

Chapter 2

Copper: σ -SiH Coordination to Cu(I)

Abstract This chapter gives firstly an introduction concerning σ -complexes and in particular σ -SiH complexes. Afterwards, the obtained results concerning the coordination of diphosphino-hydrosilanes to Cu(I) will be described.

2.1 Introduction

2.1.1 σ -Bond Coordination to Transition Metals

The activation of σ -bonds by transition metals to undergo oxidative addition is a fundamental reaction in the field of coordination chemistry. Coordination of a σ -bond to a metal center to form a σ -complex is generally involved on the way to complete bond cleavage (Fig. 2.1). Such complexes that may be observed or even isolated, play key roles as intermediates or transition states in oxidative addition processes.

The field of σ -complexes evolved significantly following the pioneering studies of Kubas et al. [1, 2] in 1980s. The finding that an intact dihydrogen molecule coordinates to a transition metal was at first highly debated [2], but the relevance of this discovery for transition metal-catalyzed bond activation processes was soon recognized and stimulated the field of coordination chemistry.

The coordination of a σ -bond is nowadays well understood and can be considered as an early state of bond activation or “arrested oxidative addition” [3]. The precise understanding of the bonding interaction in a σ -complex is therefore of paramount importance for synthetic applications, as knowledge of structure and reactivity of such complexes will lead to more active and selective catalysts. The side-on coordination of σ -bonds has become a textbook example for weak metal-ligand interactions [4] and a number of complexes containing HH [2], HSi [3, 5–8] HB [9], HC [10–12], SiSi [13–16] and even CC [17–19] bonds has been characterized.

A σ -complex can be described as a 3-center 2-electron interaction where a σ -bond acting as a 2-electron donor is coordinated in a side-on fashion (η^2) to a

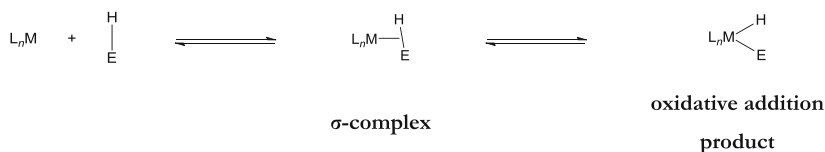


Fig. 2.1 Oxidative addition reaction at a transition metal complex with intermediacy of a σ -complex

metal, in close relationship to the Dewar-Chatt-Duncanson model that rationalizes the bonding interaction of an alkene (or an alkyne) to a metal center to form a π -complex. The σ -orbital of the ligand overlaps with a vacant metal d-orbital which leads to donation of electron density from the ligand to the metal. Furthermore, such a complex may be stabilized by backbonding, i.e. retrodonation of electron density from the metal to the ligand by interaction of a filled metal orbital of suitable symmetry with the σ^* -orbital of the ligand (Fig. 2.2).

In analogy to other 3-center 2-electron bonds involving p-block elements like in polyboranes or carbonium ions, the bonding situation of a σ -complex cannot be depicted by a single Lewis structure and is therefore also categorized as a “non-classical interaction”.

Equally important and closely related to σ -complexes are agostic interactions. Originally, this weak bonding interaction was defined as the intramolecular 3-center 2-electron coordination of a CH-bond to a transition metal, i.e. the ligand coordinating to a metal center is tethered to a CH-bond that is interacting in a side-on fashion with the same metal [20]. Over time, the term was watered down and used as well for other 3-center 2-electron interactions such as $M(\sigma\text{-SiH})$, $M(\sigma\text{-BH})$, $M(\sigma\text{-CC})$, etc. A recent contribution of Brookhart and Green who originally coined the term “agostic” points out that “*agostic*” is not synonymous with “3-center 2-electron” and should be used exclusively for CH bonds [10]. We decided to follow these recommendations and intramolecular σ -interactions other than with CH bonds are not called agostic in this manuscript. Nevertheless, we are well aware of the widespread use of the term agostic and the arguments for it in this terminology issue [2, 3, 5, 17].



Fig. 2.2 General bonding scheme for a σ -complex

2.1.2 σ -SiH Complexes

Although the first reported complex featuring a coordinated σ -bond in 1969 contained actually a hydrosilane [21], the field of σ -complexes and the systematic investigation thereof started to evolve only with the discovery of the first σ -H₂ complex in the early 1980s (vide supra) [1, 3]. With the growing interest in this type of weak bonding interaction, the experimental observation and theoretical understanding of σ -SiH complexes greatly advanced and had direct impact on SiH-bond activation processes such as hydrosilylation reactions.

The η^2 -bonding scheme of hydrosilanes is essentially the one described above (see 2.1.1). However, even though a hydrosilane moiety often resembles dihydrogen in terms of reactivity, there are important differences to the more frequently encountered H₂ ligand: the SiH bond is weaker than the one of H₂ (ca. 75–100 kcal/mol vs. 104 kcal/mol), having a bonding SiH orbital higher in energy and an antibonding SiH orbital lower in energy, which makes an SiH moiety a better σ -donor and a better π -acceptor than H₂. Furthermore, the H₂ ligand coordinates in a symmetric fashion, while the SiH-bond coordination is necessarily dissymmetric (Fig. 2.3). The inherent difference in electronegativity of Si and H (1.9 vs. 2.1 on the Pauling scale) as well as the electronic influence of the substitution pattern on silicon modulate the donation and backdonation components.

Furthermore, the approach of a hydrosilane moiety to a metal center is strongly affected by the steric situation determined by the substituents at silicon, in contrast to the small H₂ molecule [3, 5].

2.1.3 Experimental Identification of σ -SiH Interactions

The characterization of σ -SiH complexes is well-established and is based mainly on NMR and IR spectroscopy as well as single crystal X-ray or neutron diffraction analysis.

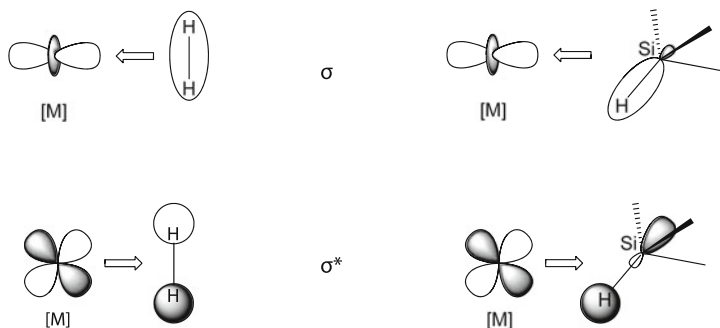


Fig. 2.3 σ -H₂ (left) versus σ -SiH (right) coordination at a transition metal

A typical NMR signature for the coordination of σ -SiH-bonds to transition metals is the decrease of the silicon-hydrogen coupling constant ($^1J_{\text{SiH}}$) as compared to the non-coordinated ligand [3, 5]. Known silane complexes are associated with coupling constants down to 40–70 Hz, but σ -SiH complexes featuring $^1J_{\text{SiH}}$ values at around 100 Hz have been reported as well [22, 23]. In general, it holds that the more activated the σ -SiH-bond is, the lower the $^1J_{\text{SiH}}$ value.

Another valuable and informative indicator is the Si–H stretching frequency ($\nu(\text{SiH})$): coordination of the σ -SiH bond results in a decrease of its bond strength and therefore $\nu(\text{SiH})$ is redshifted upon coordination. Broad, intense bands observed in the region between 1650 and 1800 cm^{-1} are considered to be indicative of η^2 -SiH-bond coordination.

Structural information can be obtained by single crystal X-ray diffraction analysis. Close proximity to the metal center of both hydrogen and silicon and an elongation of the SiH bond may hint to coordination. However, the precise localization of hydrogen atoms close to heavy elements is inherently difficult by X-ray crystallography even with high-quality measurements. Single crystal neutron diffraction circumvents this limitation, but crystals of sufficient size and quality are often not easily to obtain. Furthermore, beam time at one of the few neutron sources in Europe is scarce and necessitates not negligible effort to obtain.

Nowadays, high-level DFT computational studies are able to reproduce with high precision experimentally obtained structural and spectroscopic data. The accurate localization of hydrogen atoms in a given structure can be performed by computational means in combination with and complementary to X-ray diffraction analyses [24, 25].

Although the field of σ -SiH complexes is in general well developed and examples exist for virtually all transition metals, there was no example involving a coinage metal to be found in the literature, except for a computational analysis [26, 27]. Therefore we aimed at investigating the coordination of σ -SiH bond to group 11 metal centers.

2.2 σ -SiH Complexes of Cu

Isolation of 1st-row transition metal σ -complexes is generally more challenging than for the heavier metals, due to their less diffuse d-shell that hampers significant overlap with σ -orbitals. In the case of cationic metal centers, the positive charge leads to further contraction of the 3d-shell which makes effective backdonation of electron density from the metal to the σ^* -orbital difficult. The isolation of a σ -complex of copper is therefore expected to be non-trivial.

2.2.1 Synthesis and Characterization of Cu(I) Complexes

Ambiphilic chelating phosphine ligands have been used successfully to investigate the coordination of Lewis acids to transition metals [28, 29]. This chelating approach was extrapolated to the coordination and activation of σ -SiSi bonds at Cu (I) and Au(I) [30, 31]. In case of copper, this strategy led to the isolation of the first structurally characterized σ -complex of a coinage metal (Fig. 2.4).

This finding prompted us to investigate the capability of copper to bind other σ -bonds. The chelate assistance approach was extrapolated here to σ -SiH bonds. For that purpose, we turned our interest to a diphosphine-hydrosilane ligand, namely, $[\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{SiH}(\text{Me})(o\text{-C}_6\text{H}_4)\text{PPh}_2]$ (**1**). This ligand has recently attracted much interest with group 8–10 metals (Ru, Rh, Ir, Ni, Pd, and Pt) [23, 32–39]. The central σ -SiH bond is readily activated by these metals, and the ensuing diphosphine-silyl pincer complexes were found to possess versatile reactivity [33, 34] and interesting catalytic properties [37, 38]. Noteworthy, the σ -SiH complexes en route to the PSiP pincer complexes have recently been intercepted and characterized with Ni, Pd, and Pt [38, 39].

For the purpose of comparison, a palladium complex of **1** (Fig. 2.5), reported by the Iwasa et al., is discussed here in more detail [23]. The key feature of the ^1H solution NMR spectrum of this palladium complex is the 1J_{SiH} coupling constant of 110 Hz at the upper range of reported SiH coupling constants for hydrosilane σ -complexes. The molecular structure in the solid state has been determined by single crystal X-ray diffraction analysis: The palladium atom of this compound exhibits a distorted tetrahedral environment, with a triphenylphosphine ligand and the two phosphine donor arms of **1** forming the base of a tetrahedron and the tethered SiH-moiety completing the coordination sphere in the apical position. The SiH bond length is 1.60(3) Å, which is significantly longer than the SiH bond of

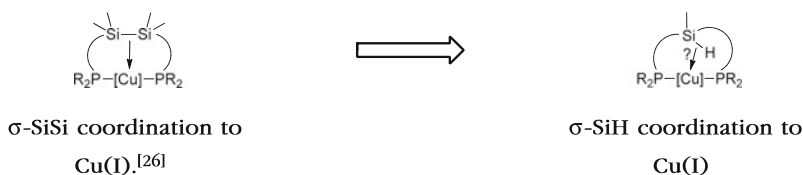


Fig. 2.4 Coordination of a SiSi bond and hypothetical/envisioned coordination of a hydrosilane to Cu(I)



Fig. 2.5 Iwasa's Pd σ -SiH complex and corresponding key experimental data

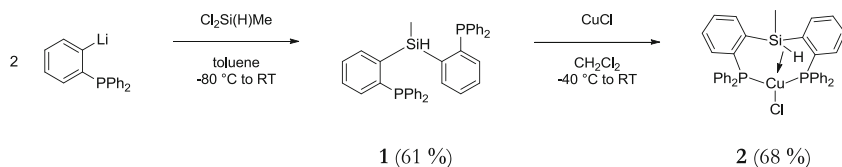
non-coordinated **1** (1.484 Å, calculated, *vide infra*), but relatively short in comparison with the majority of reported σ -SiH complexes (ca. 1.6 Å up to 1.9 Å) [3, 5]. Vibrational spectroscopic data were not attributed.

The comparatively small metric and spectroscopic changes in the SiH moiety were attributed to only weak backdonation from Pd to the σ^* orbital of the SiH bond.

We prepared the diphosphine-hydrosilane ligand **1** by slight modification of the reported procedure, coupling two equivalents of isolated *ortho*-lithiated triphenylphosphine with dichloromethylsilane (Scheme 2.1) [32]. After purification by column chromatography **1** was obtained in 61 % yield. Coordination to copper was achieved by reacting **1** with 1 eq. of CuCl in dichloromethane (addition at -40 °C and warm-up to room temperature over 1 h). The progress of the reaction is easily followed visually as the initial suspension of CuCl progressively turns to a clear solution. Copper complex **2** was isolated as a white solid (68 % yield) after precipitation with pentane.

Complex **2** displays a single resonance signal at $\delta = -7.6$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, in agreement with the symmetric coordination of the two phosphorus atoms. The associated ^{29}Si NMR signal appears as a triplet ($J_{\text{SiP}} = 23$ Hz) at $\delta = -30$ ppm. These data are very similar to those of the free ligand **1** ($\delta_{\text{Si}} = -24$ ppm, $J_{\text{SiP}} = 20$ Hz) and indicate the retention of the hydrosilane motif upon coordination. The slight high-field shift of the ^{29}Si NMR signal (by 6 ppm) is hardly informative at this stage. It may result from a weak interaction of the hydrosilane motif with copper or simply from some modification of the geometry around silicon upon coordination. A similar high-field shift was observed upon coordination of a related diphosphine-dimethylsilane ligand to gold, without any interaction of the metal center with the silane motif [40]. The ^1H NMR signal for the hydrogen atom bound to silicon is shifted downfield by ~ 1.1 ppm compared to that of the free ligand (from $\delta = 5.48$ ppm in **1** to $\delta = 6.63$ ppm in **2**). Most indicative is the associated $^1J_{\text{SiH}}$ coupling constant measured from the ^{29}Si satellites of the ^1H NMR signal (Fig. 2.6).

It decreases from 204 Hz in the free ligand **1** to 180 Hz in complex **2**, suggesting some weakening of the SiH bond. However, the relatively large $^1J_{\text{SiH}}$ coupling constant of **2** compared to reported σ -SiH complexes and in particular compared to Iwasa's related σ -SiH palladium complex (*vide supra*, $^1J_{\text{SiH}} = 110$ Hz) suggests only weak interaction of the σ -SiH-bond with copper. To confirm this bonding picture, we then turned to infrared spectroscopy: The Si–H vibration band is found



Scheme 2.1 Synthesis of ligand **1** and Cu(I) complex **2**

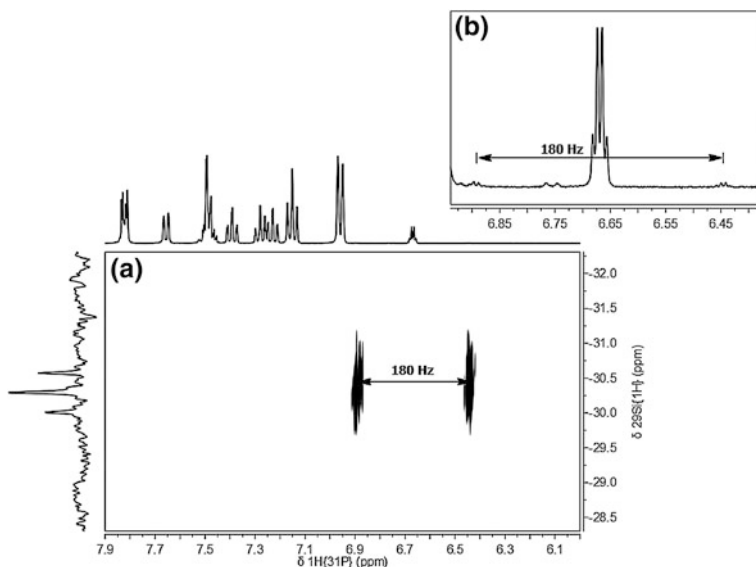


Fig. 2.6 Determination of $^1J_{\text{SiH}}$ for complex **2**: **a** ^1H - ^{29}Si -HMBC spectrum; inset **b** magnification of the SiH signal in the $^1\text{H}\{^{31}\text{P}\}$ spectrum showing the ^{29}Si satellites

at 1996 cm^{-1} in complex **2**, versus 2142 cm^{-1} in the free ligand. This variation confirms the weakening of the σ -SiH bond upon coordination and again follows the usual trend of η^2 -SiH complexes, albeit with a significantly weaker magnitude (bands in the range 1650 – 1800 cm^{-1} are usually observed) [3, 5]. To gain further insight into the structure of this complex, crystals were grown by slow diffusion of pentane into a dichloromethane solution of **2** at $-30\text{ }^\circ\text{C}$, and an X-ray diffraction analysis was performed (Fig. 2.7).

The copper center of **2** is surrounded by the two phosphorus atoms and the chlorine atom, organized in a trigonal-planar arrangement [$\text{PCuP} = 115.66(2)^\circ$, sum of angles around Cu: 359.7°]. Interestingly, the silicon atom is also located close to copper. The Cu–Si distance [$2.9977(5)\text{ \AA}$] is beyond the sum of the covalent radii ($2.43\text{ \AA}$) [41], but well within the sum of the van der Waals radii ($4.10\text{ \AA}$) [42]. This is consistent with a possible participation of the σ -SiH bond in the coordination, as suggested by the NMR and IR data. Even though the obtained X-ray data are of acceptable quality, the margin errors for the associated SiH and CuH distances are large and make small changes in the SiH bond distance insignificant. Therefore, discussions of these structural parameters are not meaningful at this point. In order to gain more insight into the structure of copper complex **2** with regard to precise hydrogen atom localization and to obtain subsequently a more detailed picture of the bonding situation in **2** and related complexes, DFT calculations have thus been carried out (see Sect. 2.2.3).

We envisioned increasing the electrophilicity of the metal to explore how this affects the coordination of σ -SiH bonds to copper. For that purpose, **2** was reacted

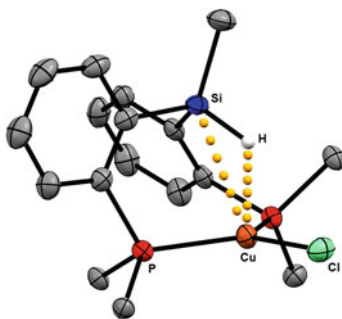
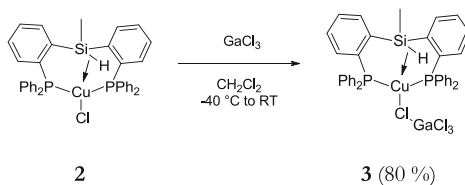


Fig. 2.7 Molecular structure of **2** determined by single crystal X-ray diffraction. Solvent molecules, phenyl substituents (with exception of the *ipso* carbon atoms) at phosphorus and hydrogen atoms, except the one at Si, are omitted for clarity. Selected bond lengths [Å] and angles [°]: CuH 2.00(2), HSi 1.42(2), CuCl 2.2287(5), CuP1 2.2557(6), CuP2 2.2783(5), SiCu 2.9977(5), P1CuP2 115.66(2), P1CuCl 122.10(2), ClCuP2 121.94(2), SiHCu 122(1)



Scheme 2.2 Synthesis of Cu(I) complex **3**

with one equivalent of GaCl_3 and the new complex **3** was isolated in 80 % yield (Scheme 2.2).

The ^{31}P and ^{29}Si NMR data for **3** (^{31}P : $\delta = -5.0$ ppm and ^{29}Si : $\delta = -30$ ppm, $J_{\text{SiP}} = 23$ Hz) very much resemble those of **2**, suggesting that the two complexes adopt similar coordination modes. Notably, the characteristic features suggesting the presence of a weak interaction between the σ -SiH bond and the copper center in **2** are also met in **3**, even to a slightly greater extent: the $^1J_{\text{SiH}}$ coupling constant is further decreased down to 170 Hz and, concomitantly, the $\nu(\text{SiH})$ band is further shifted to lower frequency at 1973 cm^{-1} (Table 2.1).

These data may suggest a slight strengthening of the σ -SiH bond coordination from **2** to **3**. Crystals of **3** were grown from a dichloromethane/pentane solution at $-60\text{ }^\circ\text{C}$, and its molecular structure was elucidated by an X-ray diffraction analysis (Fig. 2.8).

Accordingly, the Lewis acid GaCl_3 interacts strongly with the chloride at copper, but without completely abstracting it. The CuCl distance is significantly elongated [$\text{CuCl} = 2.359(1)\text{ \AA}$ in **3** vs. $2.229(1)\text{ \AA}$ in **2**], so that complex **3** can be formally considered as a tight ion pair [$(\mathbf{1})\text{Cu}^+\cdots\text{ClGaCl}_3^-$]. Here also the silicon atom comes close to copper, at an even shorter distance [$\text{CuSi} = 2.815(1)\text{ \AA}$] than in complex **2**. Since the overall geometry around copper in **3** is otherwise similar to

Table 2.1 Selected experimental data for ligand **1** and complexes **2** and **3**

	Free ligand 1	CuCl complex 2	CuClGaCl ₃ complex 3
$\delta^{29}\text{Si}$	−24	−30	−30
J_{PSi}	20	23	23
$\delta^1\text{H}$	5.48	6.63	6.44
$^1J_{\text{SiH}}$	204	180	170
ν_{SiH}	2142	1996	1973
MSi	—	2.997(1)	2.815(1)
PMP	—	115.66(2)	120.13(2)

NMR chemical shifts in ppm, coupling constants in Hz, $\nu(\text{SiH})$ stretching frequencies in cm^{-1} (IR), MSi distances in Å, and PMP bond angles in deg (X-ray)

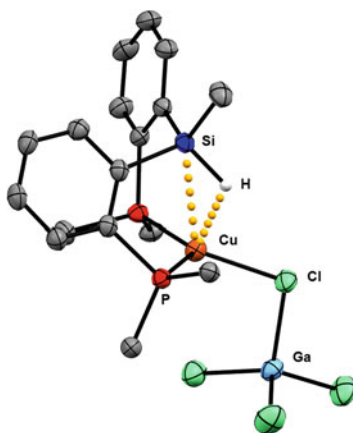


Fig. 2.8 Molecular structure of **3** determined by single crystal X-ray diffraction. Solvent molecules, phenyl substituents (with exception of the ipso carbon atoms) at phosphorus and hydrogen atoms, except the one at Si, are omitted for clarity. Selected bond lengths [Å] and angles [°]: CuCl 2.3587(6), CuH 1.88(2), HSi 1.45(2), CuP1 2.2535(6), CuP2 2.2471(6), CuSi 2.8148(5), ClGa 2.2421(5), P2CuCl 119.18(2), ClCuP1 118.69(2), P2CuP1 120.13(2), SiHCu 115(1), CuClGa 104.10(2)

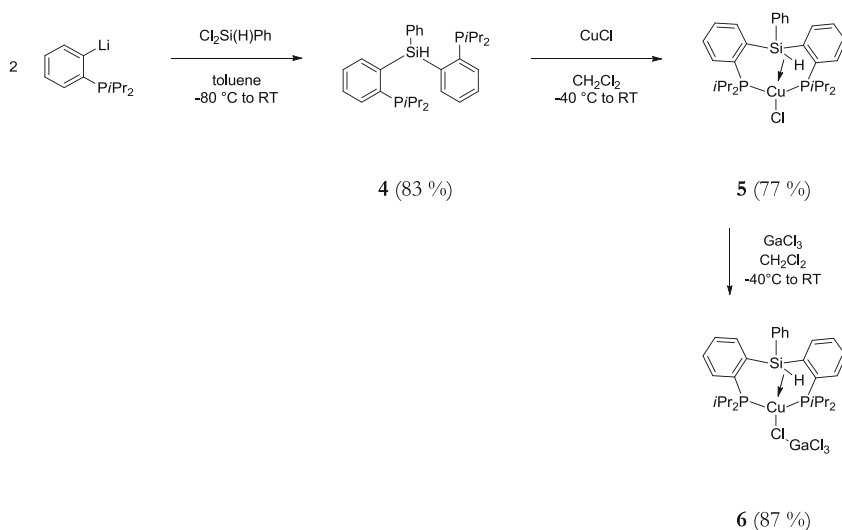
that of the CuCl complex **2** [trigonal-planar arrangement, quasi-unchanged PCuP bite angle at 120.13(2)°], the shortening of the CuSi distance most likely results from electronic rather than geometric factors. The structural features of **3** are consistent with the spectroscopic data and suggest indeed a slightly stronger coordination of the σ -SiH bond upon decreasing the electron density at copper.

Next, the influence of the substitution pattern at the phosphine donor groups and at the central silicon atom of the ligand on the coordination of the hydrosilane moiety to Cu(I) was investigated. An electron-withdrawing substituent on silicon should diminish the electron density of the SiH bond, while at the same time more basic phosphine sites would electronically enrich the copper center. We expected that both contributions should increase the backdonation from copper to SiH and

therefore stabilize the η^2 -SiH bond. Ligand **4** ($[i\text{Pr}_2\text{P}(o\text{-C}_6\text{H}_4)\text{SiH}(\text{Ph})(o\text{-C}_6\text{H}_4)\text{P}i\text{Pr}_2]$) featuring diisopropylphosphine donors and a (phenyl)hydrosilane motif was synthesized in order to fine-tune the strength of the intramolecular σ -bond of the corresponding Cu(I) complexes. **4** was prepared similarly to **1**. The reaction of 2 equivalents of *o*-lithiated diisopropylphenyl phosphine with dichlorophenylsilane gave **4** in 83 % yield after workup by crystallization. As for **2**, the synthesis of the copper(I) complex was performed by reaction of **4** with CuCl at low temperature (Scheme 2.3). Subsequent work-up by precipitation gave CuCl complex **5** in 77 % yield. Generation of a more electrophilic copper species was achieved by reaction of **5** with GaCl₃ at -40°C to give complex **6** in 87 % yield.

The spectroscopic data of **4**, **5** and **6** are somewhat similar to those of **1**, **2** and **3**, respectively (Table 2.2). A notable feature of the ^1H NMR spectrum of **4** is the $^1J_{\text{SiH}}$ value of 220 Hz. The free ligand **4** exhibits a single resonance at $\delta = -0.8$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Upon coordination to copper the ^{31}P NMR signal is shifted to lower field ($\delta = 16.9$ ppm) and is broadened, indicating a symmetric environment for the two phosphorus donor arms in **5** while at the same time the SiH coupling constant decreases ($^1J_{\text{SiH}} = 180$ Hz), pointing at the coordination of the hydrosilane moiety to the CuCl fragment. With the formation of the GaCl₃ adduct (**6**) featuring a less electron-rich copper center, a further decrease of $^1J_{\text{SiH}}$ down to 170 Hz is observed (Table 2.2).

Even though Δ^1J_{SiH} , the difference between the SiH coupling constant of free ligand and the copper complexes, is slightly bigger for the couple in the isopropyl phosphine series than for the diphenylphosphine complexes (40 and 50 Hz for **5** and **6** vs. 24 and 34 Hz for **2** and **3**), the absolute values of $^1J_{\text{SiH}}$ of **5** and **6** are still not in the range expected for typical σ -SiH complexes (vide supra). An analysis of



Scheme 2.3 Synthesis of ligand **4** and its corresponding Cu(I) complexes **5** and **6**

Table 2.2 Selected experimental data for ligand **4** and complexes **5** and **6**

	Free ligand 4	CuCl complex 5	CuClGaCl ₃ complex 6
$\delta^{29}\text{Si}$	-27	-34	-35
J_{PSi}	22	19	26
$\delta^1\text{H}$	6.42	7.11	7.19
$^1J_{\text{SiH}}$	220	180	170
ν_{SiH}	2165	2043	1978
MSi	—	2.8833(6)	2.837(2)
PMP	—	140.19(2)	137.69(8)

NMR chemical shifts in ppm, coupling constants in Hz, $\nu(\text{SiH})$ stretching frequencies in cm^{-1} (IR), MSi distances in Å, and PMP bond angles in deg (X-ray)

the IR spectra of **4**, **5** and **6** points into the same direction: $\nu(\text{SiH})$ decreases from 2165 cm^{-1} in the free ligand to 2043 cm^{-1} in the CuCl complex and is further redshifted to 1978 cm^{-1} in **6** which is in the same region as for the diphenylphosphino complexes. These spectroscopic characteristics suggest, once again, only weak bonding of the hydrosilane moiety to the copper center and no significant influence of the substitution pattern on silicon and phosphorus on this coordination.

Crystals of **5** and **6** were grown and the molecular structures of these complexes were determined by an X-ray diffraction analysis (Fig. 2.9) in order to analyze as well their structural features.

The coordination environment of Cu in **5** and **6** resembles the complexes of the diphenylphosphine series, both for the copper chloride complex and the GaCl₃ adduct, with the copper center being surrounded by the two phosphine arms and the

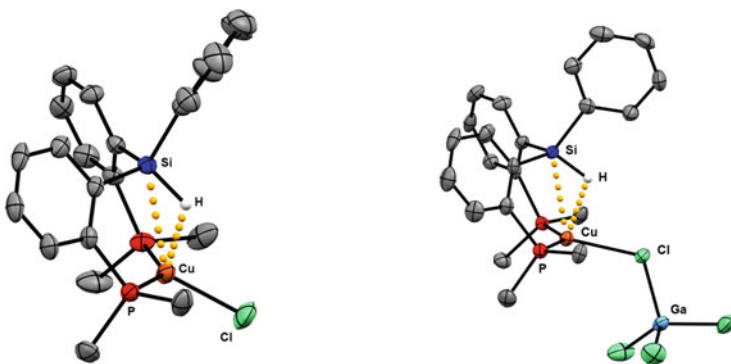


Fig. 2.9 Molecular structures of **5** (left) and **6** (right) determined by single crystal X-ray diffraction. Isopropyl substituents at phosphorus are simplified. Solvent molecules and hydrogen atoms, except the ones at Si, are omitted for clarity. Selected bond lengths [Å] and angles [°]: **5**: ClCu 2.2681(6), CuH 1.91(2), HSi 1.40(2), CuSi 2.8833(6), CuP1 2.2330(7), CuP2 2.2339(7), ClCuP 107.67(2), P1CuP2 140.19(2), P2CuCl 110.36(2), CuHSi 120(1); **6**: ClCu 2.473(2), CuH 2.08(9), HSi 1.40(6), CuP1 2.230(2), CuP2 2.256(2), ClGa 2.231(2), CuSi 2.837(2), ClCuP1 106.51(7), ClCuP2 115.30(7), P2CuP1 137.69(8), CuHSi 108(5), CuClGa 117.79(9)

chloride atom in a trigonal-planar arrangement. The PCuP angle is significantly opened for **5** [PCuP = 140.19(2)°] and **6** [PCuP = 137.69(8)°], compared to **2** and **3**. The CuCl distances for **5** and **6** are in the same range as observed before: 2.2681 (6) Å for the copper chloride complex and 2.473(2) Å in the GaCl₃ adduct, suggesting for **6** as well the formulation as a tight ion pair: [(**4**)Cu⁺...ClGaCl₃⁻].

The most striking feature is the short CuSi distance in **5** (2.8833(6) Å). This distance is further shortened upon formation of the GaCl₃ adduct **6** (2.837(2) Å). In accordance with the spectroscopic data, this shortening can be ascribed to a strengthened η^2 -SiH coordination to copper.

Overall, the structural parameters confirm the picture of weak bonding of the SiH bond to Cu(I) in complexes **5** and **6**.

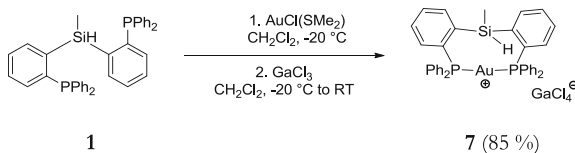
Although the modified substitution pattern shows a certain influence on the spectroscopic and structural features of the σ -SiH complexes, its impact is rather small. Even though some characteristics of **5** and **6** may suggest a marginal strengthening of the σ -SiH coordination to Cu, its magnitude is not significant.

The only weak strengthening is maybe due to the negative influence of the electron rich phosphine donor arms on the donation from SiH to Cu(I): Overall, the effects of increased backdonation and decreased donation might cancel out and the bond strength does not change after all.

2.2.2 Comparison to a Corresponding Au(I) Complex

In the group, it was shown previously that the coordination of diphosphine-disilane ligands proceeds very differently with copper and gold: side-on coordination of the σ -SiSi bond was observed with copper [30], while gold undergoes spontaneous oxidative addition and forms bis(silyl) gold(III) complexes [31]. This prompted us to investigate the influence of the metal center on the coordination behavior of the diphosphine-hydrosilane ligand. The gold complex **7** was prepared by reacting **1** with AuCl(SMe₂) and GaCl₃ in dichloromethane at low temperature (Scheme 2.4).

The spectroscopic and crystallographic data for complex **7** markedly deviate from those of the copper complexes **2** and **3** and reveal a rather different bonding situation in the gold complex. Indeed, the ¹J_{SiH} coupling constant (204 Hz) and ν (SiH) stretching frequency (2141 cm⁻¹) for **7** are the same as those of the free ligand **1**, suggesting that the σ -SiH bond does not interact with the metal in this



Scheme 2.4 Synthesis of Au(I) complex **7**

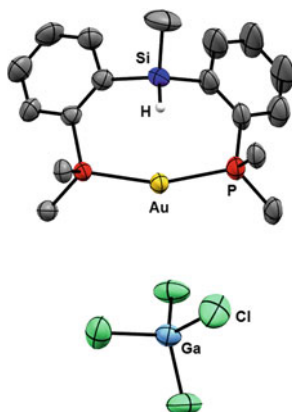


Fig. 2.10 Molecular structure of **7** determined by single crystal X-ray diffraction. Solvent molecules, phenyl substituents (with exception of the *ipso* carbon atoms) at phosphorus and hydrogen atoms, except the one at Si, are omitted for clarity. Selected bond lengths [Å] and angles [°]: AuH 2.63(4), HSi 1.33(4), AuP1 2.294(1), AuP2 2.285(1), AuCl 3.285(1), AuSi 3.166(1), P1AuP2 159.92(4), AuHSi 101(2)

case. This is consistent with the molecular structure of **7** as determined by single-crystal X-ray diffraction analysis (Fig. 2.10).

The gold complex **7** adopts a discrete ion pair structure $[(\mathbf{1})\text{Au}^+, \text{GaCl}_4^-]$ [shortest $\text{Au}\cdots\text{Cl}$ distance at 3.285(1) Å] with a wide P Au P bite angle [159.92(4)°], but the silicon atom remains far away from gold. Indeed, the AuSi distance in **7** [3.166(1) Å] substantially exceeds the CuSi distances in **2** and **3** [2.997(1) and 2.815(1) Å, respectively], although the covalent radii of gold and copper are very similar (1.36 and 1.32 Å, respectively) [41]. The comparison of complexes **2**, **3** and **7** provides further support for the participation of the σ -SiH bond in the coordination to copper, but not to gold. The bonding situation in the gold complex **7** contrasts with the oxidative addition process observed with the σ -SiSi bond to give a disilyl gold(III) complex [31]. In complex **7**, the metal center accommodates a quasi-linear bis(phosphine)Au⁺ arrangement. Comparatively, copper is more Lewis acidic [43] and the coordination of the pendant SiH or SiSi bond is favorable. In addition, the fact that the silicon atom remains remote from gold in complex **7** indicates that the coordination of the σ -SiH bond to copper in complexes **2** and **3**, although favored by the two phosphine anchors, is not imposed geometrically.

2.2.3 Computational Analysis

A detailed computational study was carried out in collaboration with the group of Dr. K. Miqueu (Université de Pau) in order to (i) further analyze the structural features of the diphosphine-silane complexes **2** and **3**, (ii) probe the influence of the

electron density at the metal center, and (iii) shed light on the nature of the σ -SiH/metal interaction. DFT calculations were performed at the B3PW91/SDD + f (Cu,Au), 6–31G** (other atoms) level of theory. The full substitution pattern of the diphosphine-silane ligand was retained in order to take reliably into account electronic and steric factors. The optimized structure of the CuCl complex **2*** reproduces the one determined crystallographically, with deviations of only 0.03 Å in the CuSi distance and 7° in the PCuP bond angle (Tables 2.1 and 2.3). Most informative is the localization of the hydrogen atom at silicon and the associated Si-H bond length. Accordingly, the σ -SiH bond is predicted to slightly elongate upon coordination, from 1.484 Å in the free ligand **1*** to 1.499 Å in complex **2***. The significance of this variation is corroborated by comparing copper and gold. Indeed, the σ -SiH bond length computed for the gold complex **7*** (1.481 Å) is essentially identical to that of the free ligand (and the silicon atom remains far away from gold at 3.269 Å). This confirms that the side-on coordination of the σ -SiH bond to copper in complex **2** is not a geometric artifact but indeed the result of a bonding interaction.

The next point was to assess how the electrophilicity of copper affects its interaction with the σ -SiH bond. For that purpose, DFT calculations were carried out on complex **3***, featuring the tight $\text{Cu}^+ \cdots \text{ClGaCl}_3^-$ ion pair structure, and on the cationic complex **3****, featuring a naked copper center (without counteranion contact, Fig. 2.11).

Here, the σ -SiH bond length was found to increase from 1.499 Å in **2*** to 1.513 Å in **3****, and concomitantly, the CuSi distance shortens from 3.021 Å in **2*** to 2.808 Å in **3**** (Table 2.3).

Besides these structural features, spectroscopic data were also computed, in particular the $^1J_{\text{SiH}}$ coupling constant. The values measured experimentally by ^1H NMR for complexes **2** and **7** as well as the free ligand **1** were well reproduced

Table 2.3 Selected computational data for ligand **1** and complexes **2***, **3***, **3**** and **7**

	Free ligand 1*	Cu complex 2*	Cu complex 3*	“Naked” Cu complex 3**	Au complex 7*
Si–H	1.484	1.499	1.501	1.513	1.481
M–H	–	2.020	1.987	1.966	2.721
M–Si	–	3.021	2.972	2.808	3.269
PMP	–	122.40	128.41	154.84	155.41
$^1J_{\text{SiH}}$	–198.6	–176.4	–164.2	–143	–201.1
ΔE_{NBO}					
$\sigma_{\text{SiH}} \rightarrow \text{Lp}^*$ (M)	–	8.4	12.4	14.3	–
$s(\text{M}) \rightarrow \sigma^*_{\text{SiH}}$	–	0.9	1.1	1.3	0.25

Bond lengths/distances in Å, bond angles in deg, $^1J_{\text{SiH}}$ coupling constants in Hz, and NBO delocalization energies in kcal/mol

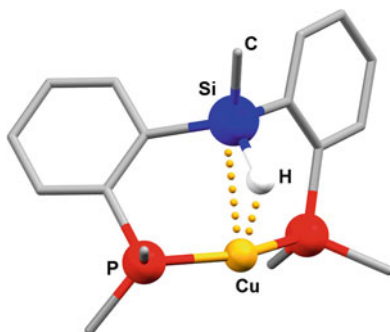


Fig. 2.11 Computed molecular structure of the naked Cu complex **3****, without any counteranion contact. Phenyl substituents (with exception of the *ipso* carbon atoms) at phosphorus and hydrogen atoms, except the one at Si, are omitted for clarity

theoretically using the GIAO method with the IGLOO II basis set (maximum deviation of only 6 Hz; see Tables 2.1 and 2.3).

The geometric variations were compared with the corresponding spectroscopic data. A quasi-linear correlation was found between the σ -SiH bond length and the $^1J_{\text{SiH}}$ coupling constant (Fig. 2.12). This behavior contrasts with the V-type correlation found between the σ -SiH bond length and the $^1J_{\text{SiH}}$ coupling constant for cationic silane complexes of ruthenium [44].

The two extreme situations are met with the free ligand **1*** on the one hand (distance SiH = 1.484 Å, $^1J_{\text{SiH}}$ = -198.6 Hz) and the cationic complex **3**** on the other hand (distance SiH = 1.513 Å, $^1J_{\text{SiH}}$ = -143.0 Hz). Although the interaction between the σ -SiH bond and the copper center is weak in all copper complexes, the

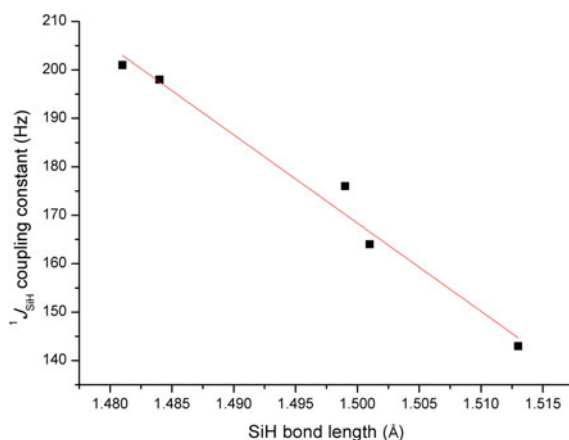


Fig. 2.12 Plot of computed $^1J_{\text{SiH}}$ coupling constant (using the GIAO method with IGLOO II basis set) versus SiH bond length predicted computationally at the B3PW91/SDD + f(Cu,Au),6-31G** (other atoms) level of theory demonstrating a linear relationship between the SiH bond length and the corresponding $^1J_{\text{SiH}}$ values for **7***, **1***, **2***, **3*** and **3**** (from left to right)

structural and spectroscopic variations observed theoretically along the series $2^* \rightarrow 3^* \rightarrow 3^{**}$ clearly indicate a progressive strengthening of the σ -SiH/Cu interaction upon increasing the electrophilicity of copper, in agreement with the experimental observations. We then examined in more detail the bonding situation in complexes 2^* , 3^* and 3^{**} via natural bond orbital (NBO) analysis. At the second-order perturbation level, donor-acceptor interactions from the σ -SiH bond to the metal center were found in all of the copper complexes 2^* , 3^* , and 3^{**} (Fig. 2.13), but not in the gold complex 7^* . The associated delocalization energies ΔE_{NBO} increase from 8 kcal/mol in 2^* to 12 kcal/mol in 3^* and 14 kcal/mol in 3^{**} , providing further confirmation of the gradual strengthening of the interaction upon increasing the electrophilicity of the copper center. The relative contributions of Si and H in the involved σ -SiH bond orbital remain essentially the same upon coordination and do not vary significantly with the electron density at copper (36–41 % for Si and 58–61 % for H). Noteworthy, only insignificant backdonation from copper to σ^* -SiH was found in 2^* , 3^* and 3^{**} ($\Delta E_{\text{NBO}} < 1.5$ kcal/mol), indicating that the coordination of the SiH bond to copper arises essentially, if not exclusively, from σ -SiH $\rightarrow$ Cu donation.

According to these NBO analyses, coordination of the σ -SiH bond to copper is very similar in nature and magnitude to that of the σ -SiSi bond we reported previously. On the basis of steric and orbital grounds, the formation of σ -complexes is a priori less favorable with disilanes than with hydrosilanes [45], but it is likely that geometric factors also play a role in our systems (the σ -SiSi bond was included within the chelating ligand backbone, while the σ -SiH bond is necessarily external). Finally, as spontaneous oxidative addition of the σ -SiSi bond had been observed at gold [31], a similar process with the σ -SiH bond of the copper complex 3^* and gold complex 7^* was considered theoretically. The structures of the corresponding Cu(III) and Au(III) complexes were optimized, and oxidative addition of the σ -SiH bond was found to be strongly disfavored energetically in both cases (by 34.5 kcal/mol for 3^* and 15.9 kcal/mol for 7^*), in agreement with the experimental observations. While σ -SiH coordination is stronger to Cu, oxidative addition of the

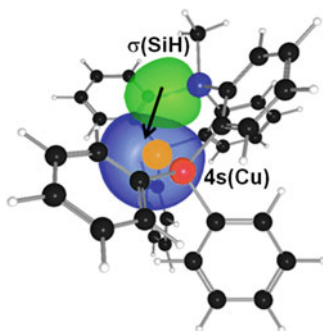


Fig. 2.13 Representation of the NLMOs on Cu and the SiH fragment, determined by an NBO analysis, illustrating the σ -SiH $\rightarrow$ Cu donation for complex 3^{**}

σ -SiH bond is easier for Au. This contrast illustrates that Lewis acidity of a metal and its tendency to undergo oxidative addition do not necessarily show parallel trends. The reader will encounter these aspects again in Chaps. 3 and 5 where they are discussed in more detail in the context of gold chemistry.

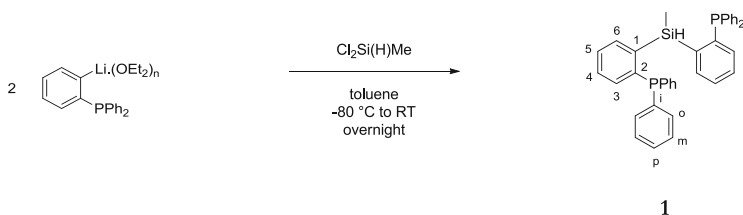
2.2.4 Conclusion

This study provides evidence for the coordination of σ -SiH bonds to copper. The diphosphine-hydrosilanes **1** and **4** are shown experimentally and computationally to engage in weak σ -SiH/Cu interactions. The ensuing copper complexes **2**, **3**, **5** and **6** stand as the first σ -SiH complexes involving a coinage metal. The spectroscopic and geometric features typically associated with the coordination of σ -SiH bonds to transition metals (decrease of the $^1J_{\text{SiH}}$ coupling constant and $\nu(\text{SiH})$ stretching frequency, elongation of the SiH bond) are also met here with copper, albeit with a substantially weaker magnitude. Variation of the substitution pattern at the phosphine donor arms and at the hydrosilane moiety in **5** and **6** does only have minor influence on the strength of the σ -SiH coordination to copper as evidenced by the similar spectroscopic and structural properties. According to DFT calculations, the coordination of the SiH bond to copper arises from weak σ -SiH $\rightarrow$ Cu donation, and Cu $\rightarrow$ σ^* -SiH back-donation is negligible. Consistently, the coordination of the σ -SiH bond slightly strengthens when the electrophilicity of copper is increased by (partial) chloride abstraction.

On the other hand, the σ -SiH bond remains pendant in the related gold complex **7**. Neither σ -bond coordination nor oxidative addition of the SiH bond is observed here. More insight into the parameters that govern σ -bond activation processes with gold is given in Chap. 5.

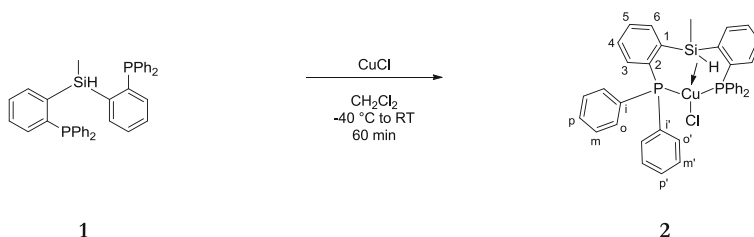
2.3 Experimental Part

2.3.1 Diphosphine-Hydrosilane Ligand (1)



A solution of dichloro(methyl)silane (229 μ L, 2.2 mmol) in toluene (2 mL) was added dropwise to a solution of *o*-lithiated triphenylphosphine (1.765 g, 4.65 mmol) in toluene (13 mL) at -80 $^{\circ}$ C. The solution was allowed to warm to room temperature overnight, after which volatiles were removed under vacuum. The resulting orange oil was purified by column chromatography (eluent: pentane/dichloromethane 9:1) to give the desired diphosphine (**1**) as a white solid. Yield: 1.020 g (61 %). **Mp**: 151 $^{\circ}$ C; **^{1} H NMR** (400 MHz, CD_2Cl_2): δ 7.75–7.57 (m, 2H, H_{ar}), 7.43–7.20 (m, 16H, H_{ar}), 7.19 – 6.96 (m, 10H, H_{ar}), 5.48 (tq, $^4J_{\text{HP}} = 5.6$ Hz, $^3J_{\text{HH}} = 3.85$ Hz, $^1J_{\text{HSi}} = 204$ Hz, 1H, SiH), 0.73 (dt, $^3J_{\text{HH}} = 3.85$ Hz, $^5J_{\text{HP}} = 0.9$ Hz, 3H, SiCH₃); **$^{31}\text{P}\{^1\text{H}\}$ NMR** (162 MHz, CD_2Cl_2): δ -13.2 (s); **$^{29}\text{Si}\{^1\text{H}\}$ NMR** (60 MHz, C_6D_6): δ -24 (t, $^3J_{\text{SiP}} = 20$ Hz); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (100 MHz, C_6D_6): δ 145.0 (dd, $^2J_{\text{CP}} = 46.8$ Hz, $^4J_{\text{CP}} = 3.5$ Hz, C_1), 144.4 (d, $^1J_{\text{CP}} = 11.2$ Hz, C_2), 138.4 (d, $^1J_{\text{CP}} = 12.4$ Hz, C_i), 137.3 (dd, $^3J_{\text{CP}} = 15.4$ Hz, $^5J_{\text{CP}} = 2.4$ Hz, C_3), 134.6 (s, C_p), 133.9 (m, C_o , C_m), 129.9 (s, C_5), -2.3 (t, $^4J_{\text{CP}} = 8.7$ Hz, SiCH₃), signals of C_4 and C_6 overlap with the solvent signal; **IR**: $\nu(\text{SiH})$: 2142 cm^{-1} ; **HRMS (ESI $^{+}$)**: calcd for $[\text{M} + \text{H}]^{+} = \text{C}_{37}\text{H}_{33}\text{P}_2\text{Si}^{+}$: 567.1827. Found: 567.1827.

2.3.2 Coordination of **1** to Copper Chloride (**2**)

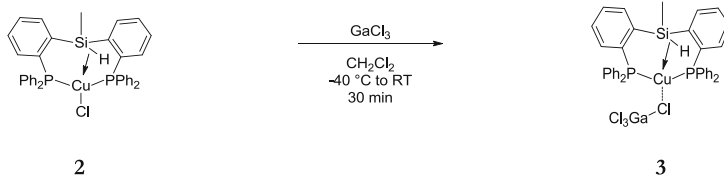


This atom labeling scheme was as well used for the NMR assignments of complexes **3** and **7**.

A solution of diphosphine-hydrosilane ligand **1** (100 mg, 0.18 mmol) in dichloromethane (3 mL) was added at -40 $^{\circ}$ C to a dispersion of copper chloride (17.5 mg, 0.18 mmol) in dichloromethane (1 mL). The reaction mixture was stirred for 60 min while warming up to room temperature. The colorless solution was concentrated to a volume of about 1 mL. Upon addition of pentane (5 mL), **2** precipitates as a white solid which was separated by filtration and dried under vacuum. Yield: 80 mg (68 %). Crystals suitable for X-ray diffraction analysis were grown at -30 $^{\circ}$ C from a saturated solution of **2** in dichloromethane layered with pentane. **Mp**: 215 $^{\circ}$ C (decomposition); **^{1} H NMR** (400 MHz, CD_2Cl_2): δ 7.85–6.86 (m, 28H, H_{ar}), 6.63 (qt, $^3J_{\text{HH}} = 3.4$ Hz, $^4J_{\text{HP}} = 6.7$ Hz, $^1J_{\text{HSi}} = 180$ Hz, 1H, SiH), 0.46 (d, $^3J_{\text{HH}} = 3.4$ Hz, 3H, SiCH₃); **$^{31}\text{P}\{^1\text{H}\}$ NMR** (162 MHz, CD_2Cl_2): δ -7.6 (s);

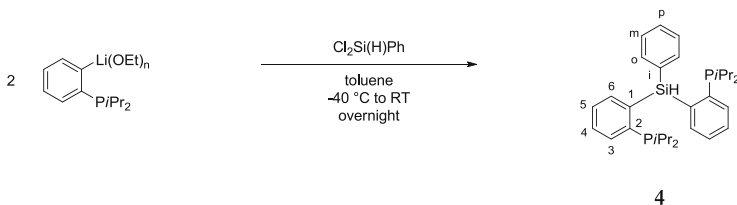
$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CD_2Cl_2): δ -30 (t, $^3J_{\text{SiP}} = 23$ Hz); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (100 MHz, CD_2Cl_2): δ 141.5 (*virtual t*, AA'X, $N = 19.2$ Hz, C_1), 139.6 (*virtual t*, AA'X, $N = 16.1$ Hz, C_2), 135.3 (*virtual t*, AA'X, $N = 7.5$ Hz, C_3), 134.5 (*virtual t*, AA'X, $N = 7.8$ Hz, C_o or C_m), 133.5 (*virtual t*, AA'X, $N = 18.4$ Hz, C_i), 133.0 (*virtual t*, AA'X, $N = 7.4$ Hz, C_o or C_m), 132.7 (s, C_4), 131.7 (*virtual t*, AA'X, $N = 15.6$ Hz, C_i), 130.2 (s, C_5), 129.7 (*virtual t*, AA'X, $N = 2.6$ Hz, C_6), 129.4 (s, C_p), 129.3 (s, $\text{C}_{p'}$), 128.7 (*virtual t*, AA'X, $N = 4.9$ Hz, C_o or C_m), 128.3 (*virtual t*, AA'X, $N = 4.6$ Hz, C_o or C_m), -4.1 (t, $^4J_{\text{PC}} = 3.7$ Hz, SiCH_3); **IR**: $\nu(\text{SiH})$: 1996 cm^{-1} (br); **HRMS (ESI+)**: calcd for $[\text{M}-(\text{Cl}^-)]^+ = \text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCu}^+$: 629.1045. Found: 629.1054. **Elt. Anal.**: calcd for $\text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCuCl} + \text{CH}_2\text{Cl}_2$: C, 60.80; H, 4.57. Found: C, 61.28; H, 4.54.

2.3.3 Reaction of **2** with GaCl_3 (**3**)



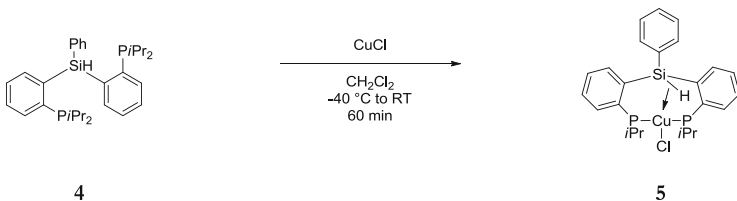
A solution of GaCl_3 (13.2 mg, 0.08 mmol) in dichloromethane (1 mL) was added to a solution of **2** (50 mg, 0.08 mmol) in dichloromethane (2 mL) at $-40\text{ }^\circ\text{C}$. The mixture was stirred for 30 min while warming up to room temperature, then concentrated to a volume of about 1 mL. Complex **3** precipitated upon addition of pentane (3 mL). The colorless solid was separated from the supernatant by filtration and dried under vacuum. Yield : 51 mg (80 %). Crystals suitable for X-ray diffraction analysis were grown at $-60\text{ }^\circ\text{C}$ from a saturated solution in dichloromethane layered with pentane. **Mp**: $119\text{ }^\circ\text{C}$; **^1H NMR** (400 MHz, CD_2Cl_2): δ 8.15–6.60 (m, 28H, H_{ar}), 6.44 (mbr, $^1J_{\text{HSi}} = 170$ Hz, 1H, SiH), 0.32 (mbr, 3H, SiCH_3); **$^{31}\text{P}\{^1\text{H}\}$ NMR** (162 MHz, CD_2Cl_2): δ -5.0 (sbr); **$^{29}\text{Si}\{^1\text{H}\}$ NMR** (79 MHz, CD_2Cl_2): δ -30 (t, $^3J_{\text{SiP}} = 23$ Hz); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (75 MHz, CD_2Cl_2): δ 140.7 (*virtual t*, AA'X, $N = 18.7$ Hz, C_1), 139.1 (*virtual t*, AA'X, $N = 16.1$ Hz, C_2), 134.2 (*virtual t*, AA'X, $N = 7.6$ Hz, C_3), 133.9 (*virtual t*, AA'X, $N = 7.9$ Hz, C_o or C_m), 132.3 (*virtual t*, AA'X, $N = 18.1$ Hz, C_i), 132.1 (*virtual t*, AA'X, $N = 7.3$ Hz, C_o or C_m), 131.9 (s, C_4), 130.9 (*virtual t*, AA'X, $N = 15.6$ Hz, C_i), 129.3 (s, C_5), 128.8 (*virtual t*, AA'X, $N = 2.6$ Hz, C_6), 128.3 (s, C_p), 128.2 (s, $\text{C}_{p'}$), 127.9 (*virtual t*, AA'X, $N = 5.1$ Hz, C_o or C_m), 127.3 (*virtual t*, AA'X, $N = 4.6$ Hz, C_o or C_m), -4.8 (t, $^4J_{\text{PC}} = 3.9$ Hz, SiCH_3); **IR**: $\nu(\text{SiH})$: 1973 cm^{-1} (br); **HRMS (ESI+)**: calcd for $[\text{M}-(\text{GaCl}_4^-)]^+ = \text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCu}^+$: 629.1045. Found: 629.1054. **Elt. Anal.**: calcd for $\text{C}_{37}\text{H}_{32}\text{P}_2\text{SiCuGaCl}_4 + \text{C}_5\text{H}_{12}$: C, 55.20; H, 4.85. Found: C, 54.87; H, 4.52.

2.3.4 Diphosphine-Hydrosilane Ligand (4)



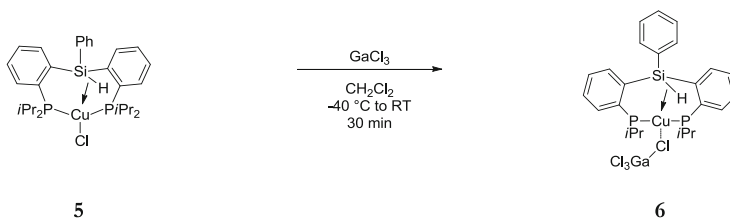
A solution of dichloro(phenyl)silane (308 μL , 2.10 mmol) in toluene (2 mL) was added dropwise to a solution of *o*-lithiated diisopropyl(phenyl)phosphine (1.154 g, 4.19 mmol) in toluene (4 mL) at -40°C . The solution was allowed to warm up to room temperature overnight, after which volatiles were removed under vacuum. The resulting white solid was recrystallized from a saturated dichloromethane solution layered with pentane to give the desired product as colorless crystals. Yield: 940 mg (83 %). **Mp**: 139°C ; $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): δ 7.60–6.95 (m, 13H, H_{ar}), 6.42 (t, $^4J_{\text{HP}} = 8$ Hz, $^1J_{\text{HSi}} = 220$ Hz, 1H, SiH), 2.10 (septd, $^2J_{\text{HP}} = 2$ Hz, $^3J_{\text{HH}} = 7$ Hz, 2H, CH_{iPr}), 2.03 (septd, $^2J_{\text{HP}} = 2$ Hz, $^3J_{\text{HH}} = 7$ Hz, 2H, CH_{iPr}), 1.01 (dd, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 7$ Hz, 6H, $\text{CH}_{3\text{iPr}}$), 0.99 (dd, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 7$ Hz, 6H, $\text{CH}_{3\text{iPr}}$), 0.77 (dd, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 6$ Hz, 6H, $\text{CH}_{3\text{iPr}}$), 0.75 (dd, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 6$ Hz, 6H, $\text{CH}_{3\text{iPr}}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ -0.8 (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ -27 (t, $^3J_{\text{SiP}} = 22$ Hz) $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): δ 144.7 (d, $^1J_{\text{CP}} = 44.0$ Hz, C_1), 137.4 (d, $^2J_{\text{CP}} = 14.3$ Hz, C_3), 136.5 (s, C_5), 132.0 (m, C_2), 129.3 (s, C_4 or C_6), 128.9 (s, C_o or C_m), 128.8 (s, C_o or C_m), 127.9 (s, C_4 or C_6), 127.5 (s, C_p), 25.0 (d, $^1J_{\text{CP}} = 20.1$ Hz, CH_{iPr}), 24.9 (d, $^1J_{\text{CP}} = 20.1$ Hz, CH_{iPr}), 20.1 (m, $\text{CH}_{3\text{iPr}}$); **IR**: $\nu(\text{SiH})$: 2165 cm^{-1} ; **HRMS (ESI+)**: calcd for $[\text{M} + \text{H}]^+ = \text{C}_{30}\text{H}_{43}\text{P}_2\text{Si}^+$: 493.2609. Found: 493.2604; **Elt. Anal.**: calcd for $\text{C}_{30}\text{H}_{42}\text{P}_2\text{Si}$: C, 73.13; H, 8.60. Found: C, 71.33; H, 8.24.

2.3.5 Coordination of 4 to Copper Chloride (5)



A solution of diphosphine-hydrosilane ligand (**4**) (200 mg, 0.41 mmol) in dichloromethane (3 mL) was added at $-40\text{ }^{\circ}\text{C}$ to a dispersion of copper(I) chloride (40.2 mg, 0.41 mmol) in dichloromethane (2 mL). The reaction mixture was stirred for 60 min while warming up to room temperature. The colorless solution was concentrated to a volume of about 1.5 mL. Complex **5** precipitated upon addition of pentane (5 mL). The colorless solid was separated from the supernatant by filtration and dried under vacuum. Yield: 187 mg (77 %). Crystals suitable for X-ray diffraction analysis were grown at $-30\text{ }^{\circ}\text{C}$ from a saturated solution of **5** in dichloromethane layered with pentane. **Mp**: $204\text{ }^{\circ}\text{C}$ (decomposition); ^1H NMR (400 MHz, CD_2Cl_2): δ 7.80–7.30 (m, 13H, H_{ar}), 7.11 (t, $^4J_{\text{HP}} = 7\text{ Hz}$, $^1J_{\text{HSi}} = 180\text{ Hz}$, 1H, SiH), 2.59 (m, 4H, CH_{iPr}), 1.29–1.23 (m, 12H, $\text{CH}_{3\text{iPr}}$), 1.17 (m, 6H, $\text{CH}_{3\text{iPr}}$), 0.99 (m, 6H, $\text{CH}_{3\text{iPr}}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 16.9 (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CD_2Cl_2): δ -34 (t, $^3J_{\text{SiP}} = 19\text{ Hz}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): δ 143.2 (*virtual t*, AA'X, $N = 18.0\text{ Hz}$, C_1), 137.9 (*virtual t*, AA'X, $N = 11.8\text{ Hz}$, C_2), 136.5 (*virtual t*, AA'X, $N = 7.3\text{ Hz}$, C_3), 136.2 (s, C_4 or C_6), 133.8 (*virtual t*, AA'X, $N = 4.9\text{ Hz}$, C_i), 132.0 (s, C_5), 129.7 (s, C_p), 129.2 (s, C_o or C_m), 129.1 (s, C_o or C_m), 127.9 (s, C_4 or C_6), 25.2 (*virtual t*, AA'X, $N = 10.2\text{ Hz}$, CH_{iPr}), 22.1 (*virtual t*, AA'X, $N = 8.0\text{ Hz}$, CH_{iPr}), 19.3 (*virtual t*, AA'X, $N = 3.1\text{ Hz}$, $\text{CH}_{3\text{iPr}}$), 19.2 (*virtual t*, AA'X, $N = 6.0\text{ Hz}$, $\text{CH}_{3\text{iPr}}$), 18.9 (*virtual t*, AA'X, $N = 3.1\text{ Hz}$, $\text{CH}_{3\text{iPr}}$), 16.4 (s, $\text{CH}_{3\text{iPr}}$); **IR**: $\nu(\text{SiH})$: 2043 cm^{-1} (wbr); **HRMS** (ESI $^{+}$): calcd for $[\text{M}(\text{Cl})]^+ = \text{C}_{30}\text{H}_{42}\text{P}_2\text{SiCu}^+$: 555.1827. Found: 555.1831; **Elt. Anal.**: calcd for $\text{C}_{30}\text{H}_{42}\text{P}_2\text{SiCuCl}$: C, 60.90; H, 7.15. Found: C, 60.17; H, 7.28.

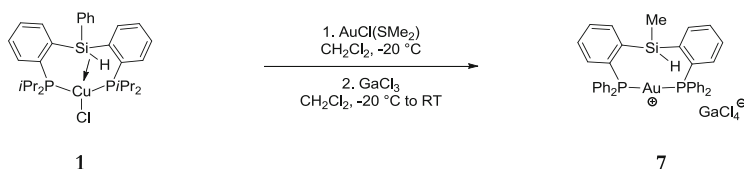
2.3.6 Reaction of **5** with GaCl_3 (**6**)



A solution of GaCl_3 (29.8 mg, 0.17 mmol) in dichloromethane (2 mL) was added to a solution of **5** (100 mg, 0.17 mmol) in dichloromethane (3 mL) at $-40\text{ }^{\circ}\text{C}$. The mixture was stirred for 30 min while warming up to room temperature, then concentrated to a volume of about 1.5 mL. Complex **6** precipitated upon addition of pentane (4 mL). The colorless solid was separated from the supernatant by filtration and dried under vacuum. Yield: 113 mg (87 %). Crystals suitable for X-ray diffraction analysis were grown at $-30\text{ }^{\circ}\text{C}$ from a saturated solution in

dichloromethane layered with pentane. **Mp**: 220 °C (decomposition); ^1H NMR (400 MHz, CD_2Cl_2): δ 7.88–7.33 (m, 13H, H_{ar}), 7.19 (t, $^4J_{\text{HP}} = 5$ Hz, $^1J_{\text{HSi}} = 170$ Hz, 1H, SiH), 2.63 (m, 4H, CH_{iPr}), 1.31 (m, 6H, $\text{CH}_{3\text{iPr}}$), 1.16 (m, 12H, $\text{CH}_{3\text{iPr}}$), 0.96 (m, 6H, $\text{CH}_{3\text{iPr}}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 19.4 (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CD_2Cl_2): δ -35 (t, $^3J_{\text{SiP}} = 26$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): δ 142.0 (*virtual t*, AA'X, $N = 16.1$ Hz, C_1), 137.0 (*virtual t*, AA'X, $N = 7.0$ Hz, C_3), 136.3 (s, C_4 or C_6), 134.8 (*virtual t*, AA'X, $N = 16.0$ Hz, C_2), 132.6 (s, C_5), 131.4 (m, C_i), 130.5 (s, C_p), 130.1 (s, C_o or C_m), 130.0 (s, C_o or C_m), 128.3 (s, C_4 or C_6), 24.5 (*virtual t*, AA'X, $N = 10.6$ Hz, CH_{iPr}), 21.8 (*virtual t*, AA'X, $N = 10.4$ Hz, CH_{iPr}), 19.3 (m, $\text{CH}_{3\text{iPr}}$), 16.1 (s, $\text{CH}_{3\text{iPr}}$); **IR**: $\nu(\text{SiH})$: 1978 cm^{-1} (wbr); **HRMS (ESI+)**: calcd for $[\text{M}-(\text{GaCl}_4^-)]^+ = \text{C}_{30}\text{H}_{42}\text{P}_2\text{SiCu}^+$: 555.1827. Found: 555.1832.

2.3.7 Coordination of **1** to Gold(I) (**7**)



A solution of the diphosphine-hydrosilane ligand **1** (100 mg, 0.18 mmol) in dichloromethane (3 mL) was added at -20°C to a solution of chloro(dimethylsulfide)gold (52 mg, 0.18 mmol) in dichloromethane (1 mL). The reaction mixture was stirred for 20 min before a solution of GaCl_3 (31 mg, 0.18 mmol) in dichloromethane (1 mL) was slowly added at -20°C . The mixture was allowed to warm up to room temperature under stirring for 30 min. The solution was then concentrated under vacuum to a volume of about 2 mL, filtered and layered with pentane (5 mL) to give **7** as yellowish crystals upon crystallization at -60°C over 3 days. Yield: 149 mg (85 %). **Mp**: 194 °C; ^1H NMR (400 MHz, CD_2Cl_2): δ 8.15–8.05 (m, 2H, H_{ar}), 7.73–7.38 (m, 24H, H_{ar}), 7.00–7.15 (m, 2H, H_{ar}), 6.88 (q, $^3J_{\text{HH}} = 3.6$ Hz, $^1J_{\text{HSi}} = 204$ Hz, 1H, SiH), 0.52 (d, $^3J_{\text{HH}} = 3.6$ Hz, 3H, SiCH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 45.4 (s); $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CD_2Cl_2): δ -37 (t, $^3J_{\text{SiP}} = 15$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 141.4 (*virtual t*, AA'X, $N = 14.6$ Hz, C_1), 137.1 (*virtual t*, AA'X, $N = 7.7$ Hz, C_3), 134.5 (*virtual t*, AA'X, $N = 8.2$ Hz, C_o or C_m), 133.9 (*virtual t*, AA'X, $N = 4.4$ Hz, C_4 or C_6), 133.2 (*virtual t*, AA'X, $N = 14.6$ Hz, C_o or C_m), 132.7 (s, C_p), 132.4 (s, $N = 14.6$ Hz, C_p), 132.3 (*virtual t*, AA'X, $N = 29.1$ Hz, C_2), 131.4 (s, C_5), 130.6 (*virtual t*, AA'X, $N = 4.4$ Hz, C_4 or C_6), 129.7 (*virtual t*, AA'X, $N = 5.3$ Hz, C_o or C_m), 129.6 (*virtual t*, AA'X, $N = 5.3$ Hz, C_o or C_m), 127.1 (*virtual t*, AA'X, $N = 29.7$ Hz, C_i), 126.3

(virtual t, AA'X, $N = 30.3$ Hz, C_i), -0.9 (t, $^4J_{CP} = 2.3$ Hz, $SiCH_3$); **IR**: $\nu(SiH)$: 2141 cm^{-1} ; **HRMS (ESI+)**: calcd for $[M]^+ = C_{37}H_{32}P_2SiAu^+$: 763.1414. Found: 763.1423. **Elt. Anal.**: calcd for $C_{37}H_{32}P_2SiAuGaCl_4$: C, 45.52; H, 3.41. Found: C, 45.38; H, 3.11.

2.3.8 Computational Details

Calculations were carried out with the Gaussian 09 program package [46] on the ligand **1*** and complexes **2***, **3***, **3**** and **7*** at the DFT level of theory using the hybrid functional B3PW91 [47, 48]. B3PW91 is Becke's three parameter functional, with the non-local correlation provided by the Perdew 91 expression. Cu, Au and Ga were treated with the Stuttgart-Dresden set-RECP (relativistic effective core potential) in combination with its adapted basis set [49–52]. The latter has been augmented by a set of polarization functions (f for the metal atoms and d for the Ga atom) [53]. All the other atoms (C, H, Si, P, Cl) have been described with a 6-31G (d, p) double- ζ basis set [54]. Geometry optimizations were carried out without any symmetry restrictions; the nature of the extrema was verified with analytical frequency calculations. The bonding situation in all complexes was studied using Natural Bond Orbital analysis (NBO-5 program) [55–58]. J_{SiH} coupling constants were evaluated by employing the direct implementation of the Gauge Including Atomic Orbitals (GIAO) method at the B3PW91 density functional level of theory [59–61]. The IGLOO II basis set was used for Si and P atoms [62].

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