Ligand Exchange between Arylcopper Compounds and Bis(hypersilyl)tin or Bis(hypersilyl)lead: Synthesis and Characterization of Hypersilylcopper and a Stannanediyl Complex with a Cu–Sn Bond

Jan Klett, Karl W. Klinkhammer,* and Mark Niemeyer*[a]

Dedicated to Professor Gerhard Fritz on occasion of his 80th birthday

Abstract: Bis(hypersilyl)tin (**1**) and bis(hypersilyl)lead (**2**) [hypersilyl = Hyp = tris(trimethylsilyl)silyl] undergo ligand exchange reactions with other carbene homologues to yield heteroleptic distannenes or diplumbenes. Here we report the extension of this reaction principle to coordinatively unsaturated arylcopper(I) compounds. The primary reaction products are probably adducts with the carbene homologues as Lewis base and the arylcopper compounds as Lewis acids. This is followed by rearrangement to the adducts HypCu–E(Hyp)Ar* (E = Sn (**6**) and Pb (**7**); Ar* = $C_6H_3Mes_2$-2,6) of hypersilylcopper (**9**) and the heteroleptic stannanediyl or plumbanediyl. The complex may be the final product or may dissociate into its component parts, free hypersilylcopper (**9**) and the appropriate heteroleptic carbene homologue. The colorless hypersilylcopper forms a trimer $(\mathbf{9})_3$ in the solid state with short Cu $\cdots$ Cu contacts (238.4–241.5 pm). All observed Cu–Si bonds are relatively long. However, shorter distances (234.9–237.4 pm) alternate with longer ones (246.5–249.2 pm), such that quasi-monomeric hypersilylcopper units can be identified. The dark green complex **6** exhibits a shorter Cu–Si bond (227.3 pm). The Sn–Cu bond length was determined to be 249.9 pm. The turquoise plumbanediyl Pb(Hyp)Ar* (**8**) is the first strictly monomeric mixed aryl silyl derivative, even in the solid state. The steric repulsions are obviously less than in the parent homoleptic compounds because the Pb–C bond in **8** is shorter (229.0 pm) and the C-Pb-Si angle (109.2°) is markedly smaller.

Keywords: copper · lead · low-valent compounds · rearrangements · tin

Introduction

Triorganylsilylcopper compounds are important reagents in organic synthesis. They are usually prepared in situ and can be used, for example, for the functionalization of alkenes under mild conditions.[1] We are currently investigating the synthesis, molecular structure, and reactivity of compounds with Cu–Si bonds. Generally, information on the structure of silylcopper compounds is very limited.[2, 3] This is surprising since such species could have some significance in the important Müller–Rochow industrial process.

The reaction of alkali metal silanides with copper halides often does not yield the desired metathesis products cleanly. Apparently, the great reduction potential of the silanide anions gives rise to different side reactions.[3] In 1988 however, Cowley et al. reported the preparation of the first neutral silylcopper compound from lithium triphenylsilanide and copper chloride in the presence of trimethylphosphane. The complex $Ph_3SiCu(PMe_3)_3$ was isolated in 60 % yield and characterized by X-ray crystallography.[2] Some years later, the reaction of the tris(tetrahydrofuran) solvate of hypersilyllithium with copper halides was examined by Stalke and co-workers.[3] They obtained the metastable, light-sensitive, and thermally labile halogenohypersilylcuprates $[Li(thf)_4][Cu_5Cl_4Hyp_2]$[3a] and $[Cu_2Hyp_2BrLi(thf)_3]$[3b] in low yields. The identity of these highly reactive compounds was confirmed unambiguously by X-ray crystallography. However, not all the main products of the observed redox reactions were identified. It is not yet known if the isolated cuprates are intermediates of these redox processes or lie on secondary reaction paths.

Results and Discussion

Herein, we report a novel method for the synthesis of silylcopper compounds which is related to the recently published ligand exchange reactions of stannanediyls and plumbanediyls.[4] It was shown that bis(hypersilyl)tin (**1**) and bis(hypersilyl)lead (**2**) react quantitatively with homoleptic

---

[a] Priv.-Doz. Dr. K. W. Klinkhammer, Dr. M. Niemeyer, J. Klett
Institut für Anorganische Chemie der Universität
Pfaffenwaldring 55, D-70569 Stuttgart (Germany)
Fax: (+49) 711-6854241
E-mail: kw@iac.uni-stuttgart.de
niemeyer@iac.uni-stuttgart.de

diaryl derivatives Ar_2E (Ar = aryl; E = Sn, Pb) to yield the heteroleptic compounds Ar(Hyp)E [Eq. (1)].[5]

$$\mathrm{EAr_2 + E'[Si(SiMe_3)_3]_2 \longrightarrow E[Si(SiMe_3)_3]Ar + E'[Si(SiMe_3)_3]Ar} \qquad (1)$$

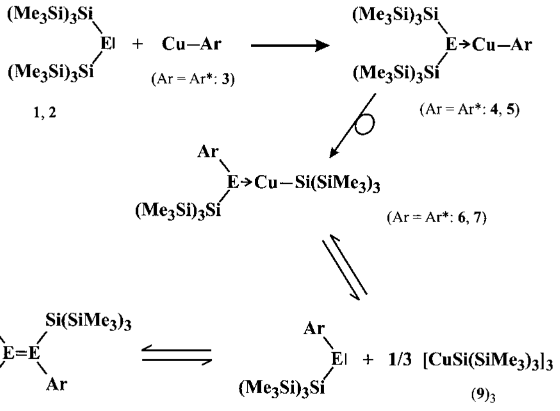
E, E' = Ge, Sn, Pb

The carbene-homologous diaryl compounds Ar_2E are replaced by the recently described arylcopper compound CuAr* (**3**)[6] (Ar* = $C_6H_3Mes_2$-2,6, Mes = $C_6H_2Me_3$-2,4,6) which is allowed to react with **1** or **2** in benzene solution. The solutions change color immediately from brown to green or blue to blue-green, respectively. Crystallization from *n*-pentane affords the dark green complex **6** in 65 % yield or the turquoise compound **8** in 73 % yield. According to spectroscopic results and a single-crystal X-ray study, compound **6** can be described as the donor–acceptor complex Ar(Hyp)Sn–CuHyp of heteroleptic aryl(hypersilyl)stannanediyl and hypersilylcopper **9**. In contrast, an X-ray structure revealed **8** to be the heteroleptic aryl(hypersilyl)plumbanediyl. Thus, ligand exchange reactions as described in Equations (2) and (3) must have been taken place.

$$\underset{\mathbf{3}}{\mathrm{CuAr^*}} + \underset{\mathbf{1}}{\mathrm{Sn[Si(SiMe_3)_3]_2}} \longrightarrow \underset{\mathbf{6}}{\mathrm{(Me_3Si)_3SiCu{-}Sn[Si(SiMe_3)_3]Ar^*}} \qquad (2)$$

$$\underset{\mathbf{3}}{\mathrm{CuAr^*}} + \underset{\mathbf{2}}{\mathrm{Pb[Si(SiMe_3)_3]_2}} \longrightarrow \underset{\mathbf{9}}{\mathrm{(Me_3Si)_3SiCu}} + \underset{\mathbf{8}}{\mathrm{Pb[Si(SiMe_3)_3]Ar^*}} \qquad (3)$$

The first step of the exchange is probably the formation of the primary adducts **4** and **5**, in which the bis(hypersilyl) metal compounds **1** and **2** are bonded to the arylcopper compound CuAr* (Scheme 1). Apparently, subsequent multistep rearrangement reactions with aryl- or hypersilyl-bridged intermediates lead to the adducts of the heteroleptic carbene-homologues to hypersilylcopper Ar(Hyp)Sn–CuHyp (**6**) and Ar(Hyp)Pb–CuHyp (**7**). Only **6** seems to be stable, whereas **7** decomposes into the fragments hypersilylcopper (**9**) and plumbanediyl **8**.



Scheme 1. Proposed pathways for the reaction of arylcopper compounds with **1** and **2**. E = Sn, Pb. Ar = $C_6H_2Me_3$-2,4,6; Ar* = $C_6H_3Mes_2$-2,6.

Unfortunately, it was not possible to isolate pure **9** from the greenish colored *n*-pentane mother liquor of compound **8**. The impure **9** obtained was always contaminated with **3** and arene Ar*H. Attempts to sublime the crude material at about 10^{-4} mbar were not successful, because **9** rapidly decomposed to a black tar above about 60 °C. However, it was possible to isolate a few colorless rods of **9** after storing the oily mother liquor of **8** in a freezer at 6 °C for several weeks. The crystals were suitable for X-ray crystallography and Raman spectroscopy. NMR spectroscopic data for hypersilylcopper were obtained readily from freshly prepared reaction mixtures of **2** and **3**. The stannanediyl adduct **6** is slightly more thermally stable than **9**, although complete decomposition was observed after heating a [D$_6$]benzene solution for several days at 50 °C. According to the NMR spectroscopic data, the remaining solution contained **3**, free arene Ar*H, and what was assumed to be the heteroleptic stannanediyl Ar*(Hyp)Sn. In contrast, the heteroleptic plumbanediyl **8** is much more thermally stable. It can be heated in solution at 50 °C for several days without decomposition.

The introduction of less bulkier substituents on copper dramatically changes the course of the reaction. When the carbene-homologues **1** and **2** were allowed to react with mesitylcopper, for example, the formation of complicated mixtures of hypersilyl-containing compounds was indicated by NMR spectroscopy. The only products which could be identified unambiguously were the heteroleptic alkene homologues Mes(Hyp)E=E(Hyp)Mes (E = Sn, Pb) which precipitated in small quantities as crystalline material from solutions of the crude dark oily products in *n*-pentane. Free hypersilylcopper, however, could not be detected. Evidently, ligand exchange again took place, but in the present case, the dimerization of the heteroleptic carbene homologues is an important side reaction to the formation of, presumably, copper(I) complexes, indicated by the absence of free hypersilylcopper (Scheme 1). The structure analysis of the heteroleptic alkene homologues, which will be discussed in detail elsewhere,[7] reveals the shortest Sn=Sn and Pb=Pb double bonds (E = Sn: 270.2 pm; E = Pb: 290.3 pm) observed so far. This is attributed to the electronic influence of the hypersilyl group and the relatively small mesityl substituent.

Solid-state structures: The X-ray crystal structure analysis shows that **6** may be interpreted as a donor–acceptor complex with the heteroleptic stannanediyl Ar*HypSn as donor and hypersilylcopper as acceptor (Figure 1). As expected for a complex of this kind, a trigonal planar tin atom and a linearly coordinated copper atom with an Si-Cu-Sn angle of 179.37(4)° are observed. The tin atom is displaced by 11.9 pm with respect to the η^1-coordinated aryl ring plane. The most striking structural feature of **6**, however, is the presence of a Cu–Sn bond. The Cu–Sn distance of 249.92(5) pm is slightly shorter than the sum of the covalent radii (257 pm).[8] To our knowledge, **6** is the first structurally characterized compound with a Cu–Sn bond.[9, 10] However, a related Ag^I–Sn^{II} species, [N=C=S–Ag(thf)–Sn{CH(SiMe$_3$)$_2$}$_2$]$_2$, was reported very recently by Lappert et al;[11] the Ag–Sn bond in this dimeric complex is 259.8 pm in length. Notably, the first structurally authenticated complexes with Cu–Ge bonds were obtained only very recently by Bochkarev and co-workers.[12] The germylcuprate [Yb(thf)$_6$][Cu(GePh$_3$)$_2$][12a] and the germylcopper compound (C$_6$F$_5$)$_3$GeCu(PPh$_3$)$_2$[12b] have Cu–Ge distances of 233.7 pm (av) and 234.8–238.2 pm, respectively. These

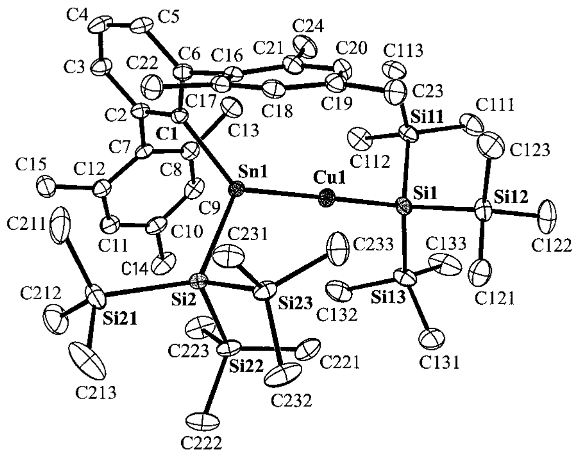


Figure 1. Molecular structure of **6** with 30 % thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected intramolecular distances [pm] and angles [°]: Cu1–Si1 227.27(11), Cu1–Sn1 249.92(5), Sn1–C1 216.6(3), Sn1–Si2 259.66(11), Si1–Si11 233.8(2), Si1–Si12 233.8(2), Si1–Si13 234.1(2), Si2–Si21 233.8(2), Si2–Si22 235.22(14), Si2–Si23 236.0(2), av Si1*n*–C1*nm* 187.9, av Si2*n*–C2*nm* 186.8; Si1-Cu1-Sn1 179.37(4), C1-Sn1-Cu1 128.57(9), C1-Sn1-Si2 114.53(9), Cu1-Sn1-Si2 116.90(3), Cu1-Si1-Si11 107.79(5), Cu1-Si1-Si12 109.37(5), Cu1-Si1-Si13 115.32(6), Sn1-Si2-Si21 123.80(5), Sn1-Si2-Si22 100.08(5), Sn1-Si2-Si23 102.74(5), Sn1-C1-C2 117.3(2), Sn1-C1-C6 122.3(3), C2-C1-C6 120.4(3).

values are consistent with the smaller covalent radius of Ge (122 pm compared to 140 pm for Sn[8]).

With a value of 227.3(1) pm, the Cu–Si bond length in **6** is shorter than the sum of the covalent radii (234 pm[8]). A similar distance of 226.6(2) pm was observed in the terminally bonded hypersilyl group of the A-shaped contact ion pair $[Cu_2Hyp_2BrLi(thf)_3]$[3b] and some *tert*-butanolato(hypersilyl)-cuprates $M^I[t\text{BuOCuHyp}]\cdot$toluene ($M^I$ = Na, K, Cs)[7] which also feature two-coordinate copper and four-coordinate silicon (Table 1). Longer Cu–Si bonds are found in the phosphane adduct $Ph_3SiCu(PMe_3)_3$ (234.0(2) pm, coordination number (CN) Cu/Si = 4/4),[2] the cluster anion $[Cu_5Cl_4Hyp_2]$ (av 234.1 pm, CN = 3/5),[3a] the bridging hypersilyl group of $[Cu_2Hyp_2BrLi(thf)_3]$ (240.6(2) pm, CN = 2/5),[3b] and the bis(hypersilyl)cuprate K[HypCuHyp] (av 229.9 pm, CN = 2/4).[7] Thus, the length of the Cu–Si bond depends on the coordination number at both atoms and the nature of the other ligands on copper (Table 1). In accordance with a four-electron three-center bond within the Si-Cu-X fragment, a longer bond is observed if a softer X ligand is present. NBO population analyses on suitable model systems such as $[H_3Si\text{-}Cu\text{-}OH]^-$, $[H_3Si\text{-}Cu\text{-}OMe]^-$, $[H_3Si\text{-}Cu\text{-}Cl]^-$, or $[H_3Si\text{-}Cu\text{-}SiH_3]^-$ also clearly favor this point of view over the alternative model of two two-electron two-center bonds.[13] The energy that results from the interaction of the donor orbitals (lone pairs) on oxygen with the σ*(Cu–Si) orbital is estimated to be nearly one order of magnitude larger than the interaction with the empty 4p orbitals on copper.

Table 1. Cu–Si distances [pm] in structurally characterized silylcopper compounds.

Compound	*d*(Cu–Si)	CN(Cu)	CN(Si)	Ref.
$[HypCu]_3$ (**9**)	av 235.0/av 249.2	2	5	
$Ph_3SiCu(PMe_3)_3$	234.0	4	4	[2]
$[Li(thf)_4][Cu_5Cl_4Hyp_2]$	av 233.4/av 234.8	3	5	[3a]
$[Cu_2Hyp_2BrLi(thf)_3]$	226.6/240.6	2	4/5	[3b]
Ar*HypSn-CuHyp (**6**)	227.3	2	4	
$Na[t\text{BuO-Cu-Hyp}]\cdot C_7H_8$	223.5	2	4	[7]
$K[t\text{BuO-Cu-Hyp}]\cdot C_7H_8$	222.6	2	4	[7]
$Cs[t\text{BuO-Cu-Hyp}]\cdot C_7H_8$	223.0	2	4	[7]
$[Li_7(Ot\text{Bu})_6][Cu_2Hyp_3]$	av 231.4/av 238.7	2	4/5	[7]
K[Hyp-Cu-Hyp]	av 229.9	2	4	[7]

In **6**, the arrangement of the substituents on the tin atom reflects interligand repulsion. Therefore, the central plane of the aryl ligand is almost orthogonal (91.4°) to the plane which is defined by C1, Sn1, Cu1, Si1, and Si2. As a consequence, the *ortho*-mesityl groups point into the free space above and below of this plane. Furthermore, the hypersilyl substituent of the stannanediyl fragment is tilted with respect to the Si2–Sn1 vector, and the Sn1-Si2-Si21 angle in the trimethylsilyl group, which is almost ecliptic to C1 (Si21-Si2-Sn1-C1 18.1°), is widened to 123.8°. The different Cu1-Sn1-C1 and Cu1-Sn1-Si2 angles of 128.57(9)° and 116.90(3)° are the result of the greater steric demand of the Ar* ligand.[14] The relatively wide C1-Sn1-Si2 angle of 114.53(9)°is identical with the related angle on tin in the recently reported $SnAr^*_2$ (114.7(2)°).[15] The observed Sn1–Si2 distance of 259.7(1) pm is significantly shorter than the mean distance of 267.2 pm in $SnHyp_2$[5] or 262.4(1) pm in $Sn(Hyp)\{C_6H_2\text{-}(CF_3)_3\text{-}2,4,6\}$,[4a] and is probably a result of changes in hybridization at tin. A similar trend is found for the Sn1–C1 bond length of 216.6(3) pm which is about 5–11 pm shorter than the corresponding distances in other reported arylstannanediyl species.[16] The Si–Si bonds lie in the normal range observed for other hypersilyl compounds (233–238 pm). Notably the Si1–Si1*n* distances (av. 233.9 pm) are slightly shorter than the Si2–Si2*n* bond lengths (235.0 pm). This is in agreement with a more crowded environment in the stannanediyl fragment compared to the hypersilylcopper part.

The X-ray structure analysis shows **8** to be monomeric in the solid state (Figure 2). This is also the case for the related homoleptic compounds $PbHyp_2$[5] and $PbAr^*_2$,[15] whereas the known heteroleptic aryl(hypersilyl)plumbanediyls Pb-

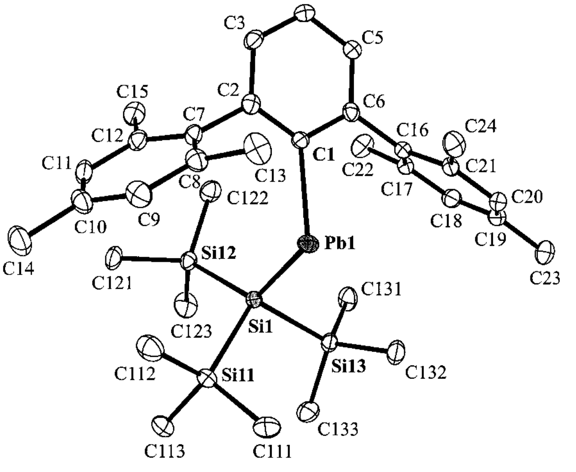


Figure 2. Molecular structure of **8** with 30 % thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected intramolecular distances [pm] and angles [°]: Pb(1)–C(1) 229.0(4), Pb1–Si1 271.20(12), Si1–Si12 234.0(2), Si1–Si13 234.0(2), Si1–Si11 234.8(2), av Si–C 187.4; C1-Pb1-Si1 109.17(11), Si12-Si1-Si13 111.39(7), Si11-Si1-Si12 109.19(6), Si11-Si1-Si13 104.67(7), Pb1-Si1-Si12 127.84(6), Pb1-Si1-Si13 104.44(5), Pb1-Si1-Si11 96.43(6), Pb1-C1-C2 121.8(3), Pb1-C1-C6 117.1(3), C2-C1-C6 120.0(4).

(Hyp)Ar (Table 2) exist as dimers in the solid state. The angle of 109.2(1)° at the two-coordinate lead atom is about 5° smaller than in the homoleptic compounds (av. 114.7° for $PbHyp_2$,[5] 114.5(6)° for $PbAr^*_2$[15]). It is remarkable that the Pb–C bond of 229.0(4) pm is considerably shorter than the values found in most of the other structurally characterized aryl-substituted plumbylenes and diplumbenes (Table 2). However, an even shorter Pb–C bond of 222.8(9) pm was recently observed in the mixed aryl(arylthio)plumbylene Pb(Tbt)(STbt) (Tbt = 2,4,6-$\{(Me_3Si)_2CH\}_3C_6H_2$).[26] In contrast, the Pb–Si distance in **8** (271.2(1) pm) and other hypersilyl-substituted plumbanediyls (270 ± 2 pm)[4, 5] remains rather constant.

Table 2. Characteristic structural parameters and ^{207}Pb NMR chemical shifts in known plumbanediyls with organyl and silyl substituents.

Compound[a]	Pb–C/Pb–Si	R-Pb-R′	$\delta(^{207}Pb)$	Ref.
$PbAr^*_2$	233/–	114.5	3870	[15]
$Pb(Arf)_2$	av 236.6/–	94.5	4878	[20]
$Pb(Tmbp)_2$	av 236.7/–	103.0	6927	[4b]
Pb(Tmbp)(*i*Tmbp)	234.4 (aryl), 247.6 (alkyl)/–	94.8	5067	[4b]
$Pb(Siam)_2$	240.4	117.1	10050	[21]
$Pb[CH(SiMe_3)_2]_2$	231.5/–	93.4	9112	[22]
Pb(Trip)Tbt	–	–	8888	[23]
Pb(Tbm)Tbt	–	–	8873	[23]
$[PbTrip_2]_2$	av 230.0	97.8, 102.3	–	[24]
$Pb(Hyp)_2$	–/268.2–270.8	113.6–115.7	–	[5]
Pb(Ar*)Hyp	229.0/271.2	109.2	10510	
$[Pb(Arf)Hyp]_2$	236.9/270.5	96.7	–	[4a]
$[Pb(Mes)Hyp]_2$	231.4/268.1	102.5	–	[7]
$[Pb(Trip)Hyp]_2$	229.6/271.7	108.8	–	[4c]
$[Pb(Tmbp)Hyp]_2$	237/270.9	106.0	7545	[4b]
$PbSil_2$	–/277.6	105.8	–	[25]

[a] Abbreviations: Arf = $C_6H_2(CF_3)_3$-2,4,6; Tmbp = C_6H*t*Bu-2-Me_3–4,5,6; *i*Tmbp = $CH_2(C_6H$*t*Bu-3-Me_2-5,6); Siam = $\{(Me_3Si)_2CSiMe_2CH_2$-}; Trip = C_6H_2*i*Pr_3-2,4,6; Tbt = $C_6H_2[CH(SiMe_3)_2]_3$-2,4,6; Tbm = $C_6H_2(CH_2SiMe_3)_3$-2,4,6; Mes = $C_6H_2Me_3$-2,4,6; Sil = Si{[N(*neo*-C_5H_{11})]$_2$(2,3-C_6H_4)]}[N$(SiMe_3)_2$].

The arrangement of the substituents is very similar to that in the related complex **6** of the homologous tin compound. Therefore, the ring plane of the coordinated aryl substituent is almost perpendicular (85.2°) to the plane defined by C1, Pb1, and Si1. Furthermore, one trimethylsilyl group exhibits an ecliptic conformation to the aryl ligand, with respect to the Pb1–Si1 bond (Si12-Si1-Pb1-C1 19.6°). As a consequence, the Pb-Si1-Si12 angle is considerably widened to 127.84(6)°.

A cyclic trimer with a nearly planar Cu_3Si_3 unit is observed in the solid-state structure of hypersilylcopper **9** (Figure 3).[27] The $Si_{12}Cu_3$ core shows approximately C_{3h} symmetry. The Si-Cu-Si bridges are almost linear (174.36(4)–175.94(4)°), and the copper atoms are slightly displaced towards each other, an observation which is typical for multinuclear copper(I) compounds.[28] The resulting Cu···Cu distances of 238.45(7)–241.50(6) pm are a sign of weak attractive d^{10}–d^{10} interactions between the copper centers.[29] The central silicon atoms of the hypersilyl groups are not located symmetrically over the edges of the Cu_3 ring, but are shifted significantly towards one copper atom. Therefore, shorter Cu–Si distances of 234.9(1)–237.4(1) pm (Figure 3, solid bonds)—which are, however, longer than in most other known silyl copper derivatives (Table 1) thus reflecting the multicenter nature of the present Cu–Si bonds—alternate with longer Cu–Si bonds of 246.5(1)–249.2(1) pm (Figure 3, open bonds), leading to quasi-monomeric hypersilylcopper units with short Cu–Si bonds. Within these moieties, the central silicon atom is almost tetrahedrally coordinated. One Si_2Cu face of the tetrahedron is capped by the copper atom of a neighboring unit, which leads to an only slightly bent Si-Si-Cu fragment (157.5–164.5°). A similar situation is found for the coordination of the central carbon atom in the related alkylcopper compound $[CuCH_2SiMe_3]_4$[30] and the central silicon atoms in base-free hypersilyllithium.[31] In the copper compound, shorter (av 199 pm) and longer (204 pm) Cu–C bonds again alternate and the Si-C-Cu angle to the capping copper atom is extremely wide (154.3 and 168.2°). In hypersilyllithium, the Cu^+ ion is replaced by the smaller and harder Li^+ ion which forms additional intra- and intermolecular interactions to the methyl groups.[31] However, no extraordinarily short Cu···$(CH_3)_3$Si contacts are found in $(\mathbf{9})_3$ or in the above-mentioned alkylcopper compound. The shortest Cu–C distance in $(\mathbf{9})_3$ (Cu–C222 279.6 pm) is about 80 pm longer than a covalent copper–carbon bond. Therefore, it is unclear if the different Cu–Si distances can be attributed to particular electronic properties of the multicenter bonds or to different steric interactions of the copper atoms with one or two trimethylsilyl substituents.

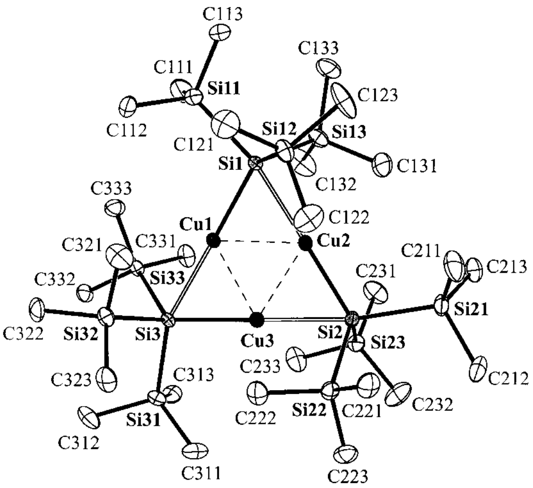


Figure 3. Molecular structure of **9** with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected intramolecular distances [pm] and angles [°]: Cu1–Si1 235.86(10), Cu1–Si3 247.74(10), Cu2–Si2 234.93(11), Cu2–Si1 246.49(10), Cu3–Si3 237.37(10), Cu3–Si2 249.20(10), Cu1···Cu3 238.45(7), Cu1···Cu2 241.50(6), Cu2···Cu3 240.79(6), Si1–Si11 237.2(2), Si1–Si12 235.84(14), Si1–Si13 236.8(2), Si2–Si21 238.11(14), Si2–Si22 238.9(2), Si2–Si23 235.7(2), Si3–Si31 237.66(14), Si3–Si32 235.69(14), Si3–Si33 236.35(13), av Si–C 187.3; Si1-Cu1-Si3 175.94(4), Si1-Cu2-Si2 174.99(4), Si2-Cu3-Si3 174.36(4), Cu1-Si1-Cu2 60.04(3), Cu2-Si2-Cu3 59.57(3), Cu1-Si3-Cu3 58.84(3), Cu1-Si1-Si11 106.51(5), Cu1-Si1-Si12 115.79(5), Cu1-Si1-Si13 116.75(5), Cu2-Si1-Si11 163.48(5), Cu2-Si1-Si12 91.01(5), Cu2-Si1-Si13 79.40(4), Cu2-Si2-Si21 109.56(5), Cu2-Si2-Si22 116.64(5), Cu2-Si2-Si23 112.09(5), Cu3-Si2-Si21 164.47(6), Cu3-Si2-Si22 77.12(4), Cu3-Si2-Si23 91.69(4), Cu3-Si3-Si31 102.96(5), Cu3-Si3-Si32 116.80(5), Cu3-Si3-Si33 121.35(5), Cu1-Si3-Si31 157.54(5), Cu1-Si3-Si32 95.06(4), Cu1-Si3-Si33 80.38(4).

Spectroscopy: NMR spectroscopic experiments clearly show that complex **6** remains intact in solution. The magnetic inequivalence of the *ortho*/*ortho′* and *meta*/*meta′* positions in the mesityl groups, as seen in the ^{13}C and ^{1}H NMR spectra, is in agreement with a rigid arrangement of the substituents. Unfortunately, it was not possible to obtain a ^{119}Sn NMR signal for **6** in [D$_6$]benzene owing to the poor solubility and limited thermal stability. The lack of a third substituent leads to a more flexible skeleton in compound **8**. Therefore, it was possible to determine the rotational barrier for the Ar* substituent by ^{1}H NMR spectroscopy (62 kJ mol^{-1}). The ^{207}Pb NMR shift of $\delta = +10510$ is observed at very low field. It is close to the value of $\delta = +10050$ ppm observed for the dialkyl plumbanediyl $\mathrm{Pb\{(Me_3Si)_2(CSiMe_2CH_2)\}_2}$.[21] ^{207}Pb NMR resonances for diorganyl plumbylenes cover a wide range of several thousand ppm (Table 2). There seems to be no obvious correlation between the ^{207}Pb NMR shift and structural parameters such as the size of the ligand or the angle at the lead center. In contrast to the central silicon atoms (M-*Si*SiMe$_3$) of other hypersilyl metal derivatives which normally exhibit resonances in the high-field region (<0 ppm), the ^{29}Si NMR resonance for the central silicon atom in **8** shows an unusually large low field shift of $\delta = +156.5$. This is only exceeded by bis(hypersilyl)lead **2** for which we have now been able to determine an even larger shift of $\delta = +198.6$.

The NMR spectra of compound **9** show no unusual features. Because we were not able to obtain a larger amount of pure **9**, it is not clear at present if the complex is also trimeric in benzene or dissociates into smaller units. However, there is no sign of hindered rotation of the hypersilyl groups at room temperature, as could be expected for such a sterically crowded molecule. In addition, the relatively long Cu–Si distances in the trimer and observations from crowded arylcopper compounds[6] are in accordance with a dissociation in solution.

Conclusions

We have shown that ligand transfer from the carbene-homologous hypersilyl derivatives **1** and **2**, which appeared to be restricted to other carbene-homologues, also occurs with coordinatively unsaturated metal derivatives such as the arylcopper compound **3**, to yield novel types of compounds such as the base-free hypersilylcopper **9** and the copper(I) stannylene complex **6**. At present, we are investigating analogous reactions with copper derivatives of less sterically demanding groups which—according to the reported results for mesitylcopper—seem to be more complicated. In addition, we wish to extend the ligand transfer reaction to derivatives of the heavier homologues of copper. Hypersilylgold, in particular, which is unknown in its base-free form, appears to be a very promising candidate for strong Au⋯Au interactions, which according to ab initio calculations,[29] should be favored by soft and electropositive substituents such as hypersilyl.

Experimental Section

General procedures: All reactions were performed with standard Schlenk techniques under an inert atmosphere of purified argon. Solvents were freshly distilled under argon from Na wire or LiAlH$_4$. The compounds **1**,[5] **2**,[5] and **3**[6] were synthesized by known literature procedures. UV spectra were obtained with a Bruins Omega 10 spectrometer. NMR spectra were recorded on Bruker AM 200 and AC 250 instruments and referenced to solvent resonances. IR spectra (Nujol mull, CsBr plates) were obtained in the range 4000–200 cm^{-1} with a Perkin-Elmer Paragon 1000PC spectrometer, the Raman spectra were recorded in the range between 800–50 cm^{-1} with a Dilor XY1024 Raman spectrometer. Mass spectra were obtained with a Varian MAT711. Melting points were determined under Ar atmosphere in sealed glass tubes.

Ar*HypSnCuHyp (6): Compound **3** (0.62 g, 1.64 mmol) in benzene (25 mL) was added with stirring at ambient temperature to **1** (1.01 g, 1.64 mmol) in benzene (15 mL). The solution immediately turned deep green and stirring was continued for 30 min. The solvent was removed under reduced pressure and the partly crystalline residue was treated with *n*-pentane (15 mL). Storage in a freezer at −60 °C afforded a dark green solid which was redissolved in a mixture of toluene and *n*-pentane (ca. 1:10). The solution was filtered over a glass filter frit and cooled to −25 °C for 12 h to give green plates of **6**, suitable for X-ray crystallographic studies. Yield: 1.06 g (65 %). M.p.: crystals turn black at about 105 °C and decompose to a black liquid at 147–149 °C. ^{1}H NMR (250 MHz [D$_6$]benzene): $\delta = 0.12$, 0.54 (Si(SiMe$_3$)$_3$), 2.08, 2.17, 2.67 ($o+p$-C*H*$_3$), 6.73, 6.94 (*m*-Mes), 6.91 (d, *m*-C$_6$H$_3$), 7.27 (t, *p*-C$_6$H$_3$). ^{13}C NMR ([D$_6$]benzene): $\delta =$ 4.3, 5.5 (Si(SiMe$_3$)$_3$), 21.1, 21.8, 23.0 ($o+p$-CH$_3$), 129.5 (*m*-C$_6$H$_3$), 129.6 (*p*-C$_6$H$_3$), 130.2, 130.3 (*m*-Mes), 135.3 (*p*-Mes), 136.1, 136.5 (*o*-Mes), 138.9 (*i*-Mes), 145.9 (*o*-C$_6$H$_3$), 162.5 (*i*-C$_6$H$_3$). EI-MS (70 eV): *m/z* (%): 680.1 (16) [Ar*HypSn$^+$], 433.1 (100) [HypSn$^+$], no Cu-containing fragments detected. UV/Vis (pentane): $\lambda_{\max}$ ($\varepsilon_{\max}$) = 674 (130), sh 480 (140), sh 400 nm (820 L cm^{-1} mol^{-1}); anal. calcd for $\mathrm{C_{42}H_{79}CuSi_8Sn}$: C 50.90, H 8.03, Cu 6.41, Si 22.67, Sn 11.98; found: C 50.62, H 8.07.

PbAr*Hyp (8) and CuHyp (9): A solution of **3** (0.43 g, 1.14 mmol) in benzene (20 mL) was added at ambient temperature to a solution of **2** (0.80 g, 1.14 mmol) in benzene (15 mL). The dark green solution was stirred for 30 min, and then the solvent was removed under reduced pressure. *n*-Pentane was added to the remaining solid and the resulting suspension was stored for 12 h at −60 °C to yield **8** as a blue-green crystalline powder (yield: 0.64 g, 73 %). Evaporation of the light-green mother liquor afforded crude **9**. Turquoise prismatic crystals (**8**) or colorless rods (**9**) suitable for X-ray crystal structure determination were either grown from hot [D$_6$]benzene or a saturated *n*-pentane solution at −60 °C. **8:** M.p.: crystals turn dark above 160 °C and decompose to a black liquid at 224–228 °C. ^{1}H NMR ([D$_8$]toluene): $\delta = 0.28$ (Si(SiMe$_3$)$_3$), 2.08 (*p*-C*H*$_3$), 2.31 (*o*-C*H*$_3$), 6.78 (*m*-Mes), 7.38 (t, *p*-C$_6$H$_3$), 7.52 (d, *m*-C$_6$H$_3$). ^{13}C NMR ([D$_6$]benzene): $\delta = 7.1$ (Si(SiMe$_3$)$_3$, ^{1}J(C,Si) = 44.0 Hz), 21.1 (*p*-CH$_3$), 21.8 (*o*-CH$_3$), 136.8 (*m*-C$_6$H$_3$), 129.8 (*p*-C$_6$H$_3$), 128.3 (*m*-Mes), 136.6 (*p*-Mes), 137.1 (*o*-Mes), 148.5 (*o*-C$_6$H$_3$), 264.9 (*i*-C$_6$H$_3$). ^{29}Si NMR ([D$_6$]benzene): $\delta = 3.5$ (Si(*Si*Me$_3$)$_3$), 156.5 (*Si*(SiMe$_3$)$_3$, ^{1}J(Si,Si) = 42.9 Hz). ^{207}Pb NMR ([D$_6$]benzene, 50 °C): $\delta = 10510$. IR (Nujol): $\tilde{\nu} = 1608$ w, 1557 vw, 1252 w, 1239 s, 1171 vw, 1084 w, 1041 w, 855 sh, 833 vs, 798 s, 749 w, 732 ms, 683 m, 621 m, 585 vw, 570 w, 545 vw, 460 vw, 437 vw, 378 cm^{-1} vw. EI-MS (70 eV): *m/z* (%): 768.3 (7) [M$^+$], 521.1 (100) [Ar*Pb$^+$/Ar*PbH$^+$]. UV/Vis (pentane): $\lambda_{\max}$ ($\varepsilon_{\max}$) = 720 (230), sh 399 nm (243 L cm^{-1} mol^{-1}); anal. calcd for $\mathrm{C_{33}H_{52}PbSi_4}$: C 51.59, H 6.82, Pb 26.97, Si 14.62; found: C 50.48, H 6.69. **9:** ^{1}H NMR ([D$_6$]benzene): $\delta = 0.52$. ^{13}C NMR ([D$_6$]benzene): $\delta = 7.0$ (^{1}J(Si, C) = 44.3 Hz). ^{29}Si NMR ([D$_6$]benzene): $\delta = -9.5$ (Si(*Si*Me$_3$)$_3$), −129.6 (*Si*(SiMe$_3$)$_3$). Raman (single crystal, <800 cm^{-1}, λ(excit.) = 647.1 nm): 744 ms, 734 sh, 681 s (ν_{as}(SiC$_3$)), 628 vs (ν_s(SiC$_3$)), 427 m (ν_{as}(SiSi$_3$)), 419 m (ν_s(SiSi$_3$)), 386 ms, 293 mw, 240 mw (ν(CuSi)), 225 sh, 176 vs, 154 sh, 75 sh, 64 vs.

X-ray crystallography: X-ray quality crystals were obtained as described above. Crystals were removed from Schlenk tubes and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber, and immediately placed in a low-temperature stream of N$_2$.[32a] All data were collected at 173 K with either a Syntex P2$_1$ (**3**) or a Siemens P4 (**4**, **5**) diffractometer. Selected data collection parameters and other crystallographic data are summarized in Table 3. Calculations were carried out with the SHELXTL PC 5.03[32b] and SHELXL-97[32c] program system installed on a local PC. The phase problem was solved by direct methods and the structures were refined on F_o^2 by full-matrix least-squares refinement. Absorption corrections were applied by the use of semiempirical ψ scans. Anisotropic thermal parameters were included for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined with a riding model, including free

Table 3. Selected crystallographic data for compounds **6**, **8**, and **9**.[a]

	6	**8**	**9**
formula	$C_{42}H_{79}CuSi_8Sn$	$C_{33}H_{52}PbSi_4$	$C_{27}H_{81}Cu_3Si_{12}$
fw	991.0	768.3	933.6
color, habit	green, plate	turquoise, block	colorless, block
cryst. size [mm]	0.40 × 0.35 × 0.05	0.40 × 0.40 × 0.25	0.80 × 0.70 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a [Å]	16.238(2)	11.5674(8)	13.237(2)
b [Å]	18.862(2)	19.468(1)	18.069(2)
c [Å]	17.985(2)	16.311(1)	21.530(3)
β [°]	91.852(8)	91.498(6)	92.47(1)
V [Å^3]	5506(1)	3671.9(5)	5145(1)
Z	4	4	4
ρ_{calc} [g cm^{-3}]	1.196	1.390	1.205
μ [cm^{-1}]	10.39	47.44	15.25
2θ range [°]	4–54	4–52	4–52
collected data	12456	14780	10449
unique data (R_{int})	12019 (0.034)	7206 (0.048)	10005 (0.039)
data with $I > 2\sigma(I)$ (N_o)	8373	5214	6680
no. of params (N_p)	563	409	483
$R1(I > 2\sigma(I))$[b]	0.0485	0.0340	0.0411
wR2 (all data)[c]	0.1021	0.0681	0.1085
GOF[d]	1.148	1.006	0.898
resd dens (e Å^{-3})	0.50/ – 0.39	0.78/ – 0.60	1.41/ – 0.48

[a] All data were collected at 173 K using $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. [b] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [d] GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}$.

rotation of methyl groups. Their isotropic thermal parameters were either allowed to refine or were constrained to 1.2 (aryl-H) or 1.5 (methyl groups) times the U_{eq} of the bonded carbon. Final R values are listed in Table 3. Important bond lengths and angles are given in the captions to Figures 1–3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114179–114181. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:(+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

We thank Dr. W. Schwarz for the X-ray data collection of compound **8** and Prof. Dr. G. Becker for his generous support of this work.

---

[1] a) I. Fleming in *Organocopper Reagents: A Practical Approach* (Ed.: R. J. K. Taylor), Oxford University Press, Oxford, **1994**, chapter 12, p. 257; b) examples for isolated silylcopper and stannylcopper compounds, which have not been structurally characterized, however: H.-F. Klein, J. Montag, U. Zucha, U. Flörke, H.-J. Haupt, *Inorg. Chim. Acta* **1990**, *177*, 35; see also: U. Schubert, B. Mayer, C. Ruß, *Chem. Ber.* **1994**, *127*, 2189.

[2] A. H. Cowley, T. M. Elkins, R. A. Jones, C. M. Nunn, *Angew. Chem.* **1988**, *100*, 1396; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1349.

[3] a) A. Heine, D. Stalke, *Angew. Chem.* **1993**, *105*, 90; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 121; b) A. Heine, R. Herbst-Irmer, D. Stalke, *J. Chem. Soc. Chem. Commun.* **1993**, 1729.

[4] a) T. Fässler, H. Grützmacher, K. W. Klinkhammer, *Angew. Chem.* **1998**, *110*, 114; *Angew. Chem. Int. Ed.* **1998**, *37*, 124; b) M. Stürmann, M. Weidenbruch, K. W. Klinkhammer, F. Lissner, H. Marsmann, *Organometallics* **1998**, *17*, 4425; c) M. Stürmann, W. Saak, M. Weidenbruch, K. W. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, 579.

[5] K. W. Klinkhammer, W. Schwarz, *Angew. Chem.* **1995**, *107*, 1448; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1334.

[6] M. Niemeyer, *Organometallics* **1998**, *17*, 4649.

[7] J. Klett, K. W. Klinkhammer, unpublished results.

[8] J. Emsley, *The Elements*, 2nd ed., Clarendon Press, Oxford, **1995**.

[9] Cambridge Structural Database, version October 1998 (F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31).

[10] Van der Waals interactions (> 300 pm) between Cu^I and Sn^{IV} centers are known: M. A. Beswick, C. J. Belle, M. K. Davies, M. A. Halcrow, P. R. Raithby, A. Steiner, D. S. Wright, *Chem. Commun.* **1996**, 2619; relatively short $Sn^{II} \cdots Cu^I$ contacts of 272.6 and 290.2 pm were observed in the cluster $Sn(mit)_6Cu_4$ (mit = 1-methylimidazol-2-thiolato): R. E. Allan, A. Bashall, J. S. Palmer, M. McPartlin, M. E. G. Mosquera, J. M. Rawson, A. E. H. Wheatley, D. S. Wright, *Chem. Commun.* **1997**, 1975.

[11] P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *Organometallics* **1998**, *17*, 2686; for a further example of Ag^I–Sn^{II} bonding see: B. Findeis, L. H. Gade, I. J. Scowen, M. McPartlin, *Inorg. Chem.* **1997**, 36, 960.

[12] a) N. A. Orlov, L. N. Bochkarev, A. V. Nikitinsky, S. F. Zhiltsov, L. N. Zakharov, G. K. Fukin, S. Y. Khorshev, *J. Organomet. Chem.* **1997**, *547*, 65; b) N. A. Orlov, L. N. Bochkarev, A. V. Nikitinsky, V. Y. Kropotova, L. N. Zakharov, G. K. Fukin, S. Y. Khorshev, *J. Organomet. Chem.* **1998**, *560*, 21.

[13] K. W. Klinkhammer, unpublished results.

[14] Based on the solid-state structure of **6**, cone angles of 192° and 206° can be calculated for the hypersilyl and Ar* groups.

[15] R. S. Simons, L. Pu, M. M. Olmstead, P. P. Power, *Organometallics* **1997**, *16*, 1920.

[16] $Sn\{C_6H_2\text{-}(CF_3)_3\text{-}2,4,6\}_2$: av 228.1 pm ref. [17], $SnMes^*_2$ ($Mes^* = C_6H_2\text{-}t Bu_3\text{-}2,4,6$): av 226.1 pm ref. [18], $SnAr^*_2$: 222.5(5) pm ref. [15], $(ClSnAr^*)_2$: 222.2(5) pm ref. [15], ISnAr** (Ar** = $C_6H_3\text{-}Trip_2\text{-}2,6$, Trip = $C_6H_2\text{-}i Pr_3\text{-}2,4,6$): 221(1) pm ref. [19], $(SiMe_3)_2NSnAr^{**}$: 222.5(5) pm ref. [19].

[17] a) H. Grützmacher, H. Pritzkow, F. T. Edelmann, *Organometallics* **1991**, *10*, 23; b) U. Lay, H. Pritzkow, H. Grützmacher, *J. Chem. Soc. Chem. Commun.* **1992**, 260.

[18] M. Weidenbruch, J. Schlaefke, A. Schäfer, K. Peters, H. G. von Schnering, H. Marsmann, *Angew. Chem.* **1994**, *106*, 1938; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1846.

[19] L. Pu, M. M. Olmstead, P. P. Power, B. Schiemenz, *Organometallics* **1998**, *17*, 5602.

[20] S. Brooker, J.-K. Buijink, F. T. Edelmann, *Organometallics* **1991**, *10*, 25.

[21] C. Eaborn, T. Ganicz, P. B. Hitchcock, J. D. Smith, S. E. Sözerli, *Organometallics* **1997**, *16*, 5621.

[22] Synthesis: a) P. J. Davidson, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1973**, 317; b) P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1976**, 2268; solid-state structure: c) K. W. Klinkhammer, M. F. Lappert, unpublished results; ^{207}Pb NMR parameters: d) B. Wrackmeyer, K. Horchler, H. Zhou, *Spectrochim. Acta* **1990**, *46A*, 809.

[23] N. Tokitoh, N. Kano, K. Shibata, R. Okazaki, *Organometallics* **1995**, *14*, 3121.

[24] M. Stürmann, W. Saak, H. Marsmann, M. Weidenbruch, *Angew. Chem.* **1999**, *111*, 145; *Angew. Chem. Int. Ed.* **1999**, *38*, 187.

[25] B. Gehrhus, P. B. Hitchcock, M. F. Lappert, *Angew. Chem.* **1997**, *109*, 2624; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2514.

[26] N. Kano, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 4237.

[27] Trimeric copper(I) complexes which feature two-coordinate copper atoms are very rare: $[Cu_3(Mes)(O_2CC_6H_5)_2]$: H. L. Aalten, G. van Koten, K. Goubitz, C. H. Stam, *Organometallics* **1989**, *8*, 2293; $[CuN(SiMePh_2)_2]_3$: H. Chen, M. M. Olmstead, S. C. Shoner, P. P. Power, *J. Chem. Soc. Dalton Trans.* **1992**, 451; $[CuC_6H_3\text{-}Ph_2\text{-}2,6]_3$: see ref. [6].

[28] G. van Koten, S. L. James, J. T. B. H. Jastrzebski in *Comprehensive Organometallic Chemistry*, vol. 3, (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**, chapter 2, p. 57.

[29] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

[30] J. A. J. Jarvis, A. Pearce, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1977**, 999.

[31] K. W. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418.

[32] a) H. Hope, *Progr. Inorg. Chem.* **1995**, *41*, 1; b) *SHELXTL PC 5.03*; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1994; c) G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Solution and Refinement; University of Göttingen, Germany, 1997.

Received: February 2, 1999 [F 1589]