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σ-SiH Complexes of Copper: Experimental Evidence and Computational Analysis

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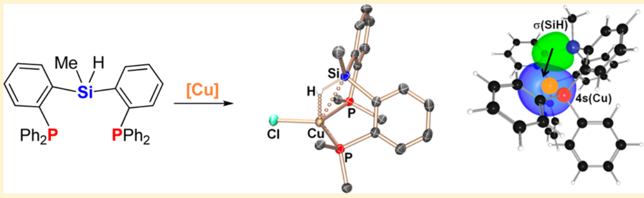
Supporting Information

ABSTRACT: Copper and gold complexes **2**−**4** of the diphosphine-hydrosilane $[Ph_2P(o\text{-}C_6H_4)]_2MeSiH$ ligand **1** have been prepared, and their bonding situation has been analyzed experimentally (NMR, IR, X-ray diffraction) and computationally (geometry optimizations, NBO analyses). The σ-SiH bond remains pendant in the gold complex **4** but engages into a weak side-on coordination to copper. This bonding interaction slightly strengthens when the metal becomes more electron deficient, consistent with essentially pure σ-SiH-to-copper donation. Complexes **2** and **3** provide very rare examples of σ-bond coordination to a coinage metal.



In the past decades, coinage metals have garnered tremendous interest in catalysis. Cu, Ag, and Au complexes have been applied successfully to a broad range of transformations with very high levels of activity and selectivity.[1] In parallel, fundamental experimental and theoretical studies have been carried out, and thereby, our knowledge of the properties and behavior of coinage metal complexes has progressed.[2,3] Such organometallic studies are all the more valuable in that the coinage metals differ markedly from the other transition metals and that their organometallic chemistry is comparatively much less known.

In this context, we have recently started to explore the ability of coinage metals to coordinate and activate σ-bonds.[4,5] It is nowadays well-established that σ-bonds can coordinate to transition metals and σ-complexes are recognized as key intermediates in the oxidative addition process.[6] Over the years, the side-on coordination of σ-bonds has in fact become a textbook example of weak metal/ligand interactions,[7] and a variety of σ-complexes have been authenticated experimentally with H−H,[6] H−Si,[8] H−B,[9] H−C,[10] C−C,[11] Si−Si,[12] etc., bonds. However, examples of σ-bond coordination remain extremely rare with the coinage metals.[13,14] Last year, we reported the first structural characterization of such a complex upon coordination of a diphosphine-disilane to copper. Weak side-on coordination of the σ-SiSi bond was identified with copper,[4] whereas oxidative addition was observed in the corresponding gold complex (Figure 1).[5]

Seeking to determine how general the coordination and activation of σ-bonds at coinage metals are and to gain more insight into the underlying factors, we became interested in studying the interactions of σ-SiH bonds with copper and gold.

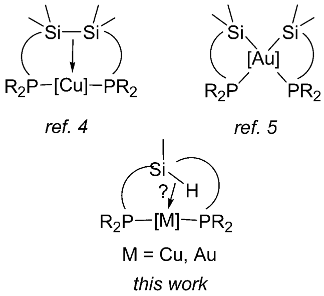


Figure 1. Schematic representation of the coordination/activation of σ-SiSi and σ-SiH bonds at copper and gold.

Hydrosilanes are involved in many transition metal catalyzed transformations, and as a matter of fact, σ-SiH complexes are the most studied class of σ-complexes after σ-H_2 complexes.[8] But very little is known about the coordination of σ-SiH bonds to the coinage metals, although copper and gold complexes are very powerful and valuable catalysts for hydrosilylation reactions and related processes.[15]

The chelating approach we used to investigate the coordination of Lewis acids[16] and σ-SiSi bonds[4,5] was extrapolated here to σ-SiH bonds (Figure 1).[17] For that purpose, we turned to a diphosphine-hydrosilane ligand, namely, $[Ph_2P(o\text{-}C_6H_4)SiH(Me)(o\text{-}C_6H_4)PPh_2]$, **1**. This ligand backbone has recently attracted much interest with group 8 to 10 metals (Ru, Rh, Ir, Ni, Pd, and Pt).[18,19] The central σ-SiH

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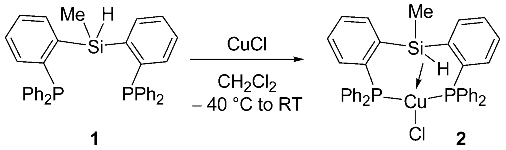
bond is readily activated by these metals, and the ensuing diphosphine-silyl pincer complexes were found to possess versatile reactivity[18b,c] and interesting catalytic properties.[18f] Noteworthily, the σ-SiH complexes en route to the PSiP pincer complexes have recently been intercepted and characterized with Ni, Pd, and Pt.[18d,g,h] Here we report a detailed experimental and computational study of the coordination of the diphosphine-hydrosilane **1** to copper and gold. We provide evidence for the coordination of the σ-SiH bond to copper, while the hydrosilane remains pendant with gold. The bonding situation has been analyzed thoroughly, and the electron density at copper has been varied to see how this affects the silane coordination.

The diphosphine-hydrosilane ligand **1** was prepared by slight modification of the reported procedure, coupling two equivalents of isolated *ortho*-lithiated triphenylphosphine with dichloromethylsilane.[18a,20] Coordination to copper was achieved by reacting **1** with CuCl in dichloromethane (addition at −40 °C and warmup 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. The formed complex **2** was isolated as a white solid (68% yield) after precipitation with pentane (Scheme 1).

Scheme 1. Coordination of the Diphosphine-Hydrosilane 1 to Copper Chloride



Complex **2** displays a single resonance signal at $\delta = -7.6$ ppm in the ^{31}P NMR spectrum, in agreement with the symmetric coordination of the two phosphorus atoms. The associated ^{29}Si NMR signal appears as a triplet ($J_{SiP} = 23$ Hz) at $\delta = -30$ ppm. These data are very similar to those of the free ligand **1** ($\delta = -24$ ppm, $J_{SiP} = 24$ 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.[21] The ^{1}H 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 $^{1}J_{SiH}$ coupling constant measured from the ^{29}Si satellites of the ^{1}H NMR signal. It decreases from 204 Hz in the free ligand **1** to 180 Hz in complex **2**, suggesting some weakening of the Si−H bond. The decrease of $^{1}J_{SiH}$ is a well-established signature for the coordination of σ-SiH bonds to transition metals.[8] Known silane complexes are associated with coupling constants down to 40−70 Hz, and usually the more activated the σ-SiH bond is, the lower the $^{1}J_{SiH}$ value. Thus, the relatively large $^{1}J_{SiH}$ coupling constant of **2** suggests only weak interaction of the σ-SiH bond with copper. To confirm this bonding picture, we then turned to infrared spectroscopy, the ν_{SiH} stretching frequency being another useful descriptor.[8] The corresponding vibration band is found at 1996 cm^{-1} in complex **2**, vs 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).[8]

To gain further insight into the structure of complex **2**, crystals were grown from a dichloromethane/pentane solution at −30 °C, and an X-ray diffraction analysis was performed (Figure 2). The copper center of **2** is surrounded by the two phosphorus atoms and the chlorine atom, organized in a trigonal-planar arrangement [PCuP = 115.66(2)°]. Interestingly, the silicon atom also sits close to copper. The Cu−Si distance [2.997(1) Å] is beyond the sum of the covalent radii (2.43 Å),[22] but well within the sum of the van der Waals radii (4.10 Å).[23] This is consistent with a possible participation of the σ-SiH bond in the coordination, as suggested by the NMR and IR data. At this point, it is worth recalling that hydrogen atoms close to heavy elements, in particular transition metals, are inherently difficult to locate accurately by X-ray crystallography even with high-quality measurements. As a consequence, the margin errors for the associated SiH and MH distances are large and discussions of these structural parameters are hardly reliable. Computational studies do not face the same problem, and density functional theory (DFT) calculations are most useful in combination with and complement to X-ray diffraction analyses.[24] A theoretical study of **2** and related complexes has thus been carried out (*vide infra*).

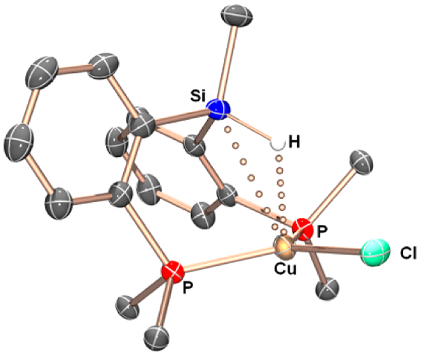
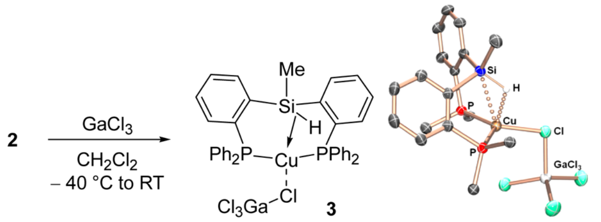


Figure 2. X-ray structure of complex **2**. Thermal ellipsoids are set at 50% probability; solvent molecules, phenyl substituents at phosphorus, and hydrogen atoms, except the one at Si, are omitted for clarity.

To explore further the coordination of σ-SiH bonds to copper, we then envisioned increasing the electrophilicity of the metal and see how this affects the spectroscopic and structural features of the complex. For that purpose, complex **2** was reacted with one equivalent of $GaCl_3$ and the new complex **3** was isolated in 80% yield (Scheme 2). The ^{31}P and ^{29}Si NMR data for **3** (^{31}P: δ −5.0 ppm and ^{29}Si: δ −30 ppm, $J_{SiP} = 23$ 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 $^{1}J_{SiH}$ coupling constant is further decreased at 170 Hz and, concomitantly, the ν_{SiH} band is further shifted to lower frequency at 1973 cm^{-1} (Table 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 °C, and its molecular structure was elucidated by X-ray diffraction analysis. Accordingly, the Lewis acid $GaCl_3$

Scheme 2. Reaction of the Diphosphine-Hydrosilane Copper Chloride Complex 2 with $GaCl_3$ and X-ray Structure of the Ensuing Complex 3[a]



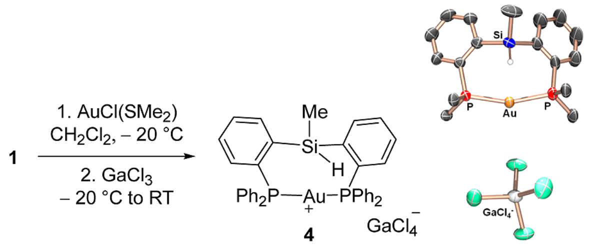
[a]Thermal ellipsoids are set at 50% probability; solvent molecules, phenyl substituents at phosphorus, and hydrogen atoms, except the one at Si, are omitted for clarity.

Table 1. Selected Experimental Data for Ligand 1 and Complexes 2–4[a]

	free ligand **1**	CuCl complex **2**	$CuClGaCl_3$ complex **3**	$Au^+GaCl_4^-$ complex **4**
δ ^{29}Si	−23	−30	−30	−37
J_{PSi}	20	23	23	15
δ ^1H	5.48	6.63	6.44	6.88
$^1J_{SiH}$	204	180	170	204
ν_{SiH}	2142	1996	1973	2141
MSi		2.997(1)	2.815(1)	3.166(1)
PMP		115.66(2)	120.13(2)	159.92(4)

[a]NMR chemical shifts in ppm, coupling constants in Hz, ν_{SiH} stretching frequencies in cm^{-1} (IR), MSi distances in Å, and PMP bond angles in deg (X-ray).

Scheme 3. Coordination of the Diphosphine-Hydrosilane 1 to Gold and X-ray Structure of the Ensuing Complex 4[a]



[a]Thermal ellipsoids are set at 50% probability; solvent molecules, phenyl substituents at phosphorus, and hydrogen atoms, except the one at Si, are omitted for clarity.

interacts strongly with the chloride at copper, but without complete abstraction. The CuCl distance is significantly elongated [CuCl = 2.359(1) Å in **3** vs 2.229(1) Å in **2**], so that complex **3** can be formally considered as a tight ion pair [(**1**)$Cu^+\cdots ClGaCl_3^-$]. Here also the silicon atom comes close to copper, at an even shorter distance [CuSi = 2.815(1) Å] than in complex **2**. Since the overall geometry around copper in **3** is otherwise similar to 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.

We have 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,[4] while gold undergoes spontaneous oxidative addition and forms bis(silyl) gold(III) complexes.[5] This prompted us to investigate the influence of the metal center on the coordination behavior of the diphosphine-hydrosilane ligand. The gold complex **4** was prepared by reacting **1** with $AuCl(SMe_2)$ and $GaCl_3$ in dichloromethane at low temperature (Scheme 3). The spectroscopic and crystallographic data for complex **4** 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 **4** are the same as those of the free ligand **1**, suggesting that the σ-SiH bond does not interact with the metal in this case. This is consistent with the molecular structure of **4** as determined by single-crystal X-ray diffraction analysis. The gold complex **4** adopts a discrete ion pair structure [(**1**)-Au^+,$GaCl_4^-$] [shortest Au···Cl distance at 3.285(1) Å] with a wide PAuP bite angle [159.92(4)°], but the silicon atom remains far from gold. Indeed, the AuSi distance in **4** [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).[22]

The comparison of complexes **2**, **3**, and **4** 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 **4** contrasts with the oxidative addition process observed with the σ-SiSi bond and is in fact reminiscent of that observed in the diphosphine-disilane silver complex.[4] In both cases, the metal center nicely accommodates quasi-linear bis(phosphine)M^+ arrangement. Comparatively, copper is more Lewis acidic[25] and the coordination of the pending σ-SiH or SiSi bond is favorable. In addition, the fact that the silicon atom remains remote from gold in complex **4** 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.

A detailed computational study was then carried out in order to (i) further analyze the structural features of the diphosphine-silane complexes, (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 same level of theory as that used previously,[4,5,21,26] i.e., B3PW91/SDD+f(Cu,Au), 6-31G**(other atoms). 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*** nicely reproduces that determined crystallographically, with deviations of only 0.03 Å in the CuSi distance and 7° in the PCuP bond angle (Table 2). 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***.[20] The meaningfulness of this variation is corroborated by comparing copper and gold. Indeed, the σ-SiH bond length computed for the gold complex **4*** (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 really the result of a bonding interaction. Besides these structural features, we also looked at spectroscopic data, in particular the $^1J_{SiH}$ coupling

Table 2. Selected Theoretical Data for Complexes **2***–**5*** and Ligand **1***[a]

	ligand **1***	CuCl **2***	$CuClGaCl_3$ **3***	Cu^+ **5***	$AuGaCl_4^-$ **4***
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
$^1J_{SiH}$	−198.6	−176.4	−164.2	−143	−201.1
ΔE_{NBO} (kcal/mol)					
σSiH→ Lp*(M)		8.4	12.4	14.3	
s(M)→σ*SiH		0.9	1.1	1.3	0.25

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

constant. The values measured experimentally by ^1H NMR for complexes **2** and **4** as well as the free ligand **1** were nicely reproduced theoretically using the GIAO method with the IGLOO II basis set (maximum deviation of only 6 Hz; see Tables 1 and 2).

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 $Cu^+GaCl_4^-$ ion pair structure, and on the cationic complex **5***, featuring a naked copper center (without counteranion contact).[20] Here, the σ-SiH bond length was found to increase from 1.499 Å in **2*** to 1.513 Å in **5***, and concomitantly, the CuSi distance shortens from 3.021 Å in **2*** to 2.808 Å in **5*** (Table 1). It is interesting at this stage to compare the geometric variations with the spectroscopic data. A quasi-linear correlation was actually found between the σ-SiH bond length and the $^1J_{SiH}$ coupling constant (see Figure S1′).[27] The two extreme situations are met with the free ligand **1*** on one hand (d_{SiH} = 1.484 Å, $^1J_{SiH}$ = −198.6 Hz) and the cationic complex **5*** one the other hand (d_{SiH} = 1.513 Å, $^1J_{SiH}$ = −143.0 Hz). Although the interaction between the σ-SiH bond and the copper center is weak in all copper complexes, the structural and spectroscopic variations observed theoretically along the series **2*** → **3*** → **5*** 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***–**5*** 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 **5***, but not in the gold complex **4***. The associated delocalization energies ΔE_{NBO} increase from 8 kcal/mol in **2*** to 12 kcal/mol in **3*** and 14 kcal/mol in **5***, providing another 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). Noteworthily, only insignificant back-donation from copper to σ*-SiH was found in **2***, **3***, and **5*** (ΔE_{NBO} < 1.5 kcal/mol), indicating that the coordination of the Si–H bond to copper arises essentially, if not exclusively, from σ-SiH→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,[28] 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,[4,9] we considered theoretically a similar process with the σ-SiH bond of the copper complex **3*** and gold complex **4***. 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 **4***), in agreement with our experimental observations. While σ-SiH coordination is stronger to Cu, oxidative addition of the σ-SiH bond is easier for Au. This contrast illustrates that Lewis acidity and a tendency to undergo oxidative addition are two different aspects of chemistry that do not necessarily show parallel trends.

This study provides evidence for the coordination of σ-SiH bonds to copper. The diphosphine-hydrosilane **1** is shown experimentally and computationally to engage in weak σ-SiH/Cu interactions. The ensuing copper complexes **2** and **3** stand as the first σ-SiH complexes involving a coinage metal. The σ-SiH bond remains pendant in the corresponding gold complex **4**. The spectroscopic and geometric features typically associated with the coordination of σ-SiH bonds to transition metals (decrease of the $^1J_{SiH}$ coupling constant and ν_{SiH} stretching frequency, elongation of the SiH bond) are also met here with copper, albeit with a substantially weaker magnitude. According to DFT calculations, the coordination of the Si–H bond to copper arises from weak σ-SiH→Cu donation, and Cu→σ*-SiH back-donation is negligible. Consistently, the coordination of the σ-SiH bond slightly strengthens when the electrophilicity of copper is increased. Future work in our group will seek to explore further the coordination and activation of σ-bonds at the coinage metals, with and without chelating assistance.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational procedures, characterization, and coordinates for the optimized structures **2***–**5***. CCDC 910791 (**2**), 910792 (**3**), and 910793 (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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