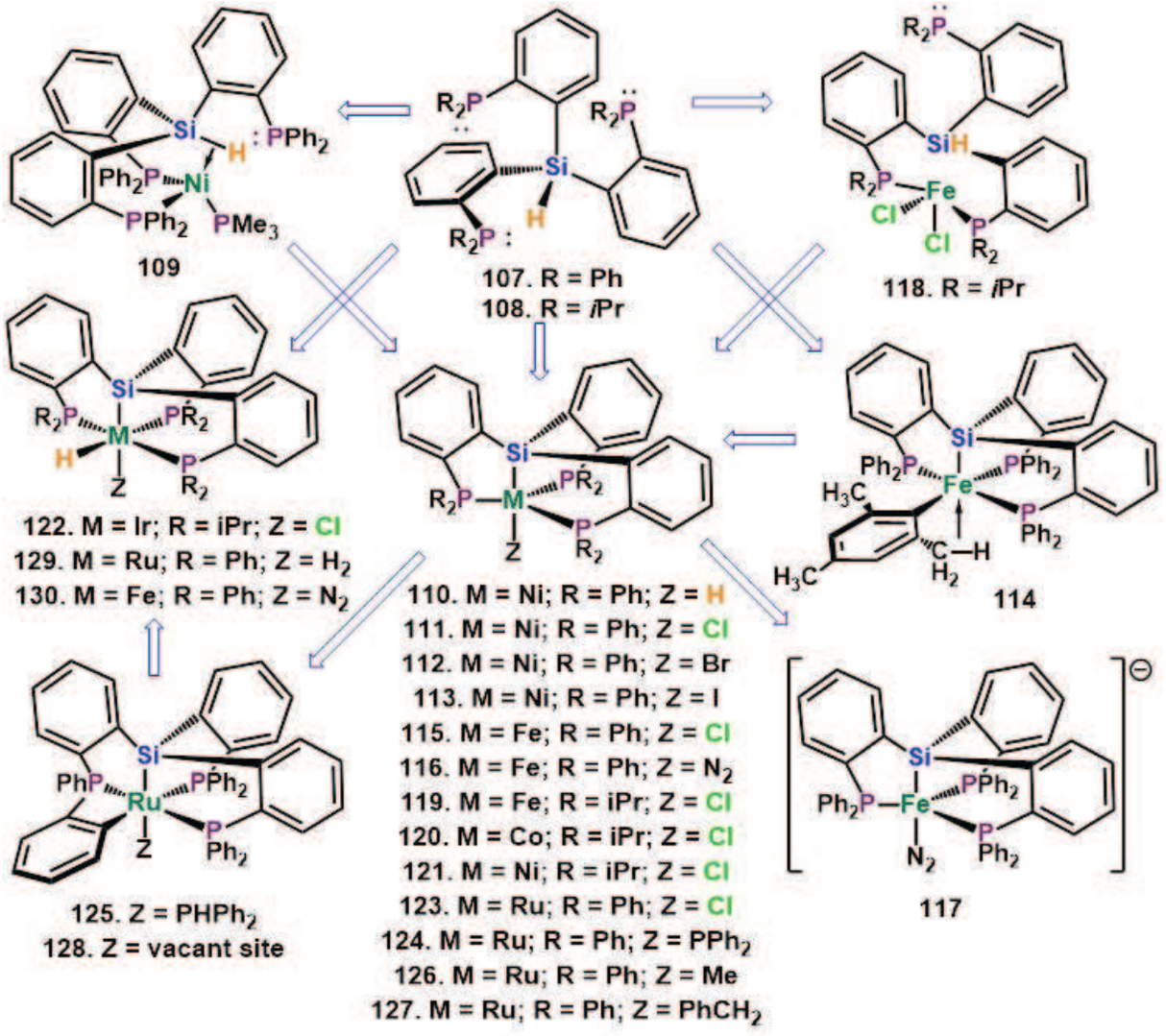


Figure 8. The chemistry of P_3Si systems [31-34].

the metal. The reaction of this agostic complex with HCl leads to the formation of complex [FeCl{(*o*-C_6H_4-PPh_2)$_3$Si}] (**115**). Subsequent reduction with Na/Hg amalgam under a N_2 atmosphere led to the Fe(I) complex [Fe(N_2){(*o*-C_6H_4-PPh_2)$_3$Si}] (**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)$_3$Si}]$^-$ (**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^{i}Pr$_2$)$_3$SiH (**108**) reacts with $FeCl_2$ at room temperature producing a species with one uncoordinated phosphorous atom and the Si—H bond intact [$FeCl_2${(*o*-C_6H_4-P*i*Pr$_2$)$_2$SiH(*o*-C_6H_4-P*i*Pr$_2$)}] (**118**); however, if the reaction was made in the presence of MeMgCl at −78°C, the desired complex [FeCl{(*o*-C_6H_4-P*i*Pr$_2$)$_3$Si}] (**119**) was isolated. The reactivity of **108** with metallic precursors $CoCl_2$, $NiCl_2$ and [Ir(μ-Cl)(COD)]$_2$ was found to yield the tripodal species [CoCl{(*o*-C_6H_4-P*i*Pr$_2$)$_3$Si}] (**120**), [NiCl{(*o*-C_6H_4-P*i*Pr$_2$)$_3$Si}] (**121**) and [IrHCl{(*o*-C_6H_4-P*i*Pr$_2$)$_3$Si}] (**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 [RuCl{(*o*-C_6H_4-PPh_2)$_3$Si}] (**123**). The exchange reaction with $LiPPh_2$ (also with $LiPiPr_2$) led to expected phosphide complex [Ru(PPh_2){(*o*-C_6H_4-PPh_2)$_3$Si}] (**124**), which decays at room temperature to the cyclometalated [Ru($PHPh_2$){Si(*o*-C_6H_4-PPh_2)$_2$(*o*-C_6H_4)P(*o*-C_6H_4)Ph}] (**125**). The reaction of **123** with stoichiometric amounts of MeLi or $PhCH_2MgCl$ leads to [Ru(Z){(*o*-C_6H_4-PPh_2)$_3$Si}] (Z = Me (**126**); $PhCH_2$ (**127**)). Successive loss of methane or toluene renders the formation of the unsaturated square pyramidal species [Ru{Si(*o*-C_6H_4-PPh_2)$_2$(*o*-C_6H_4)P(*o*-C_6H_4)Ph}] (**128**), which in turns affords under H_2 or N_2 atmospheres compounds [Ru(H_2)H{(*o*-C_6H_4-PPh_2)$_3$Si}] (**129**) and [Ru(N_2)H{(*o*-C_6H_4-PPh_2)$_3$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*-C_6H_4-PR_2)$_2$SiHMe (R = Cy (**55**), *i*Pr (**56**), *t*Bu (**57**); **Figure 5**) towards [Ir(μ-Cl)(COD)]$_2$. The complexes [IrClH{(*o*-C_6H_4-PR_2)$_2$SiMe}] (R = Cy, **75**, *i*Pr, **131**, *t*Bu, **132**) (**Figure 7** and **9**) reacted with reducing agent $Me_4N{\cdot}BH_4$ under argon to produce the tetrahydride complexes [IrH_4}{(*o*-C_6H_4-PR_2)$_2$SiMe}] (R = Cy (**133**), ^{i}Pr (**134**), ^{t}Bu(**135**)) or under dinitrogen gas to produce rare stable Ir(III) dihydride-dinitrogen complexes of formula [$IrH_2(N_2)$}{(*o*-C_6H_4-PR_2)$_2$SiMe}] (R = Cy (**136**), *i*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 [FeH{(*o*-C_6H_4-PPh_2)$_2$SiMe}(PMe_3)$_2$] (**138**) was synthesised from [Fe(PMe_3)$_4$], its *ν*(Fe—H) stretching band was found at 1870 cm^{-1} in the IR spectrum, while a triplet of doublets (td),

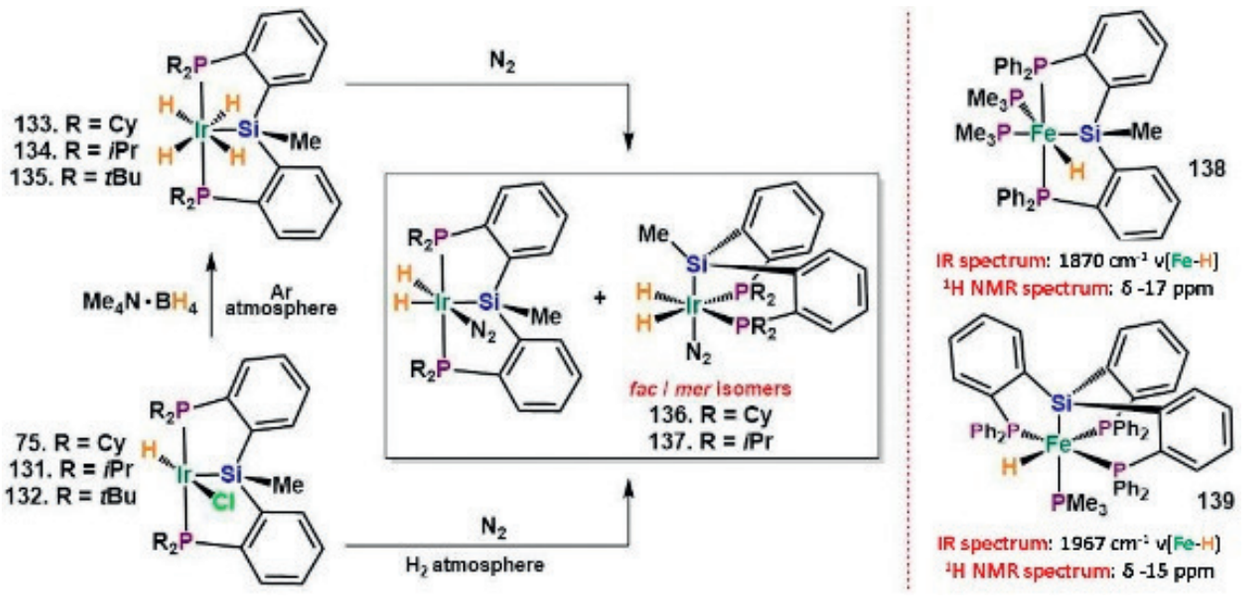


Figure 9. (Left) Chemistry of *PSiP* complexes of group 9. (Right) Related Fe octahedral complexes [35].

signal was found at δ −17.09 (J_{PH} = 71.4, 18.1 Hz) in the ^{1}H NMR spectrum. By comparison, complex [FeH{(*o*-C_6H_4-PPh_2)$_3$Si}(PMe_3)] (**139**) was characterised by a ν(Fe—H) band at 1967 cm^{-1} and a signal in ^{1}H NMR spectrum at δ −15.00 of a triplet of doublets of doublets (tdd) multiplicity with J_{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*-C_6H_4)-NMe_2}SiHMeCl and its reactivity towards organolithium {(*o*-C_6H_4Li)-P*t*Bu_2}. In this manner, the mixed-donor ligand {(*o*-C_6H_4)-P*t*Bu_2}{(*o*-C_6H_4)-NMe_2}SiHMe (**140**) was synthesised. This new-fangled ligand reacted with group 10 precursors $PdBr_2$ or [$PtCl_2$(cod)] to give the complexes [M(X){(*o*-C_6H_4)-P^tBu_2}{(*o*-C_6H_4)-NMe_2-SiMe}] (M = Pd, X = Br (**144**); M = Pt, X = Cl (**145**)), respectively. Treatment of the latter complexes with OTf- led to the formation of compounds [M(OTf){(*o*-C_6H_4)-P*t*Bu_2}{(*o*-C_6H_4)-NMe_2-SiMe}] (M = Pd (**146**); Pt (**147**)) showing in the X-ray diffraction molecular structure a distance Pd-O of 2.3518(11) Å 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 [M(X){(*o*-C_6H_4)-P*t*Bu_2-SiMe-(*o*-C_6H_4)-NMe_2}(PMe_3)] (M = Pd, X = Br (**148**); M = Pt, X = Cl (**149**)). The coordination of the *PSiN* ligand towards group 9 (Rh, Ir) and 8 (Ru) has also been studied. The complex [Ru{(*o*-C_6H_4)-P*t*Bu_2}{(*o*-C_6H_4)-CHNMe-SiMe}(η^3-cyclooctene)] (**150**) was achieved upon thermal reaction of the *PSiN* ligand with one equivalent of [Ru(2-methylallyl)$_2$(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*-C_6H_4)-PR_2}{(*o*-C_6H_4)-NMe_2}SiHMe

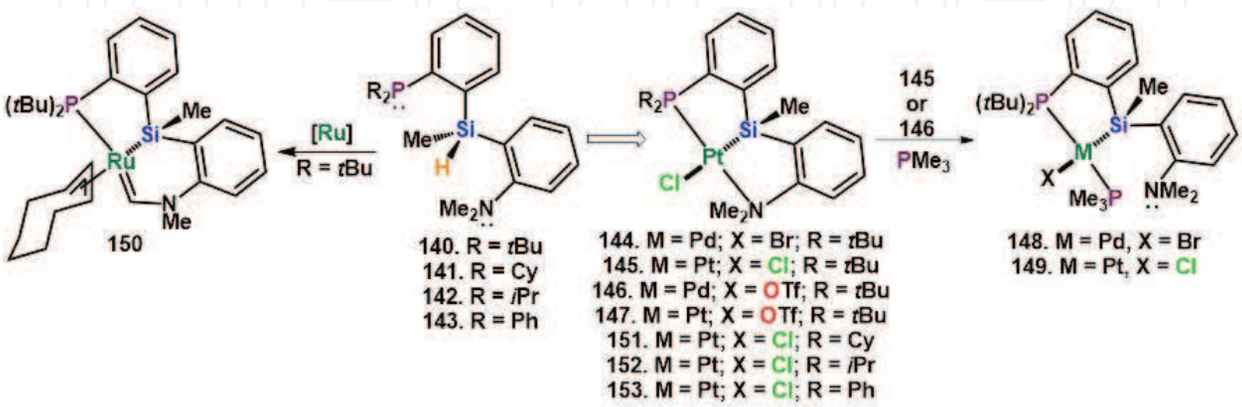


Figure 10. The chemistry of mixed *PSiN* ligands [36-37].

(R = *t*Bu (**140**); Cy (**141**); *i*Pr (**142**); Ph (**143**)) [36]. The complexes [PtCl{(*o*-C_6H_4)-PR_2(*o*-C_6H_4)-NMe_2-SiMe}] (R = *t*Bu (**145**); Cy (**151**); *i*Pr (**152**); Ph (**153**)) were synthesised by the reaction with [$PtCl_2\eta^2$-(C_2H_4)]$_2$ in the presence of Et_3N. 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(P_3Si)] tripodal systems, an extended series of organometallic species of general formulae [M(X){(*o*-C_6H_4-PR_2)$_3$Si}] or [M(L){(*o*-C_6H_4-PR_2)$_3$Si}] (R = Ph, ^{i}Pr; X = Me, Cl; L = H_2, N_2, CO, NH_3, N_3R', PMe_3) 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*-C_6H_4-P*i*Pr_2)$_{3-n}$(*o*-C_6H_4-SAd)$_n$SiH (n = 2 (**154**); 1 (**155**)) synthesised from silyl-phosphines such as (*o*-C_6H_4-P*i*Pr_2)$_2$SiHCl, **59** (**Figure 5**, section 4.1), upon lithiation of Br(*o*-C_6H_4)E (E = P*i*Pr_2 or SAd) with varying stoichiometric amounts of Li(*o*-C_6H_4)E. The reactivity of these hybrids with $FeCl_2$ afforded a new class of iron complexes featuring a S—Fe—N_2 linkage (**Figure 11**) [49]. The bulky hexa-dentate ligand {(*o*-C_6H_4-P*i*Pr_2)$_2$HSi-O-SiH(*o*-C_6H_4-P*i*Pr_2)$_2$} (**156**) was synthesised by the controlled hydrolysis of **59** (**Figure 11**). The reactivity of **59** was also reported towards $FeBr_2$ and NiX_2·DME (X = Cl or Br). The complex [$Fe_2(N_2)$(μ-H)$_2$({(*o*-C_6H_4-P*i*Pr_2)$_2$Si)$_2$O}] (**157**) was formed in an equilibrium mixture with [$Fe_2(N_2)_2$(μ-H)$_2$({(*o*-C_6H_4-P*i*Pr_2)$_2$Si)$_2$O}] (**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 NiX_2.DME (X = Cl, Br) in the presence of triethylamine, dinuclear zerovalent nickel complexes bearing both η^2-(Si—H) and η^2-H_2 moieties were observed by the group of Peters. Theoretical studies suggest that the Ni centre facilitates H atom exchange between the η^2-(Si—H) and η^2-H_2 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].

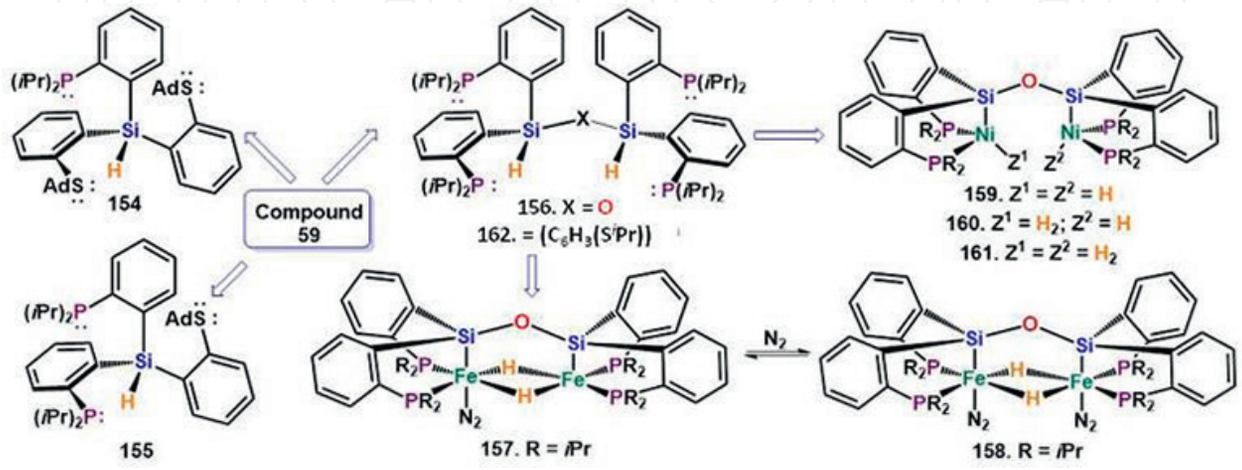


Figure 11. Chemistry of compound **59** and related reactions [49-52].

Interestingly, the synthesis of the bulkier ligand (o-C_6H_4-PiPr$_2$)$_2$HSi-(C_6H_3)SiPr-SiH(o-C_6H_4-PiPr$_2$)$_2$ (**162**) was reported very recently. The lithiation of (2,6-dibromophenyl)-isopropyl thioether with nBuLi 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 {(R_2P)$C_2B_{10}H_{10}$($SiMe_2$H)} (R = Me (**163**), OEt (**164**), Ph (**165**)) towards [Pt(η^2-C_2H_4)(PPh_3)$_3$] or [Pt(COD)$_2$], which afforded extremely uncommon *trans*-bis(P,Si-chelates) [Pt{(R_2P)$C_2B_{10}H_{10}$($SiMe_2$)}$_2$] (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(η^2-C_2H_4)(PPh_3)$_3$] towards **165** occurs via oxidative addition resulting in the mono(chelate)

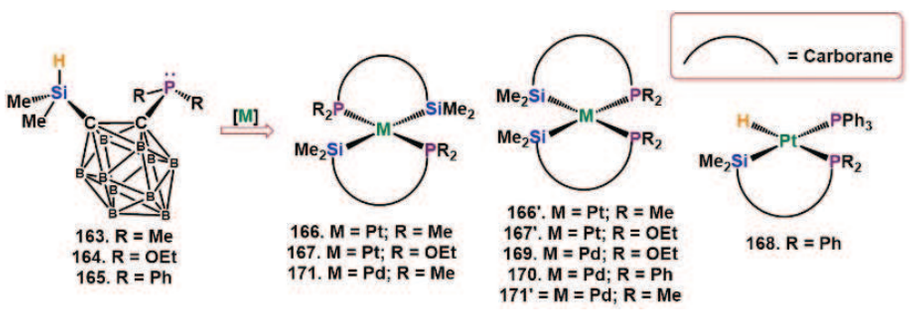


Figure 12. Bulky carborane silyl-phosphine ligands [53].

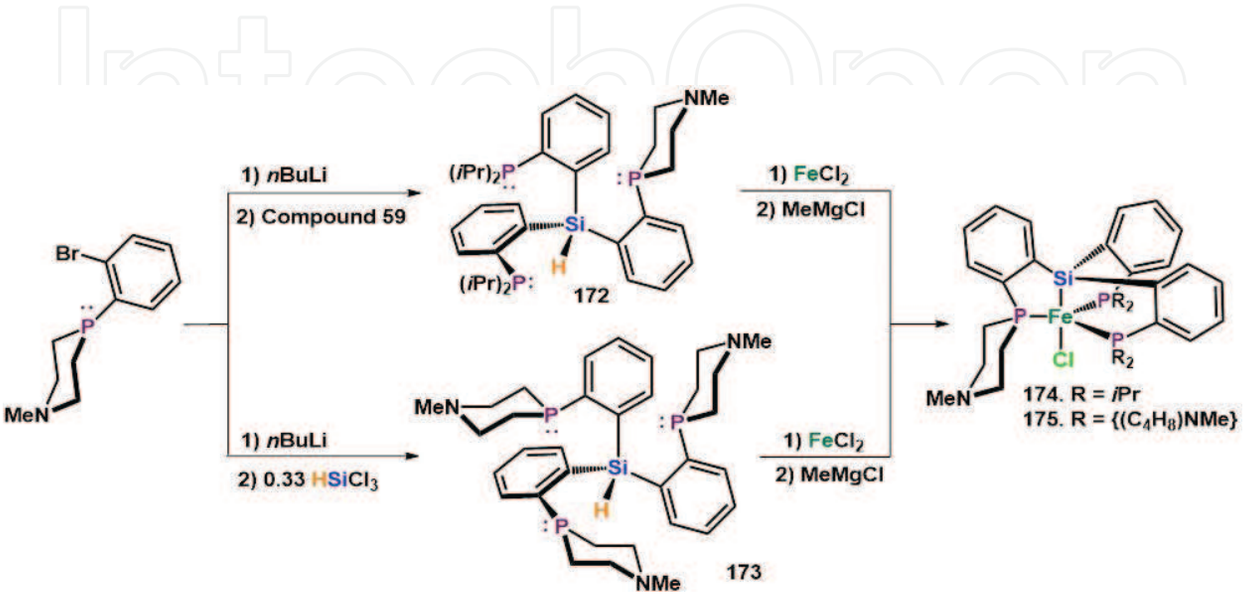


Figure 13. Syntheses of bulky cage trigonal bipyramidal iron complexes [54].

[PtH{(Ph_2P)$C_2B_{10}H_{10}$($SiMe_2$)}(PPh_3)] (**168**). These authors also investigated the reactivity of the same bulky carborane silyl-phosphines with the palladium precursor [$Pd_2(dba)_3$] and observed that depending of the substituents over the phosphorous atoms, the *cis* isomer was exclusively formed [Pd{(R_2P)$C_2B_{10}H_{10}$($SiMe_2$)}$_2$] (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{[$Ph_2P(CH_2)_3]_2$SiMe}] (**176**) [55] derived from the reaction of the ligand *PSiP* {[$Ph_2P(CH_2)_3]_2$SiHMe} (**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 C_6D_6 and C_7D_8, while in $CDCl_3$ or CD_2Cl_2 solutions, the ratio is *ca.* 83:17. Complex **176** (and **176′**) reacted with NaX (X = Br or I) leading to the corresponding complexes [IrHX{[$Ph_2P(CH_2)_3]_2$SiMe}] ((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(O_3SCF_3) to produce the isomers *syn* **179** and *anti* **179′** with general formula [IrH(O_3SCF_3){[$Ph_2P(CH_2)_3]_2$SiMe}]; likewise the reactivity of **176** with AgX or HX (X = PF_6) in the presence of a neutral ligand afforded the mixture of the respective *syn*/*anti* cationic species [IrH(L)$_2$){[$Ph_2P(CH_2)_3]_2$SiMe}]$^+$[PF_6]$^-$ (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 Ph_2P[(*o*-C_6H_4)CH_2SiMe_2H} (**183**) towards the complexes [$RuH_2(\eta^2\text{-}H_2)(PCy_3)_2$] (**184**) and [Ru(cod)(cot)]. Complex **185** resulted from the substitution of two molecules of dihydrogen and two of the ligands PCy_3 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 H_2, 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

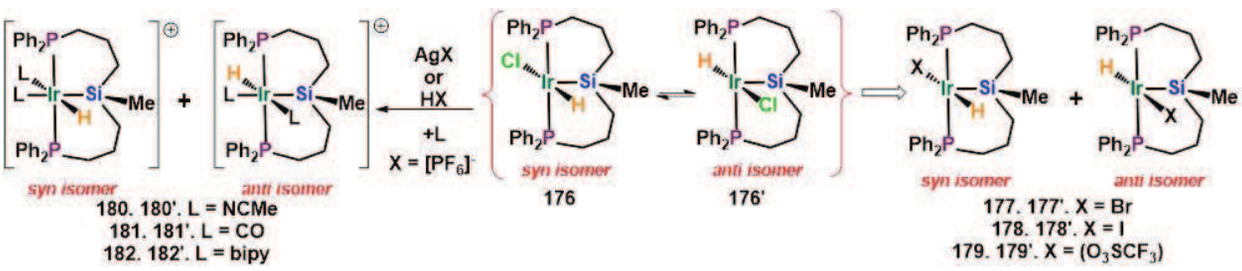


Figure 14. The chemistry of [IrP_2Si] [56, 57].

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 H_2 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*-C_6H_4)CH_2SiMe_2H}$_2$ (**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 PCy_3 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 η^2-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

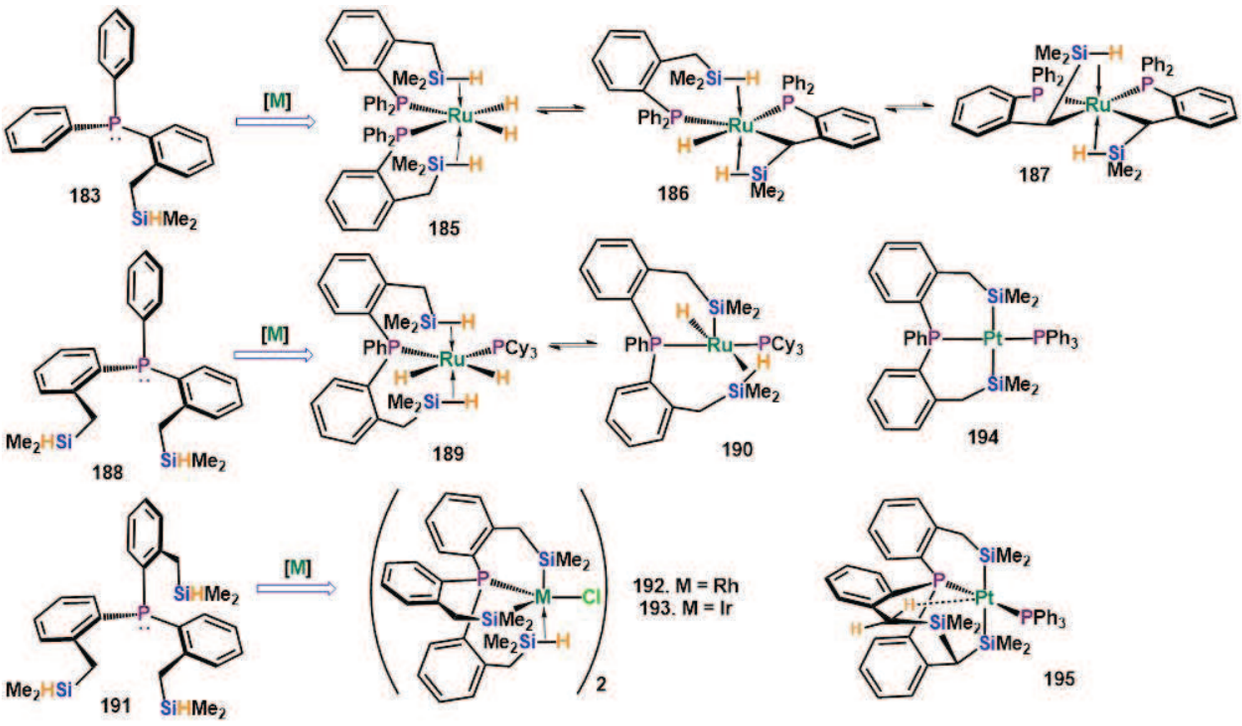


Figure 15. Chemistry of silyl-benzyl phosphines bi-, tri- and tetradentate [58-60].

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)° 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** + H_2 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 $P\{(o\text{-}C_6H_4)CH_2SiMe_2H\}_3$ (**191**) was also investigated with compounds $[M(\mu\text{-}Cl)(cod)]_2$ (M = Rh, Ir) [60] and with $[Pt(PPh_3)_3]$ [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, d^8 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 ^{i}PrOH 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.

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Conflict of interest

The authors declare no conflict of interest.

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References

[1] Holmes-Smith RD, Osei RD, Stobart SR. Phosphinoalkylsilanes: Synthesis and spectroscopic properties of phosphino(silyl)methanes, 1-phosphino-2-silylethanes, and 1-phosphino-3-silylpropanes. Journal of the Chemical Society, Perkin Transactions. 1983; **I**:861-866

[2] Auburn MJ, Holmes-Smith RD, Stobart SR. (Phosphinoalkyl)silyl complexes: 3. "Chelate-assisted" hydrosilylation: Formation of enantiomeric and diasteroisomeric iridium(III) complexes with chelating (phosphinoethyl)silyl ligands. Journal of the American Chemical Society. 1984;**106**:1314-1318

[3] Auburn MJ, Stobart SR. (Phosphinoalkyl)silyl complexes. 5. Synthesis and reactivity of congeneric chelate-stabilized disilyl complexes of rhodium(III) and iridium (III): Cholorobis[[(diphenylphosphino)ethyl]dimethylsilyl] rhodium and -iridium. Inorganic Chemistry. 1985;**24**(3):318-323

[4] Zhu J, Lin Z, Marder TB. Trans influence of boryl ligands and comparison with C, Si, and Sn ligands. Inorganic Chemistry. 2005;**44**(25):9384-9390

[5] Koller SG, Martín-Romo R, Melero JS, Colquhoun VP, Schildbach D, Strohmann C, et al. Structural consequences of an extreme difference between the trans influence of the donor atoms in a palladacycle. Organometallics. 2014;**33**(24):7329-7332

[6] Kim Y-J, Park J-I, Lee S-C, Osakada K, Tanabe M, Choi J-C, et al. Cis and trans isomers of $Pt(SiHAr_2)_2(PR_3)_2$ (R = Me, Et) in the solid state and in solutions. Organometallics. 1999; **18**(7):1349-1352

[7] Kohtaro O, Makoto T. Platinum and palladium complexes with metal–silicon bonds. New bonding, structures, and chemical properties. Bulletin of the Chemical Society of Japan. 2005;**78**(11):1887-1898

[8] Cuevas-Chávez CA, Zamora-Moreno J, Muñoz-Hernández MA, Bijani C, Sabo-Etienne S, Montiel-Palma V. Stabilization of trans disilyl coordination at square-planar platinum complexes. Organometallics, ASAP article, 2017. DOI: 10.1021/acs.organomet.7b00566

[9] Mitton SJ, McDonald R, Turculet L. Synthesis and characterization of neutral and cationic platinum(II) complexes featuring pincer-like Bis(phosphino)silyl ligands: Si−H and Si−Cl bond activation chemistry. Organometallics. 2009;**28**(17):5122-5136

[10] Shimada S, Tanaka M. Group 10 transition-metal complexes with metal–silicon bonds derived from 1,2-disilylbenzenes and bis(2-silylphenyl)silane. Coordination Chemistry Reviews. 2006;**250**(9):991-1011

[11] Shimada S, Tanaka M, Honda K. Unusual reactivity of 1,2-disilylbenzene toward Pt(0) complexes. Isolation of the first $Pt^{IV}Si_4P_2$ and dinuclear, mixed-valence $Pt^{II}Pt^{IV}Si_4P_4$ complexes. Journal of the American Chemical Society. 1995;**117**(31):8289-8290

[12] Joslin FL, Stobart SR. (Phosphinoalkyl)silanes. 2. Synthesis and spectroscopic properties of poly(phosphinoalkyl)silanes. Inorganic Chemistry. 1993;**32**:2221-2223

[13] Mitton SJ, McDonald R, Turculet L. Nickel and palladium silyl pincer complexes: Unusual structural rearrangements that involve reversible Si-C(sp^3) and Si-C(sp^2) bond activation. Angewandte Chemie (International Edition in English). 2009;**48**(45):8568-8571

[14] Mitton SJ, McDonald R, Turculet L. Facile intramolecular silicon–carbon bond activation at Pt(0) and Pt(II) centers. Polyhedron. 2013;**52**:750-754

[15] Takaya J, Iwasawa N. Hydrocarboxylation of allenes with CO_2 catalized by silyl pincer-type palladium complexes. Journal of the American Chemical Society. 2008;**130**:15254-15255

[16] Takaya J, Kirai N, Iwasawa N. Efficient synthesis of diborylalkenes from alkenes and diboron by a new PSiP-pincer palladium-catalyzed dehydrogenative borylation. Journal of the American Chemical Society. 2011;**133**(33):12980-12983

[17] Kirai N, Iguchi S, Ito T, Takaya J, Iwasawa N. PSiP-pincer type palladium-catalyzed dehydrogenative borylation of alkenes and 1,3-dienes. Bulletin of the Chemical Society of Japan. 2013;**86**(7):784-799

[18] Takaya J, Iwasawa N. Silyl ligand mediated reversible beta-hydrogen elimination and hydrometalation at palladium. Chemistry—A European Journal. 2014;**20**(37):11812-11819

[19] Korshin EE, Leitus G, Shimon LJW, Konstantinovski L, Milstein D. Silanol-based pincer Pt(II) complexes: Synthesis, structure, and unusual reactivity. Inorganic Chemistry. 2008;**47**(16):7177-7189

[20] Morgan E, MacLean DF, McDonald R, Turculet L. Rhodium and iridium amido complexes supported by silyl pincer ligation: Ammonia N-H bond activation by a [PSiP]Ir complex. Journal of the American Chemical Society. 2009;**131**:14234-14236

[21] Takaya J, Iwasawa N. Bis(o-phosphinophenyl)silane as a scaffold for dynamic behavior of H–Si and C–Si bonds with palladium(0). Organometallics. 2009;**28**(23):6636-6638

[22] Takaya J, Iwasawa N. Reaction of bis(o-phosphinophenyl)silane with $M(PPh_3)_4$ (M = Ni, Pd, Pt): Synthesis and structural analysis of η^2-(Si–H) metal(0) and pentacoordinate silyl metal(II) hydride complexes of the Ni triad bearing a PSiP-pincer ligand. Dalton Transactions. 2011;**40**(35):8814-8821

[23] Joost M, Mallet-Ladeira S, Miqueu K, Amgoune A, Bourissou D. σ-SiH complexes of copper: Experimental evidence and computational analysis. Organometallics. 2013; **32**(3):898-902

[24] MacInnis MC, McDonald R, Ferguson MJ, Tobisch S, Turculet L. Four-coordinate, 14-electron Ru(II) complexes: Unusual trigonal pyramidal geometry enforced by bis(phosphino) silyl ligation. Journal of the American Chemical Society. 2011;**133**(34):13622-13633

[25] Li Y-H, Ding X-H, Zhang Y, He W-R, Huang W. Synthesis, characterization, and catalytic behavior of a PSiP pincer-type ruthenium(II) complex. Inorganic Chemistry Communications. 2012;**15**:194-197

[26] MacInnis MC, MacLean DF, Lundgren RJ, McDonald R, Turculet L. Synthesis and reactivity of platinum group metal complexes featuring the new pincer-like bis(phosphino) silyl ligand $[K_3$-$(2\text{-}Ph_2PC_6H_4)_2SiMe]$-([PSiP]): Application in the ruthenium-mediated transfer hydrogenation of ketones. Organometallics. 2007;**26**:6522-6525

[27] Kirai N, Takaya J, Iwasawa N. Two reversible sigma-bond metathesis pathways for boron-palladium bond formation: Selective synthesis of isomeric five-coordinate borylpalladium complexes. Journal of the American Chemical Society. 2013;**135**(7):2493-2496

[28] Takaya J, Kirai N, Iwasawa N. Mechanistic studies on the stereoisomerization between two stereoisomeric, isolable five-coordinate borylpalladium(II) complexes bearing a phenylene-bridged PSiP-pincer type ligand. Organometallics. 2014;**33**(6):1499-1502

[29] Wu S, Li X, Xiong Z, Xu W, Lu Y, Sun H. Synthesis and reactivity of silyl iron, cobalt, and nickel complexes bearing a [PSiP]-pincer ligand via Si–H bond activation. Organometallics. 2013;**32**(11):3227-3237

[30] MacInnis MC, Ruddy AJ, McDonald R, Ferguson MJ, Turculet L. Synthesis and characterization of five-coordinate, 16-electron RuII complexes supported by tridentate bis(phosphino)silyl ligation. Dalton Transactions. 2016;**45**(40):15850-15858

[31] Xu S, Li X, Zhang S, Sun H. Synthesis and characterization of stable tripodal silyl iron and nickel complexes. Inorganica Chimica Acta. 2015;**430**:161-167

[32] Mankad NP, Whited MT, Peters JC. Terminal Fe(I)-N2 and Fe(II)…H-C interactions supported by tris(phosphino)silyl ligands. Angewandte Chemie (International Edition in English). 2007;**46**(30):5768-7571

[33] Whited MT, Mankad NP, Lee Y, Oblad PF, Peters JC. Dinitrogen complexes supported by tris(phosphino)silyl ligands. Inorganic Chemistry. 2009;**48**:2507-2517

[34] Takaoka A, Mendiratta A, Peters JC. E−H bond activation reactions (E = H, C, Si, Ge) at ruthenium: Terminal phosphides, silylenes, and germylenes. Organometallics. 2009; **28**(13):3744-3753

[35] Fang H, Choe YK, Li Y, Shimada S. Synthesis, structure, and reactivity of hydridoiridium complexes bearing a pincer-type PSiP ligand. Chemistry, an Asian Journal. 2011; **6**(9):2512-2521

[36] Ruddy AJ, Mitton SJ, McDonald R, Turculet L. 'Hemilabile' silyl pincer ligation: Platinum group PSiN complexes and triple C-H activation to form a (PSiC)Ru carbene complex. Chemical communications (Cambridge, England). 2012;**48**(8):1159-1161

[37] Takaya J, Ito S, Nomoto H, Saito N, Kirai N, Iwasawa N. Fluorine-controlled C-H borylation of arenes catalyzed by a PSiN-pincer platinum complex. Chemical Communications. 2015;**51**(100):17662-17665

[38] Mankad NP, Müller P, Peters JC. Catalytic N-N coupling of aril azides to yield azoarenes via trigonal bipyramid iron-nitrene intermediates. Journal of the American Chemical Society Communications. 2010;**132**:4083-4085

[39] Lee Y, Mankad NP, Peters JC. Triggering N2 uptake via redox-induced expulsion of coordinated NH3 and N2 silylation at trigonal bipyramidal iron. Nature Chemistry. 2010;**2**(7):558-565

[40] Lee Y, Peters JC. Silylation of iron-bound carbon monoxide affords a terminal Fe carbyne. Journal of the American Chemical Society. 2011;**133**(12):4438-4446

[41] Fong H, Peters JC. Hydricity of an Fe-H species and catalytic CO_2 hydrogenation. Inorganic Chemistry. 2015;**54**(11):5124-5135

[42] Rittle J, Peters JC. Proton-coupled reduction of an iron cyanide complex to methane and ammonia. Angewandte Chemie (International Edition in English). 2016;**55**:1-5

[43] Rittle J, Peters JC. An Fe-N_2 complex that generates hydrazine and ammonia via Fe=NNH_2: Demonstrating a hybrid distal-to-alternating pathway for N_2 reduction. Journal of the American Chemical Society. 2016;**138**(12):4243-4248

[44] Mankad NP, Müller P, Peters JC. Catalytic N−N coupling of aryl azides to yield azoarenes via trigonal bipyramid iron−nitrene intermediates. Journal of the American Chemical Society. 2010;**132**(12):4083-4085

[45] Takaoka A, Peters JC. A homologous series of cobalt, rhodium, and iridium metalloradicals. Inorganic Chemistry. 2012;**51**(1):16-18

[46] Suess DL, Tsay C, Peters JC. Dihydrogen binding to isostructural S = (1/2) and S = 0 cobalt complexes. Journal of the American Chemical Society. 2012;**134**(34):14158-14164

[47] Tsay C, Peters JC. Thermally stable N_2 and H_2 adducts of cationic nickel(II). Chemical Science. 2012;**3**(4):1313-1318

[48] Takaoka A, Gerber LC, Peters JC. Access to well-defined ruthenium(I) and osmium(I) metalloradicals. Angewandte Chemie (International Edition in English). 2010;**49**(24):4088-4091

[49] Takaoka A, Mankad NP, Peters JC. Dinitrogen complexes of sulfur-ligated iron. Journal of the American Chemical Society. 2011;**133**(22):8440-8443

[50] Rittle J, McCrory CCL, Peters JC. A 10^6-fold enhancement in N_2-binding affinity of an $Fe_2(\mu\text{-}H)_2$ core upon reduction to a mixed-valence $Fe^{II}Fe^{I}$ state. Journal of the American Chemical Society. 2014;**136**(39):13853-13862

[51] Connor BA, Rittle J, VanderVelde D, Peters JC. A Ni0(η^2-(Si–H))(η^2-H_2) complex that mediates facile H atom exchange between two σ-ligands. Organometallics. 2016;**35**(5):686-690

[52] Creutz SE, Peters JC. Diiron bridged-thiolate complexes that bind N_2 at the Fe(II)Fe(II), Fe(II)Fe(I), and Fe(I)Fe(I) redox states. Journal of the American Chemical Society. 2015; **137**(23):7310-7313

[53] Lee Y-J, Lee J-D, Kim S-J, Keum S, Ko J, Suh I-H, et al. Synthesis, structure, and DFT calculation of (phosphino-o-carboranyl)silyl group 10 metal complexes: Formation of stable trans-Bis(P,Si-chelate)metal complexes. Organometallics. 2004;**23**(2):203-214

[54] Creutz SE, Peters JC. Exploring secondary-sphere interactions in Fe-N x H y complexes relevant to N_2 fixation. Chemical Science. 2017;**8**(3):2321-2328

[55] Brost RD, Bruce GC, Joslin FL, Stobart SR. Phosphinoalkylsilyl complexes. 12. Stereochemistry of the tridentate Bis(diphenylphosphinopropyl)silyl (biPSi) framework: Complexation that introduces "face discrimination" at Coordinatively unsaturated metal centers. X-ray crystal and molecular structures of Pt[SiMe($CH_2CH_2CH_2PPh_2)_2$]Cl, IrH[SiMe($CH_2CH_2CH_2PPh_2)_2$]Cl, and RuH[SiMe($CH_2CH_2CH_2PPh_2)_2$]$(CO)_2$. Organometallics. 1997;**16**(26):5669-5680

[56] Sola E, Garcia-Camprubi A, Andrés JL, Martin M, Plou P. Iridium compounds with κ-P,P,Si (biPSi) pincer ligands: Favoring reactive structures in unsaturated complexes. Journal of the American Chemical Society. 2010;**132**:1911-1921

[57] Garcia-Camprubi A, Martin M, Sola E. Addition of water across Si-Ir bonds in iridium complexes with kappa-P,P,Si (biPSi) pincer ligands. Inorganic Chemistry. 2010; **49**(22):10649-10657

[58] Montiel-Palma V, Muñoz-Hernandez MA, Ayed T, Barthelat JC, Grellier M, Vendier L, Sabo-Etienne S. Agostic Si-H bond coordination assists C-H bond activation at ruthenium in bis(phosphinobenzylsilane) complexes. Chemical Communications. 2007;**0**(38):3963-3965

[59] Montiel-Palma V, Muñoz-Hernandez MA, Cuevas-Chavez CA, Vendier L, Grellier M, Sabo-Etienne S. Phosphinodi(benzylsilane) PhP{(o-$C_6H_4CH_2$)$SiMe_2H$}$_2$: A versatile"PSi_2H_x" pincer-type ligand at ruthenium. Inorganic Chemistry. 2013;**52**(17):9798-9806

[60] Corona-Gonzalez MV, Zamora-Moreno J, Cuevas-Chavez CA, Rufino-Felipe E, Mothes-Martin E, Coppel Y, Muñoz-Hernandez MA, Vendier L, Flores-Alamo M, Grellier M, Sabo-Etienne S, Montiel-Palma V. A family of rhodium and iridium complexes with semirigid benzylsilyl phosphines: From bidentate to tetradentate coordination modes. Dalton Transactions. 2017;**46**(27):8827-8838

[61] Shimizu H, Nagasaki I, Matsumura K, Sayo N, Saito T. Developments in asymmetric hydrogenation from an industrial perspective. Accounts of Chemical Research. 2007; **40**(12):1385-1393

[62] Colacot T. Nobel Prize in Chemistry. Timely recognition for Rh, Ru and Os-catalysed chiral reactions. Platinum Metals Review. 2001, 2002;**46**(2):82-83

[63] Ikariya T, Murata K, Noyori R. Bifunctional transition metal-based molecular catalysts for asymmetric syntheses. Organic & Biomolecular Chemistry. 2006;**4**(3):393-406

[64] Tamao K, Sumitani K, Kumada M. Selective carbon-carbon bond formation by crosscoupling of Grignard reagents with organic halides. Catalysis by nickel-phosphine complexes. Journal of the American Chemical Society. 1972;**94**(12):4374-4376

[65] Hua X, Masson-Makdissi J, Sullivan RJ, Newman SG. Inherent vs apparent chemoselectivity in the Kumada–Corriu cross-coupling reaction. Organic Letters. 2016; **18**(20):5312-5315

[66] Yoshikai N, Matsuda H, Nakamura E. Hydroxyphosphine ligand for nickel-catalyzed cross-coupling through nickel/magnesium bimetallic cooperation. Journal of the American Chemical Society. 2009;**131**(27):9590-9599

[67] Liu N, Wang Z-X. Kumada coupling of aryl, heteroaryl, and vinyl chlorides catalyzed by amido pincer nickel complexes. The Journal of Organic Chemistry. 2011; **76**(24):10031-10038

[68] Xi Z, Liu B, Chen W. Room-temperature Kumada cross-coupling of unactivated aryl chlorides catalyzed by N-heterocylic carbene-based nickel(II) complexes. The Journal of Organic Chemistry. 2008;**73**(10):3954-3957

[69] Iglesias MJ, Prieto A, Nicasio MC. Kumada–Tamao–Corriu coupling of heteroaromatic chlorides and aryl ethers catalyzed by (IPr)Ni(allyl)Cl. Organic Letters. 2012; **14**(17):4318-4321

[70] Xiong Z, Li X, Zhang S, Shi Y, Sun H. Synthesis and reactivity of N-heterocyclic PSiP pincer iron and cobalt complexes and catalytic application of cobalt hydride in Kumada coupling reactions. Organometallics. 2016;**35**(3):357-363