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Activation of a σ-SnSn Bond at Copper, Followed by Double Addition to an Alkyne

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Supporting Information

ABSTRACT: Many synthetically useful copper-catalyzed transformations involve the activation of apolar or weakly polar σ-bonds (E−H and E−E′ bonds, with E = C, B, Si, Sn, etc.). Yet, little is known so far about the associated elementary steps, and it is highly desirable to gain better knowledge regarding the way σ-bonds can be activated by copper to help further development in this area. To this end, we became interested in investigating the coordination and activation of apolar or weakly polar σ-bonds at copper using chelating assistance. Here we report investigations of gold and copper complexes deriving from the diphosphine-stannane [$Ph_2P(o\text{-}C_6H_4)Me_2Sn{-}SnMe_2(o\text{-}C_6H_4)PPh_2$] **1**. The σ-SnSn bond of **1** readily undergoes oxidative addition at both gold and copper, giving bis(stannyl) Au^+ and Cu^+ complexes **2** and **3**. Coordination of **1** to CuBr leads to the neutral complex **4** which features more σ-SnSn complex character. The ability of complex **3** to undergo insertion reactions with alkynes was then examined. With methyl propiolate, a clean reaction occurred, and the bis-stannylated alkene copper complex **5** was isolated. The structures of ligand **1** and complexes **2**−**5** have been unambiguously determined by multinuclear NMR spectroscopy and crystallography. These results substantiate the ability of copper to promote the addition of apolar σ-bonds to CC multiple bonds via a 2e redox sequence and draw thereby an unprecedented parallel with the group 10 metals.

■ INTRODUCTION

Copper occupies a forefront position in transition metal chemistry, and it is certainly one of the most, if not *the* most, widely used metal in organic synthesis.[1] Over the years, copper complexes have found widespread applications in stoichiometric and catalytic transformations, with always increasing activity, selectivity, and functional group tolerance. But the considerable synthetic development of copper chemistry contrasts with the relatively poor understanding of the involved mechanisms. In fact, what is known for the other transition metals often does not apply to copper because of the specific properties of this metal, and our knowledge of the fundamental behavior of copper complexes remains quite superficial. However, the past decade has witnessed significant advances in the understanding of copper chemistry.

This is particularly true for the activation of aryl halides and, more generally, for the processes of C−X bond activation/formation relevant to Ullmann-type couplings.[2] In the two most often invoked mechanisms, aryl halides are activated either by a radical pathway or by concerted oxidative addition, and direct evidence has been reported recently for both routes.[3] Thanks to meticulous investigations, the groups of Stahl, Ribas, and others have been able to characterize well-defined aryl copper(III) species relevant to Ullmann-type coupling reactions, and unambiguous evidence for Cu(I)/Cu(III) redox sequences has been provided for C−N, C−O, C−S, C−Se, C−P, and C−F bond formations.[4−6] In addition, studying photoinduced C−N couplings, Fu and Peters have recently demonstrated the ability of copper to promote aryl halide activation by single electron transfer.[7]

Comparatively, much less is known about the activation of apolar or weakly polar σ-bonds (E−H and E−E′ bonds, with E = C, B, Si, Sn, etc.) at copper, although these processes are involved in a broad range of synthetically useful catalytic transformations.[8] It is highly desirable to gain better knowledge on the way σ-bonds can be activated by copper to help further development in this area, not only for the optimization of catalytic properties but also for the discovery of new transformations. To this end, we investigated the coordination

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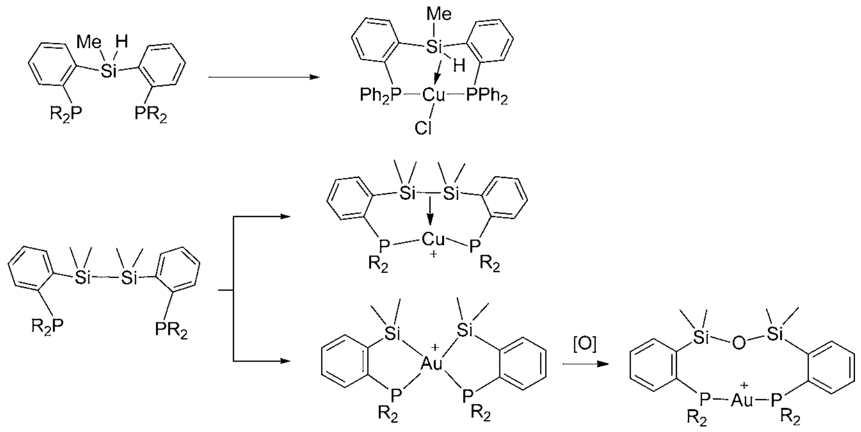
Chart 1. Interaction of σ-SiSi and σ-SiH Bonds with Copper and Gold, As Previously Observed in Phosphine-Chelated Systems



and activation of apolar or weakly polar σ-bonds at copper using chelating assistance.[9] Using phosphine anchors, we recently discovered that σ-SiSi and σ-SiH bonds can coordinate in a side-on fashion to copper, and thereby, the first σ-complexes[10] of copper[11] have been isolated and structurally characterized (Chart 1).[12] According to geometric and electronic data, the corresponding σ bonds are slightly weakened but not strongly activated upon coordination to copper. A markedly different situation was found in the related gold complexes. Oxidative addition of the σ-SiSi bond occurs spontaneously, affording bis(silyl) gold(III) complexes[13] and subsequent insertion of oxygen provided evidence for an unusual 2e redox sequence at gold.[14] To probe the ability of copper to engage into similar 2e processes, and to compare further the behavior of the two coinage metals, we decided to explore the reactivity of other σ-bonds. Herein we report a detailed investigation of gold and copper complexes deriving from a diphosphine−distannane.[15−17] Oxidative addition of the σ-SnSn bond occurs spontaneously at gold to give a bis(stannyl) gold(III) complex. The σ-SnSn bond is also activated at copper, and the degree of activation increases with the electrophilicity of the metal (CuBr/Cu$^+$). Subsequent reaction with methyl propiolate induces double stannylation of the C≡C triple bond. The structures of all of the complexes have been unambiguously determined by multinuclear NMR spectroscopy and crystallography. These results substantiate the ability of copper to promote the addition of apolar σ-bonds to CC multiple bonds via a 2e redox sequence and draw thereby an unprecedented parallel with the group 10 metals.[18]

■ RESULTS AND DISCUSSION

Theoretical Study of σ-SiSi and σ-SnSn Bond Activation at Gold and Copper. The coordination of diphosphine−disilane and diphosphine−distannane ligands [$Ph_2P(o\text{-}C_6H_4)Me_2E{-}EMe_2(o\text{-}C_6H_4)PPh_2$] (E = Si, Sn) to gold and copper was first studied theoretically to gain some insight into how the nature of the σ-EE bond influences the activation process.[19] DFT calculations were carried out at the B3PW91/SDD+pol(Au,Sn, Cu),6-31G**(P,C,H,Ga,Si,Cl) level of theory on complexes **A**−**D** (naked cationic complexes, gas phase; see Supporting Information). The main results are depicted in Figure 1. With gold, oxidative addition of the σ-EE bond is energetically favored for both silicon and tin. The Au(III) complexes $\mathbf{A}_{\mathrm{III}}$ and $\mathbf{B}_{\mathrm{III}}$ are more stable than their Au(I) isomers $\mathbf{A}_{\mathrm{I}}$ and $\mathbf{B}_{\mathrm{I}}$ featuring pendant σ-EE bonds (by 9.8 kcal/mol for silicon and 4.6 kcal/mol for tin). A different situation is predicted for copper. The ground-state structures correspond to the Cu(I) complexes $\mathbf{C}_{\mathrm{I}}$ and $\mathbf{D}_{\mathrm{I}}$ featuring side-on coordinated σ-SiSi and σ-SnSn bonds, respectively. The Cu(III) bis(silyl) complex $\mathbf{C}_{\mathrm{III}}$ is found 7.8 kcal/mol higher in energy than its Cu(I) isomer $\mathbf{C}_{\mathrm{I}}$. Of note, the corresponding Cu(III)

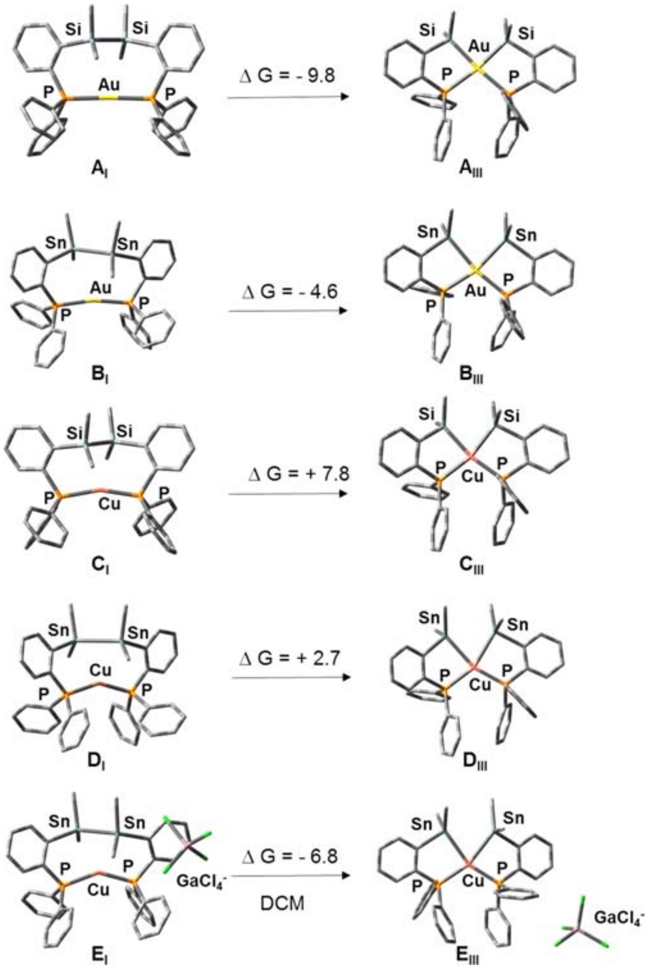


Figure 1. Computational results for the σ-SiSi and σ-SnSn bond activation at gold and copper. Optimized geometries and relative stabilities (ΔG in kcal/mol at 25 °C) of the M(I) complexes (with pendant or side-on coordinated σ-EE bonds) and M(III) complexes (resulting from oxidative addition of the σ-EE bonds).

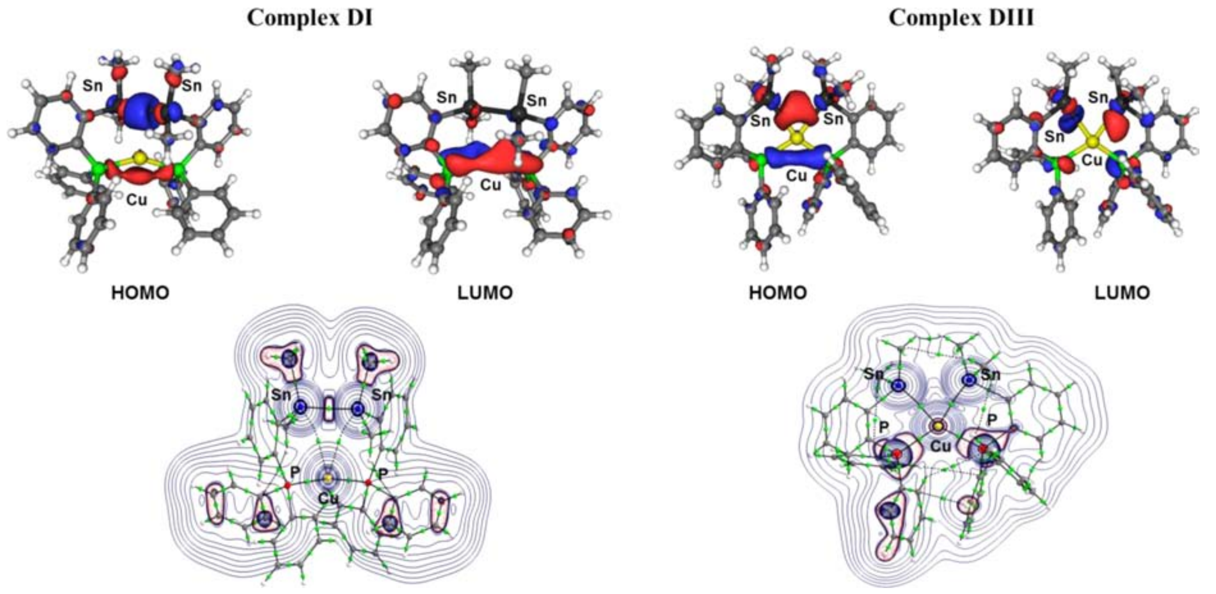


Figure 2. (a) Molekel plots (cutoff: 0.04) of the HOMO and LUMO for complexes $\mathbf{D}_\mathrm{I}$ and $\mathbf{D}_\mathrm{III}$. (b) Calculated electron-density maps for complexes $\mathbf{D}_\mathrm{I}$ and $\mathbf{D}_\mathrm{III}$ with relevant bond paths and bond critical points (green dots). Charge accumulation ($\nabla^2 \rho(r) < 0$) is printed in blue and charge depletion ($\nabla^2 \rho(r) > 0$) in red.

bis(stannyl) complex $\mathbf{D}_\mathrm{III}$ is only slightly higher in energy than its σ-SnSn Cu(I) isomer $\mathbf{D}_\mathrm{I}$ (by 2.7 kcal/mol), indicating that oxidative addition of the σ-SnSn bond at copper is about thermoneutral. Moreover, when the $GaCl_4^-$ counteranion is included and the solvent effects are taken into account (single point PCM calculations with dichloromethane), the Cu(III) bis(stannyl) complex $\mathbf{E}_\mathrm{III}$ becomes the ground state structure, about 6.8 kcal/mol more stable than the corresponding Cu(I) isomer $\mathbf{E}_\mathrm{I}$.

The electronic structure of the diphosphine–distannane copper complexes was then examined through analyses of the molecular orbitals (MO) and atom-in-molecules (AIM) calculations (Figure 2; see Supporting Information). The highest occupied molecular orbital HOMO of $\mathbf{D}_\mathrm{I}$ is mainly associated with the σ-SnSn orbital which is slightly distorted toward copper (Sn, Sn, Cu three-center interaction). The copper center has a larger contribution in the HOMO of $\mathbf{D}_\mathrm{III}$, which corresponds to a symmetric combination of σ-SnCu orbitals. The electron density maps of $\mathbf{D}_\mathrm{I}$ and $\mathbf{D}_\mathrm{III}$ are also noticeably different. While a bond path and a bond critical point (BCP) are clearly observed between the two Sn atoms of $\mathbf{D}_\mathrm{I}$ (electron density at the BCP: $\rho(r) = 0.053$ e·bohr^{-3}), such features are not found for $\mathbf{D}_\mathrm{III}$. In both complexes, BCP are localized between the two Sn atoms and the copper center, but the associated electron density is significantly higher in $\mathbf{D}_\mathrm{III}$ than in $\mathbf{D}_\mathrm{I}$ (0.048 vs 0.027 e·bohr^{-3}). All of these data suggest that $\mathbf{D}_\mathrm{I}$ is best described as a σ-SnSn complex, while $\mathbf{D}_\mathrm{III}$ is best described as a Cu(III) bis-stannyl complex.

We then sought to gain more insights into the σ-SnSn bond activation process at Au/Cu, and to this end, we explored the energy profile of the oxidative addition reaction with model complexes **B*** and **D*** (featuring Me instead of Ph groups at P) (Figure 3; see Supporting Information). For gold, a low energy pathway was found between $\mathbf{B}_\mathrm{I}$* and $\mathbf{B}_\mathrm{III}$* (the corresponding transition state is located only 4.1 kcal/mol above $\mathbf{B}_\mathrm{I}$* in energy). The activation barrier for σ-SnSn oxidative addition is higher (18 kcal/mol) with copper but remains accessible under mild conditions. The geometric features of the associated transition states (TS) differ significantly from Au to Cu. A symmetric structure with well-developed AuSn bonds (2.875 Å) is found for gold, while the TS located for Cu is dissymmetric and displays two very different SnCu distances (2.282 and 3.317 Å), suggesting asynchronous formation of the two CuSn bonds.

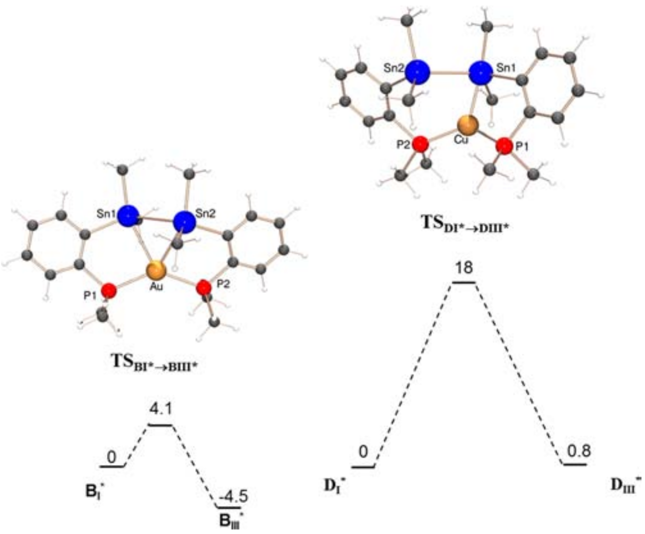
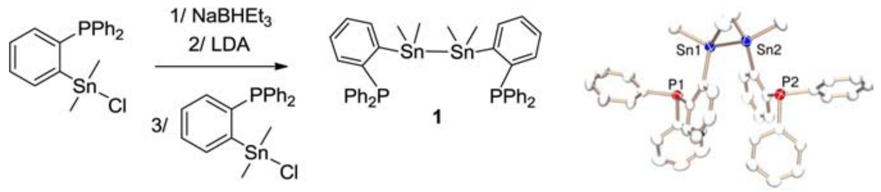


Figure 3. Energy profile (ΔG in kcal/mol) and structure of the transition states for the σ-SnSn bond activation at gold and copper (model complexes **B*** and **D***, respectively).

From these DFT calculations, diphosphine–distannanes are anticipated to behave quite differently from diphosphine–disilanes upon coordination, and oxidative addition of the σ-SnSn bond is envisioned to occur not only with gold, but also with copper. This prompted us to prepare the diphosphine–distannane **1** and to explore its coordination experimentally.

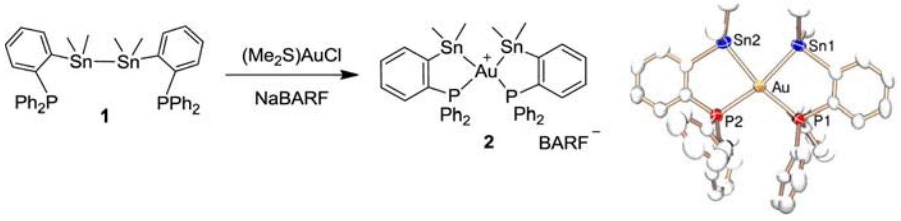
Synthesis of the Diphosphine–Distannane 1 and Coordination to Gold. Whereas the related diphosphine–disilane was readily obtained from the corresponding 1,2-dichlorodisilane,[11] the preparation of the diphosphine–

Scheme 1. Preparation and X-ray Structure of the Diphosphine−Distannane 1[a]



[a]Ellipsoids set at 50% probability; hydrogen atoms omitted for clarity. Selected bond length (Å): SnSn 2.7682(2).

Scheme 2. Coordination of the Diphosphine−Distannane 1 to Gold, Oxidative Addition of the σ-SnSn Bond[a]



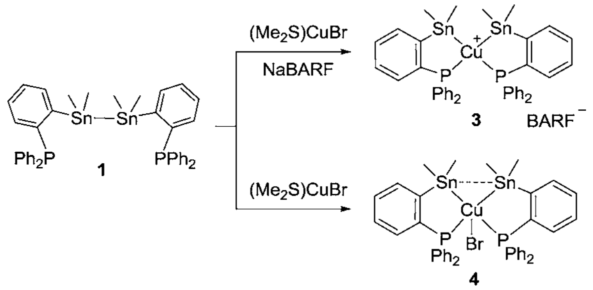
[a]Molecular structure of the ensuing bis(stannyl) gold(III) complex **2** (ellipsoids set at 50% probability; hydrogen atoms and BARF counteranion omitted for clarity). Selected bond lengths (Å) and angles (deg): P1−Au, 2.3974(10); P2−Au, 2.3919(10); Sn1−Au, 2.6293(3); Sn2−Au, 2.6335(3); P1−Au−P2, 106.74(3); Sn1−Au−Sn2, 82.027(10); P1−Au−Sn1, 85.97(2); P2−Au−Sn2, 85.30(3).

distannane **1** required a multistep sequence (Scheme 1). The key reaction is a tin−tin coupling between [2-(chlorodimethylstannyl)phenyl]diphenylphosphine[20] and the corresponding stannyl lithium species (see Supporting Information). Reductive coupling of [2-(chlorodimethylstannyl)phenyl]diphenylphosphine, as reported by Kang et al. for the preparation of $[Ph_2P\text{-}(o\text{-carboranyl})SnMe_2]_2$,[21] did not prove efficient in our case. After purification by flash chromatography, the desired ligand **1** was obtained as a white powder in 65% yield (see Supporting Information). Key spectroscopic and structural data of **1**, such as the ^{119}Sn NMR resonance signal at δ −122 ppm, the J_{P-Sn} coupling constants (130 and 82 Hz) and the SnSn bond distance (2.7682(2) Å), will be important parameters to consider later on when analyzing σ-SnSn bond activation at gold and copper.

The coordination properties of the diphosphine−distannane **1** were then investigated, starting with gold. The reaction of **1** with $(Me_2S)AuCl$ in the presence of NaBARF (BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) results in spontaneous oxidative addition of the σ-SnSn bond and gives the bis(stannyl) gold(III) complex **2** (Scheme 2). The cleavage of the σ-SnSn bond is clearly apparent in NMR, from the downfield shift of the ^{119}Sn resonance signal (δ 114.6 ppm) and the associated SnP coupling pattern ($J_{P-Sn(trans)}$ = 950 Hz and $J_{P-Sn(cis)}$ = 96 Hz). The molecular structure of **2** was unambiguously confirmed by X-ray diffraction analysis. The gold center is tetracoordinate, and the complex adopts square-planar cis geometry. The σ-SnSn bond is cleaved [the SnSn distance reaches 3.4536(4) Å in **2**], and short AuSn bonds are formed [2.6293(3) and 2.6335(3) Å, vs 2.75 Å for the sum of covalent radii[22]].[23]

Oxidative addition of the σ-SnSn bond upon coordination of **1** to gold is consistent with the computational study [the gold(III) complex $\mathbf{B}_{III}$ is favored by 4.6 kcal/mol over the corresponding gold(I) isomer $\mathbf{B}_{I}$] and parallels the σ-SiSi bond activation observed with the related diphosphine−disilane.[14a] To assess further the propensity of the σ-SnSn bond to undergo oxidative addition, we then explored the coordination of the diphosphine−distannane **1** to copper.

Scheme 3. Coordination of the Diphosphine−Distannane 1 to Copper



Coordination of the Diphosphine−Distannane to Copper (Cationic and Neutral Complexes). Reaction of **1** with $(Me_2S)CuBr$ and NaBARF afforded the cationic Cu complex **3**, which was isolated in 90% yield after workup (Scheme 3). Upon coordination, the ^{119}Sn NMR resonance signal shifts to lower field (from δ −122 ppm for **1**, to δ −13 ppm for **3**), and two very different J_{Sn-P} coupling constants, including a very large one, are observed (495 and 89 Hz). Similar features were observed for the gold complex **2**, and thus, it is likely that the σ-SnSn bond has also been activated at copper. To ascertain more precisely the molecular structure of **3**, single crystals were grown from a dichloromethane/pentane solution at −20 °C and analyzed by X-ray diffraction. Accordingly, complex **3** features a discrete ion pair structure (Figure 4, left). The related complex with $GaCl_4^-$ as a counteranion was also isolated and characterized crystallographically (see Supporting Information). The two structures are very similar and fit well with that predicted computationally. The copper center is tetracoordinate and adopts square-planar geometry,[24] with head-to-head arrangement of the two phosphino-stannyl chelates. The maximum deviation from the least-squares plane defined by the Cu, P1, P2, Sn1, and Sn2 atoms is of only 0.07 Å, and the CuSn bonds are short (2.5988(5) Å and 2.6083(5) Å, vs 2.71 Å for the sum of

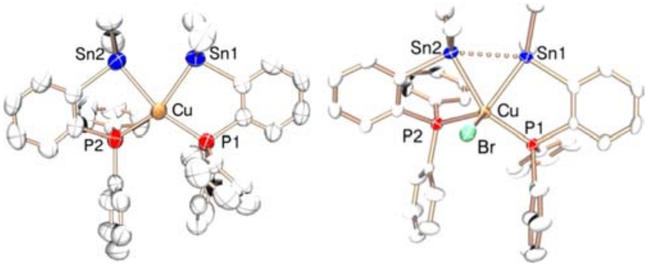


Figure 4. Molecular view of complexes **3** (left) and **4** (right) in the solid state (thermal ellipsoids set at 50% probability; hydrogen atoms, counteranion, and solvate molecules omitted for clarity). Selected bond lengths (Å) and angles (deg): P1−Cu, 2.2741(9); P2−Cu, 2.2655(9); Sn1−Cu, 2.5988(5); Sn2−Cu, 2.6083(5); Sn1−Sn2, 3.0910(4); P1−Cu−P2, 112.23(3); Sn1−Cu−Sn2, 72.829(13); P1−Cu−Sn1, 89.25(2); P2−Cu−Sn2, 85.74(3) for complex **3** and P1−Cu, 2.3059(14); P2−Cu, 2.2835(14); Sn1−Cu, 2.6698(7); Sn2−Cu, 2.6632(7); Sn1−Sn2, 2.9942(5); Cu−Br, 2.4767(8); P1−Cu−P2, 112.83(5); Sn1−Cu−Sn2, 68.311(18); P1−Cu−Sn1, 84.11(4); P2−Cu−Sn2, 87.19(4) for complex **4**.

covalent radii[22]).[25] The distance between the two tin atoms (3.0910(4) Å) is well beyond the sum of covalent radii (2.78 Å)[22] but smaller than in the gold complex **2** (3.4536(4) Å), suggesting the possible existence of some residual Sn···Sn contact in **3**.[26] However, as mentioned above, AIM calculations performed on the optimized structure $\mathbf{D}_{\mathrm{III}}$ revealed the absence of bond critical point between the two Sn atoms. Moreover, an AIM analysis carried out on the crystallographic determined geometry gave the same result (see Supporting Information). Accordingly, complex **3** is best described as a bis(stannyl) Cu(III) species.

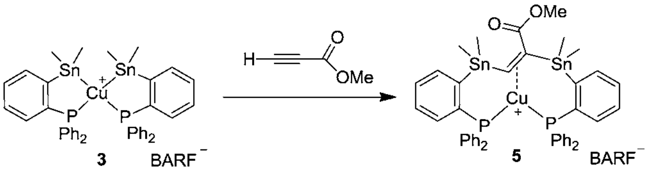
We then prepared a neutral complex related to **3** since the electron density at copper is likely to influence the extent of σ-SnSn bond activation. Indeed, we recently observed in a related study that the coordination of σ-SiH bonds to copper strengthens when the electrophilicity of the metal increases.[12b] Thus, the diphosphine−distannane **1** was reacted with $(Me_2S)CuBr$ in the absence of halide scavenger. The coordination proceeded readily, but the ensuing complex **4** proved to be extremely sensitive, precluding its isolation.[27] Decomposition occurs rapidly above −20 °C, but complex **4** could be characterized by multinuclear NMR spectroscopy at −40 °C. Most diagnostic is the ^{119}Sn NMR resonance signal found at δ −37 ppm with $J_{\mathrm{P-Sn}}$ coupling constants of 549 and 122 Hz. Fortunately, crystals were obtained from a pentane/dichloromethane at −60 °C so that the structure of **4** could be unequivocally assessed by X-ray diffraction analysis (Figure 4, right). The coordination sphere around copper can be assimilated to a tetrahedron, with the σ-SnSn bond capping the pyramidal diphosphine copper bromide moiety (sum of P1CuP2, P1CuBr, and P2CuBr bond angles = 323.28(13)°). The two Sn atoms lie close to the metal center. The Cu−Sn distances (2.6632(7) and 2.6698(7) Å) are longer than those of complex **3** (~2.60 Å) but below the sum of covalent radii (2.71 Å).[22] The σ-SnSn bond is significantly elongated (2.9942(5) Å vs 2.7682(2) Å in the free ligand **1** and 3.0910(4) Å in the cationic complex **3**). Here also, AIM calculations were performed on the solid-state geometry, but in this case, a bond path and a bond critical point (BCP) were found between the two Sn atoms [electron density at the BCP: $\rho(r) = 0.046$ e·bohr^{-3} vs 0.058 e·bohr^{-3} for a pendant σ-SnSn bond; see Supporting Information].

The structural features of complexes **3** and **4** clearly indicate substantial σ-SnSn bond activation. Coordination of the diphosphine−distannane **1** to Cu$^+$ proceeds with oxidative addition of the σ-SnSn bond to give the bis(stannylated) Cu complex **3**. The neutral CuBr complex **4** features more σ-SnSn complex character. The activation of the σ-SnSn bond at copper advances when the electrophilicity of the metal increases, suggesting that donation dominates over backdonation in this process.

Having substantiated the ability of copper to activate the σ-SnSn bond of **1**, we were then interested to study the reactivity of the bis(stannyl) Cu(III) complex **3**, in particular its ability to undergo insertion reactions so as to achieve a complete sequence akin to that commonly encountered with Pd and Pt.[18] For that purpose, we examined the reactivity of complex **3** toward alkynes.

Reaction of the Bis(stannyl) Copper Complex 3 with Methylpropiolate. Reactions of **3** with phenyl acetylene and dimethyl acetylene dicarboxylation led to a mixture of unidentified products, but with methyl propiolate (10 equiv), a clean reaction occurred within 10 h at room temperature. The bis-stannylated alkene copper complex **5** was isolated in 70% after workup (Scheme 4). The dissymmetric nature of **5** is apparent in ^{31}P NMR spectroscopy, two doublets being observed at δ = 14.9 and 9 ppm with a $J_{\mathrm{P-P}}$ coupling constant of 56 Hz. Consistently, the ^{119}Sn NMR spectrum displays two resonance signals at δ = −47 ppm and −65 ppm, in the same range than those reported for free bis(stannyl) alkenes.[28] Each ^{119}Sn NMR signal appears as a doublet of a doublet due to Sn−P couplings with the two inequivalent phosphorus atoms.

Scheme 4. Reaction of Complex 3 with Methyl Propiolate



Single crystals were grown from dichloromethane/pentane at −20 °C, and the molecular structure of complex **5** was analyzed by X-ray diffraction (Figure 5), confirming insertion of the

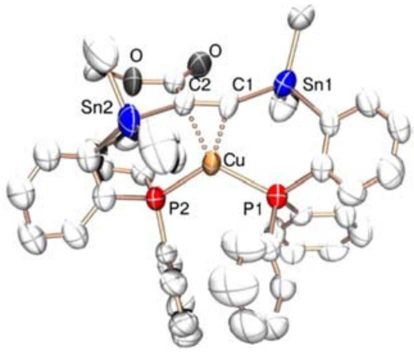


Figure 5. Molecular view of complex **5** in the solid state (thermal ellipsoids set at 50% probability; hydrogen atoms, counteranion, and solvate molecules omitted for clarity). Selected bond lengths (Å) and angles (deg): P1−Cu, 2.2817(13); P2−Cu, 2.2758(15); C1−Cu, 2.118(8); C2−Cu, 2.149(8); C1−C2, 1.394(12); P1−Cu−P2, 121.78(5).

alkyne between the two tin atoms. Complex **5** adopts a discrete ion pair structure. The copper center is surrounded by the two phosphorus atoms (PCuP = 121.78(5)°) and the bis-stannylated alkene, organized in a trigonal-planar geometry. The C═C double bond is essentially coplanar with the PCuP skeleton (the corresponding dihedral angle is of 10.39(45)°). The CuC distances (2.118(8) and 2.149(8) Å) slightly exceeds the sum of covalent radii (2.05 Å),[22] indicating relatively weak coordination of the central alkene moiety to copper.[29] Consistently, the C═C bond is short (1.394(12) Å) and only marginally deviates from planarity (the sum of bond angles at C1 and C2 = 301.9(2)° and 305.9(2)°). Notably, complex **5** is obtained as sole product, and according to the X-ray diffraction study, the two tin atoms display a trans-orientation. Thus, complex **3** reacts with methyl propiolate via trans-addition across the triple bond of the alkyne. Such a selectivity contrasts with the syn-addition usually observed upon bis-(stannylation) of alkynes with transition metals. This may not be a specific feature of copper[30] but rather the consequence of geometric constraints associated with the chelate structure of the PSnSnP system.

The reaction of the neutral copper complex **4** with methyl propiolate was also examined, for comparison. No reaction occurs at low temperature, and decomposition is observed upon warming to room temperature. No $^{31}P/^{119}Sn$ NMR signal attributable to an insertion product could be detected. The degree of activation of the σ-SnSn bond thus plays a critical role on the bis-stannylation reaction. The diphosphine−distannane **1** undergoes σ-SnSn bond activation upon coordination to Cu^+, and methyl propiolate then inserts between the two tin atoms. In this reaction sequence, copper promotes activation of the distannane followed by double addition to the C≡C triple bond. Such 2e redox transformations are well-known for the group 10 metals, in particular Pd and Pt,[18,30−32] but have no precedent with coinage metals.

■ CONCLUSION

The ability of copper to activate and functionalize σ-SnSn bonds has been evidenced using chelating assistance. Coordination of the diphosphine−distannane **1** to Au^+ and Cu^+ proceeds with oxidative addition of the σ-SnSn bond and affords the bis(stannyl) complexes **2** and **3**. The extent of σ-SnSn bond activation was found to increase with the electrophilicity of copper. The related neutral CuBr complex **4** features more σ-SnSn complex character. The bis(stannyl) copper complex **3** undergoes a clean insertion reaction with methyl propiolate to give the bis-stannylated alkene copper complex **5**. The evolution of the bonding situation along the entire sequence (activation/functionalization of the σ-SnSn bond) has been thoroughly analyzed thanks to systematic X-ray diffraction studies.

These results evidence the ability of copper to undergo two-electron redox transformations[33] and draw thereby unprecedented parallel with the group 10 metals, in particular Pd and Pt that are habitually used to promote the addition of element−element bonds to alkynes and alkenes. They also provide valuable information for the development of difunctionalization reactions with copper. Baker, Marder, and Wescott recognized early on the ability of the coinage metals to promote double addition to CC multiple bonds (diboration of vinylarenes with gold in their pioneering contribution),[34] but this remains a relatively underexplored field of research. However, recent contributions reported copper catalyzed diboration[19,35] and borastannation[35] of CC multiple bonds. Copper(I) boryl complexes are invoked as key intermediates, and redox neutral catalytic cycles are proposed. The results reported here indicate that 2e redox cycles are also viable with copper, which opens new possibilities. Future work from our group will seek to explore further the chemistry of the coinage metals and to gain better knowledge on their behavior in all elementary steps.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental conditions and procedures, theoretical details, and analytical data and crystallographic data (CIF) for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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