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A Crystalline σ Complex of Copper

Pauline Gualco,[†] Abderrahmane Amgoune,[†] Karinne Miqueu,[‡] Sonia Ladeira,[§] and Didier Bourissou*[,†]

[†]Université de Toulouse, UPS, LHFA, 118 Route de Narbonne, F-31062 Toulouse, France; CNRS, LHFA UMR 5069, F-31062 Toulouse, France

[‡]Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (UMR 5254), Equipe Chimie Physique, Université de Pau et des Pays de l'Adour, Hélioparc, 2 Avenue du Président Angot, 64053 Pau cedex 09, France

[§]Université de Toulouse, UPS, Institut de Chimie de Toulouse, FR2599, 118 Route de Narbonne, F-31062 Toulouse, France

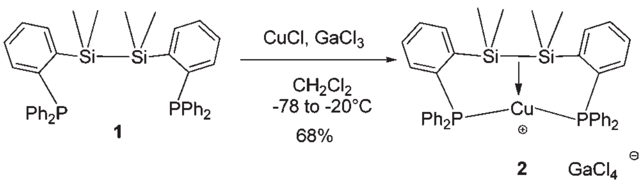
S *Supporting Information*

ABSTRACT: Over the last decades, our understanding of σ-bond activation at transition metals has progressed considerably from both fundamental and synthetic points of view thanks to the preparation and characterization of a variety of σ complexes. Here we report the synthesis and structural analysis of the first σ complex involving a coinage metal. The copper(I) complex **2** derived from the diphosphine−disilane [$Ph_2P(C_6H_4)Me_2Si-SiMe_2(C_6H_4)PPh_2$] (**1**) has been isolated and crystallographically characterized. The coordination of the Si−Si σ bond to copper was thoroughly analyzed by quantum-chemical methods.

The past decades have witnessed spectacular progress in the activation of inert, apolar σ bonds (H−H as well as E−H and E−E bonds, where E = C, Si, ...) with transition metals. The discovery that σ bonds can coordinate to transition metals without splitting clearly represented a major breakthrough,[1−3] and the ensuing so-called σ complexes are nowadays recognized as key intermediates. Of major interest is the characterization of such bonding situations via spectroscopic and structural methods in order to gain a better understanding of the factors governing the activation of σ bonds.[4] In this respect, it is striking to note that the coordination of σ bonds has been shown structurally with almost all transition metals except the coinage metals.

In recent years, coinage-metal complexes have emerged as powerful catalysts for a broad range of reactions, including σ-bond activations,[5] but σ complexes species with these metals remain very elusive. The possible existence of such a bonding situation has rarely been supported computationally,[6,7] and only recently was experimental evidence reported. The coordination of a C−H σ bond has been identified by pulsed electron paramagnetic resonance spectroscopy in a copper(II) complex of a triazamacrocylic ligand.[6] Here we report experimental and theoretical evidence for the coordination of a Si−Si σ bond to a coinage metal. In the course of our studies on unusual metal−ligand interactions supported by phosphine buttresses,[8,9] a crystalline σ complex of copper(I) was obtained from the diphosphine−disilane [$Ph_2P(C_6H_4)Me_2Si-SiMe_2(C_6H_4)PPh_2$] (**1**).

Scheme 1. Coordination of Diphosphine−Disilane 1 to Copper



Following previously reported methodologies for the synthesis of diphosphine−silane ligands,[10] **1** was prepared by treatment of 2 equiv of ortho-lithiated triphenylphosphine with 1,2-dichlorotetramethyldisilane. The copper(I) complex **2** was obtained by reacting **1** with CuCl and $GaCl_3$ in dichloromethane at low temperature (Scheme 1).[11] Decomposition occurred upon warming to room temperature, but complex **2** could be isolated in pure form (68% yield) by workup at −20 °C. Complex **2** exhibits a single ^{31}P NMR signal at 5.2 ppm, indicating the symmetric coordination of the two phosphorus atoms. The ^{29}Si NMR resonance signal for complex **2** at −23.5 ppm is shifted slightly upfield relative to that of free ligand **1** at −21.2 ppm, indicating the retention of the disilane moiety and possibly some interaction between the Si−Si σ bond and the metal center. The coordination of the Si−Si σ bond to the cationic Cu center was unambiguously evidenced structurally and theoretically.

Colorless crystals of **2** (melting point 110.9 °C) suitable for an X-ray diffraction study were obtained from a dichloromethane/pentane solution at −60 °C. The analysis showed that complex **2** adopts a discrete ion pair structure in the solid state (Figure 1). The two Si atoms lie close to the metal center, with the Cu−Si distances [2.7196(14) and 2.7212(14) Å] exceeding the sum of the covalent radii (2.43 Å)[12] by only 12%. Notably, two methyl substituents of the $SiMe_2$ moieties also lie close to the copper center, with short Cu−H contacts of 2.2262(6) and 2.3615(6) Å.[11] The coordination sphere is completed by the two phosphorus atoms [P−Cu distances = 2.2079(13) and 2.2168(13) Å], whose arrangement significantly deviates from linearity [P−Cu−P angle = 153.72(5)°]. The copper points toward the Si−Si σ bond, and overall, its geometry is halfway between trigonal-planar and T-shaped. Another salient feature is the significant lengthening of the Si−Si σ bond upon coordination [from 2.3581(11) Å in free ligand **1** to 2.4505(19) Å in **2**]. The geometric features of **2** parallel those typically associated with the coordination of σ bonds to transition metals and thus

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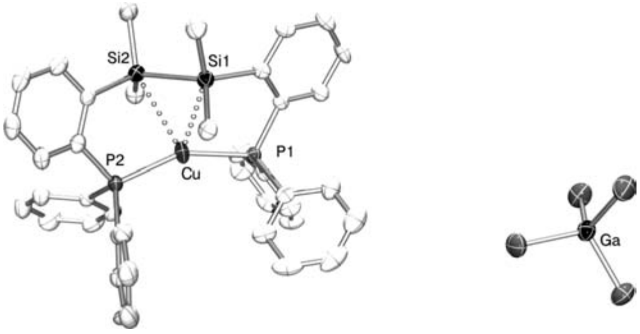
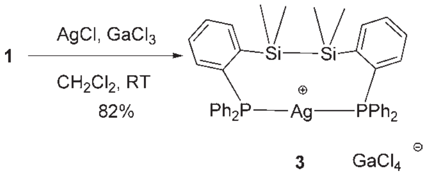


Figure 1. X-ray crystal structure of complex **2**. Thermal ellipsoids have been drawn at 50% probability, and hydrogen atoms and solvate molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−Cu, 2.2079 ± 13; P2−Cu, 2.2168 ± 13; Si1−Cu, 2.7212 ± 14; Si2−Cu, 2.7196 ± 14; Si1−Si2, 2.4505 ± 19; P1−Cu−P2, 153.72 ± 5.

Scheme 2. Coordination of Diphosphine−Disilane 1 to Silver



strongly argue in favor of side-on coordination of the disilane moiety to copper.

The coordination of **1** to silver(I) was also performed via a similar procedure to give the corresponding complex **3** in 82% isolated yield (Scheme 2). The single-crystal X-ray diffraction study revealed a markedly different bonding situation (Figure 2). The metal center is surrounded by the two phosphorus atoms [P−Ag distances = 2.4010(9) and 2.4008(9) Å]. A weak contact with one chlorine atom of the $GaCl_4^-$ counteranion [3.065(3) Å] is present, but the geometry around Ag deviates only slightly from linearity [P−Ag−P angle = 171.91(3)°].[13] The two Si atoms remain at much longer distances from the metal center than in the copper complex: the Ag−Si distances in **3** [3.4766(11) and 3.3896(11) Å] exceed the sum of the covalent radii (2.56 Å)[11] by more than 32%. In addition, the Si−Si σ bond length [2.3633(15) Å] is very similar to that in free ligand **1** and substantially shorter than that in **2**. According to these geometric data, the disilane moiety does not coordinate to the metal center in **3**.

Density functional theory calculations on the complexes **2*** and **3*** (including the $GaCl_4^-$ counteranion and having methyl or phenyl substituents on the phosphorus atoms) were carried out.[11] The optimized geometries nicely reproduced those determined crystallographically. In agreement with the geometric data, natural bond orbital (NBO) analyses identified a donor−acceptor interaction from the Si−Si σ bond to the metal center only in the copper complex **2*** (the delocalization energy found at the second-order perturbation level was $\Delta E_{\mathrm{NBO}} \sim 14-19$ kcal/mol). The coordination of the Si−Si σ bond to copper is largely dominated by Si−Si σ to Cu donation. A donor−acceptor interaction associated with Cu to Si−Si σ^* back-donation was also found, but the corresponding delocalization energy was negligible (<1 kcal/mol). Another conspicuous feature of the coordination of the disilane is the symmetry of the natural localized molecular orbital (NLMO) centered on the Si−Si σ bond, which is significantly distorted toward the metal in the copper complex **2*** but remains cylindrical in the silver complex **3*** (Figure 3). The description of **2*** as a genuine σ complex was further supported by electron localization function (ELF) analyses.[11,14] The side-on coordination of the disilane moiety in the copper complex **2*** is associated with a trisynaptic (Cu, Si, Si) ELF basin, whereas in the free ligand **1*** and silver complex **3***, the Si−Si σ bond is associated with a disynaptic (Si, Si) ELF basin.

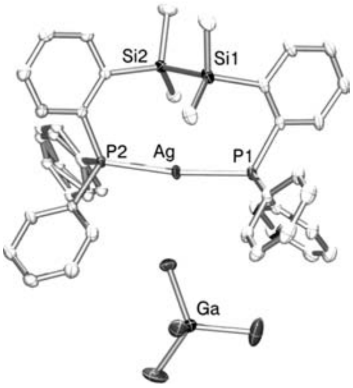


Figure 2. X-ray crystal structure of complex **3**. Thermal ellipsoids have been drawn at 50% probability, and hydrogen atoms and solvate molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−Ag, 2.4010 ± 9; P2−Ag, 2.4008 ± 9; Si1−Ag, 3.4766 ± 11; Si2−Ag, 3.3896 ± 11; Si1−Si2, 2.3633 ± 15; P1−Ag−P2, 171.91 ± 3.

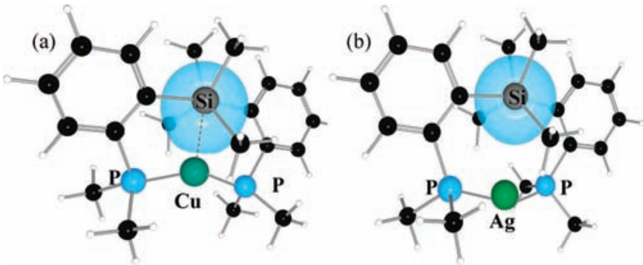


Figure 3. Three-dimensional images of the NLMOs centered on the Si−Si σ bond in complexes (a) **2a*** and (b) **3a***.

On the basis of all these experimental and theoretical data, the copper complex **2** can be unambiguously formulated as a σ complex, and as such, it provides the first structural evidence for such a bonding situation involving a coinage metal. The related silver complex **3** adopts a markedly different structure without coordination of the disilane moiety. The lower Lewis acidity of Ag(I) and its higher propensity to accommodate linear dicoordinate complexes[12] most likely explain this difference. Moreover, this indicates that diphosphine−disilane ligand **1** is relatively flexible and that the coordination of the Si−Si σ bond in **2** is supported but not geometrically imposed by the two phosphine buttresses.

Notably, the formation of σ complexes is less favorable with Si−Si bonds than with X−H bonds (X = H, C, Si, ...) on both orbital and steric grounds.[15] The directionality of the Si−Si σ bond does not permit optimal overlap, and the surrounding substituents induce substantial shielding. Although the activation of Si−Si bonds by transition metals, which is the key step for catalytic bis-silylation reactions, has been fairly well documented,[16] not much is known about Si−Si σ complexes.[17] To date, the coordination of Si−Si σ bonds had been authenticated structurally only once, in a trinuclear Pd cluster arising from the thermal condensation of $[o\text{-}C_6H_4(SiH_2)_2Pd(dmpe)]$ [dmpe =1,2-bis(dimethylphosphino)ethane].[18−21] The transient formation of an unsupported Si−Si σ complex was also recently proposed to account for the fluxional behavior of the bis-silyl Pd complex $[(dcpe)Pd(SiMe_2H)_2]$ [dcpe =1,2-bis(dicyclohexylphosphino)ethane], as observed in solution by NMR spectroscopy.[22]

In conclusion, the diphosphine−disilane copper(I) complex **2** represents the first structurally authenticated σ complex involving a coinage metal and is a very rare example of a Si−Si σ complex. Ongoing studies are aimed at further exploration of the coordination of σ bonds to coinage metals.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental conditions and procedures, theoretical details, and analytical data and crystallographic data (CIF) for compounds **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

dbouriss@chimie.ups-tlse.fr

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