Homo- and Heteroleptic Hypersilylcuprates — Valuable Reagents for the Synthesis of Molecular Compounds with a Cu−Si Bond

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Dedicated to the memory of Ron Snaith

Keywords: Copper / Silicon / Silylcuprates / Si ligands

Unsolvated hypersilanides MHyp [Hyp = $Si(SiMe_3)_3$] of the heavier alkali metals (M^I = Na, K, Cs) react with copper *tert*-butoxide in toluene to yield crystalline heteroleptic cuprates [M^I(toluene)][*t*BuOCuHyp]. These cuprates proved to be valuable sources for pure hypersilylcopper and other cuprates bearing hypersilyl ligands such as the di(hypersilyl)-cuprates $M^I[CuHyp_2]$.

Introduction

Molecular compounds with a Cu−Si bond are very important reagents in modern organic chemistry.[1] However, since they are usually prepared in situ for this purpose, only limited information about their composition and molecular structures is available. This information has mainly been derived from NMR experiments.[2] Only very few structural data for pure compounds are available to date.[3−8] This is partially related to the low kinetic stability of these cuprates and/or the fact that the reaction mixtures often contain various additives to get better regiospecificity and stereoselectivity. The first report of a crystal structure came from Cowley et al. in 1988 , who succeeded in preparing a kinetically stabilized triphenylphosphane complex of a neutral silylcopper complex and determined its structure by X-ray diffraction.[3] All efforts to isolate the pure silylcopper complex in the absence of any stabilizing donor failed however. A few years later Stalke et al. synthesized two silylcuprates as crystalline materials.[4,5] The yields were low, however, and in spite of the bulky hypersilyl substituent employed one of these cuprates, a polynuclear chlorocuprate, is extremely kinetically unstable and decomposes below −20 °C. Until 1999 when we finally succeeded in preparing the first kinetically stable unsolvated silylcopper complex as well as stable lithium cuprates in very good yields,[6,7] a few further reports were published concerning the synthesis of pure Cu^I compounds bearing silyl groups.[9−11] To the best of our knowledge, no detailed structural information about such species had been provided with the exception of two cuprates synthesized very recently by Lerner et al. by a procedure similar to the one used by Stalke.[8] We again used the mentioned hypersilyl group, but in contrast to Stalke and Lerner avoided the presence of halide anions which are thought to have a destabilizing influence on related copper derivatives with hydrocarbyl substituents. As alternative copper(I) source we used either copper *tert*-butoxide or a very bulky arylcopper derivative.

$$7\ LiHyp + 6\ CuO\mathit{t}Bu \longrightarrow [Li_7(O\mathit{t}Bu)_6][Cu_7Hyp_3] + 4\ CuHyp \quad (1)$$

$$9\ LiHyp + 6\ CuO\mathit{t}Bu \longrightarrow [Li_7(O\mathit{t}Bu)_6][Cu_2Hyp_3] + 2\ LiCu_2Hyp_3 \quad (2)$$

$$11\ LiHyp + 6\ CuO\mathit{t}Bu \longrightarrow [Li_7(O\mathit{t}Bu)_6][Cu_2Hyp_3] + 4\ LiCuHyp_2 \quad (3)$$

$$PbHyp_2 + CuAr \longrightarrow CuHyp + Pb(Ar)Hyp \quad (4)$$

The employed silanide nucleophiles were unsolvated hypersilanides of lithium [Equations (1)−(3)] and lead(II) [Equation (4)], respectively. Both reaction types, however, are not suitable for preparing large quantities of pure silylcopper derivatives. We now report the synthesis of novel hypersilyl complexes of Cu^I, the heteroleptic *tert*-butoxy(hypersilyl)cuprates of the heavier alkali metals M^I[*t*BuOCuHyp], which are easily accessible in high quantities and excellent yields. They are fairly stable under controlled conditions and, as will be seen below, have proved to be valuable starting compounds for other silyl derivatives of Cu^I.

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Table 1. Crystallographic data for M^I(toluene)[HypCuO*t*Bu] [M^I = K (**1**), Na (**2**), Cs(**3**)] and M^ICuHyp_2 [M^I = K (**4**), Na (**5**)]

	1	**2**	**3**	**4**	**5**
Formula	$C_{40}H_{88}Cu_2K_2O_2Si_8$	$C_{40}H_{88}Cu_2Na_2O_2Si_8$	$C_{40}H_{88}Cs_2Cu_2O_2Si_8$	$C_{18}H_{54}CuKSi_8$	$C_{18}H_{54}CuNaSi_8$
Molecular mass	1031.10	998.88	1218.72	597.97	581.86
Crystal System	monoclinic	triclinic	triclinic	monoclinic	triclinic
Space Group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P\bar{1}$
a [Å]	13.6489(14)	9.916(2)	9.400(2)	9.134(2)	9.442(2)
b [Å]	12.498(2)	12.329(2)	11.478(2)	12.619(3)	13.164(2)
c [Å]	18.619(2)	12.469(2)	15.454(3)	15.827(3)	16.689(3)
α [°]	90	90.82(3)	71.41(3)	90	108.495(9)
β [°]	107.762(10)	101.99(3)	81.59(3)	91.87(3)	96.201(10)
γ [°]	90	91.03(3)	81.37(3)	90	108.919(9)
V [Å^3]	3024.7(7)	1490.6(5)	1553.8(5)	1823.3(7)	1808.9(6)
Z	2	1	1	2	2
F(000)	1104	536	624	644	628
$D_{calcd.}$ [gcm^{-1}]	1.132	1.113	1.302	1.089	1.068
μ [mm^{-1}]	1.026	0.916	2.019	0.982	0.886
Crystal Size [mm^{-3}]	0.4 × 0.3 × 0.1	0.8 × 0.6 × 0.3	0.6 × 0.5 × 0.5	0.8 × 0.3 × 0.3	0.6 × 0.3 × 0.2
θ range	2.7 < θ < 28°	3.4 < θ < 27.5°	2 < θ < 28°	2 < θ < 30°	2.3 < θ < 28°
hkl ranges	$-1 < h < 18$	$0 < h < 12$	$0 < h < 12$	$-12 < h < 12$	$0 < h < 12$
	$-1 < k < 16$	$-16 < k < 16$	$-14 < k < 14$	$-8 < k < 17$	$-15 < k < 15$
	$-24 < l < 23$	$-16 < l < 15$	$-20 < l < 20$	$-22 < l < 22$	$-22 < l < 21$
No. of reflns measd.	8910	7207	7799	6919	8777
No. of unique reflns, R_{int}	7303, 0.057	6819, 0.0399	7354, 0.045	6919, 0.059	8286, 0.045
Reflections with $I > 2\sigma(I)$	2600	3891	4923	4134	4075
Parameters, restraints	320, 90	320, 220	257, 0	254, 1	368, 66
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.046,	R_1 = 0.050,	R_1 = 0.050,	*R*1 = 0.039,	*R*1 = 0.064,
	wR_2 = 0.071	wR_2 = 0.116	wR_2 = 0.112	*wR*2 = 0.085	*wR*2 = 0.146
Final *R* indices (all data)	R_1 = 0.154,	R_1 = 0.092,	*R*1 = 0.091,	*R*1 = 0.061,	*R*1 = 0.137,
	wR_2 = 0.085	wR_2 = 0.125	wR_2 = 0.131	*wR*2 = 0.089	*wR*2 = 0.166
Goodness-of-fit	0.680	0.880	0.987	0.866	0.925
Residual electron density [e·Å^{-3}]	−0.301, 0.327	−0.389, 0.739	−1.003, 0.802	−0.396, 0.441	−0.311, 0.457

Results and Discussion

Potassium hypersilanide [KHyp; Hyp = -Si(SiMe$_3$)$_3$][12] readily reacts with copper *tert*-butoxide in toluene to give a pale yellow solution from which, on cooling to −20 °C, colorless crystals precipitate. The NMR spectroscopic data indicate that the toluene solvate of heteroleptic potassium *tert*-butoxy(hypersilyl)cuprate [K(toluene)][*t*BuOCuHyp] (**1**) had formed quantitatively [Equation (5)]. This assumption was verified by an X-ray diffraction experiment on a single crystal (Table 1 and 2). Whereas in the crystalline state cuprate **1** may be stored for several months, in solution

Table 2. Selected bond lengths [pm] and angles [°] in M^I(toluene)[HypCuO*t*Bu] [M^I = K (**1**), Na (**2**), Cs(**3**)]

	1	**2**	**3**
Cu1−Si1	222.59(2)	223.47(11)	223.0(2)
Cu1−O1	188.0(3)	188.7(2)	188.1(3)
Si−Si (range)	233.2(2)−234.68(14)	233.8(2)−234.6(2)	233.5(2)−233.9(2)
M^I−O1	259.1(3)	225.5(3)	290.1(3)
M^I−O1′	266.0(2)	229.4(3)	298.5(3)
M^I···C_{arom} (range)	315(4)−338(4)	294.2(12)−356.9(8)	359.7(9)−388.4(9)
M^I···C_T [a]	302	295.2	346.5
Si1−Cu1−O1	171.70(7)	177.05(8)	174.59(11)
Cu1−O1−C1	120.4(2)	122.8(2)	119.0(3)
Cu1−O1−M^I	106.24(12)	104.55(10)	104.87(13)
Cu1−O1−$M^{I\prime}$	91.51(9)	97.85(10)	93.64(12)
M^I−O1−C1	121.1(2)	117.5(2)	119.2(3)
$M^{I\prime}$−O1−C1	118.0(2)	117.0(2)	116.8(3)
M^I−O1−$M^{I\prime}$	92.65(8)	91.24(10)	98.75(10)
O1−M^I−O1′	87.35(8)	88.76(10)	81.25(10)
Cu−Si−Si (range)	104.98(5)−120.50(6)	107.96(5)−118.76(6)	106.29(7)−117.26(7)
Si−Si−Si (range)	105.26(6)−106.63(6)	105.69(5)−106.71(5)	106.81(8)−107.49(8)

[a] C_T denotes the centroid of the carbon atoms of the aromatic ring.

it decomposes slowly even at −20 °C with precipitation of a black powder within a few weeks; this process is even faster when the solution is exposed to ambient light.

$$M^{I}Hyp + CuO\mathit{t}Bu \xrightarrow[-20°C]{\text{toluene}} [M^{I}(\text{toluene})][\mathit{t}BuOCuHyp]$$

M^{I} = Na (**2**), K (**1**), Cs (**3**) (5)

In the solid state the heterocuprate **1** consists of centrosymmetric dimers (Figure 1), where two *tert*-butoxy(hypersilyl)cuprate anions with almost linear Si−Cu−O backbones [171.70(7)°] are linked via two $[K(\text{toluene})]^{+}$ cations, thus forming planar K_2O_2 rings with alternating short and long K−O distances of 259.1(3) and 266.0(2) pm, respectively. The coordination sphere of each alkali cation is completed by an η^6-bonded toluene molecule. Due to twofold disordering of the toluene ligand the K···C distances cannot be determined to a great accuracy, but observed values between 315 and 352 pm lie in the expected range. An intriguing feature of the cuprate anion is a very short Cu−Si bond of 222.59(12) pm, which is thus far the shortest among all structurally characterized compounds with Cu−Si bonds (Table 3). The Cu−O distance, on the other hand, is comparatively long, giving rise to the description of cuprate **1** as a *loose* Lewis-acid/base adduct of hypersilylcopper and potassium *tert*-butoxide. Replacing the relatively hard Lewis base *tert*-butoxide for a softer one such as a second hypersilanide anion, or neutral ligands such as phosphanes, leads to substantial lengthening of the Cu−Si bond. We were able to synthesize and structurally characterize di(hypersilyl)cuprates with Na, K and Cs as countercations and therein found Cu−Si distances of about 230 ± 1 pm (see below).

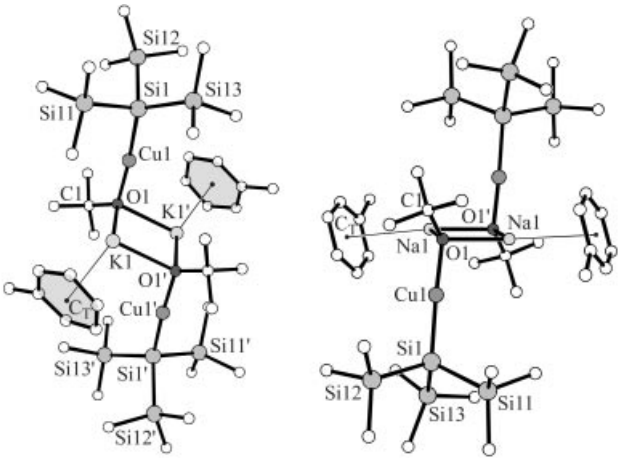

Figure 1. Molecular structures of heterocuprates **1** (left) and **2** (right); slightly differing orientations have been chosen for better illustrating the structural details; atoms are represented by spheres of arbitrary radii; the centroids of the aromatic rings are denoted by C_T; selected structural parameters are given in Table 2

Replacing K^{+} for Na^{+} or Cs^{+} does not significantly change the basicity and availability of the butoxide anion. The respective heterocuprates **2** and **3** again form dimers in the solid state (Figure 1 and 2) and in spite of different crystal structures display very similar molecular structures to the potassium derivative **1**. The observed differences such as different M^{I}−O bond lengths and different M^{I}···C distances (Table 2) can all be related to the strongly differing ionic radii of the alkali metals. Due to the much larger radius of Cs^{+} the cesium cuprate **3** exhibits — other than its relatives **1** and **2** — further aggregation in the solid state. This is accomplished by a Cs···CH_3 agostic interaction with methyl groups of neighboring cuprate dimers [Cs···C122′ 372.8(6) pm] and finally leads to one-dimensional coordination polymers (Figure 2). The cesium cuprate also differs in the fact that the solvating toluene, again bonded in an η^6-fashion, is now well ordered.

Replacing potassium for lithium, i.e. reacting lithium hypersilanide with copper *tert*-butoxide, dramatically changes the type of products obtained. Lithium *tert*-butoxide, which is presumably formed at first, doesn't give any isolable adduct with hypersilylcopper. Instead it catches Li^{+} cations from excess lithium hypersilanide to give the unique cation $[Li_7(O\mathit{t}Bu)_6]^{+}$, and — with simultaneously generated hypersilylcopper — gives rise to the formation of different homocuprates [Equations (1) − (3)], details of which have been published in a previous paper.[7]

The structural parameters of the hypersilyl group present in the cuprates **1**, **2** and **3** differ only slightly. Relatively short Si−Si bonds and Si−Si−Si angles significantly smaller than ideal tetrahedral values indicate negative charge accumulation on the hypersilyl group. An almost complete charge transfer is expected, and found, for the parent alkali metal silanides. Consequently, Si−Si bond lengths of 233 pm and Si−Si−Si angles down to 102° are observed for these compounds, whereas almost ideal tetrahedral angles are found for the derivatives of elements with a similar electronegativity as silicon (e.g. $HgHyp_2$ [13]). A relatively high negative charge of about −0.5 is verified by NBO analysis of the density derived from ab initio or DFT calculations, and is in agreement with the position of the ^{29}Si NMR resonance for the central silicon atom, which is observed at high field (δ = −147 ppm) for all cuprates **1**−**3**.

Next we discuss preliminary results for the utilization of the heterocuprates **1**−**3** in the synthesis of other cuprates. From the outcome of the reaction of lithium hypersilanide with copper *tert*-butoxide, we assumed that in the presence of (unsolvated) Li^{+} cations *tert*-butoxide anions usually do not bind to a Cu−SiR_3 moiety to form heterocuprates. Therefore we supposed that the addition of lithium salt might lead to substitution of the *tert*-butoxide ligand for the co-anion of lithium [Equation (6)].

$$[M^{I}(\text{toluene})][\mathit{t}BuOCuHyp] + LiX \longrightarrow [M^{I}][XCuHyp] + LiO\mathit{t}Bu + \text{toluene}$$

M^{I} = Na (**2**), K (**1**), Cs (**3**) (6)

Table 3. Cu−Si bond lengths [pm] in molecular compounds

Compound	Cu−Si	CN(Cu)	CN(Si)	Ref.
$Ph_3SiCu(PPh_3)_3$	234.0	4	4	3
$(HypCu)_3$	av 235.0/av 249.2	2	5	6
$HypCu(PPh_3)_2$	234.5	3	4	16
HypCuSn(Hyp)Ar[a]	227.3	2	4	6
[(toluene)Na][*t*BuOCuHyp] (**2**)	223.5	2	4	
[(toluene)K][*t*BuOCuHyp] (**1**)	222.6	2	4	
[(toluene)Cs][*t*BuOCuHyp] (**3**)	223.0	2	4	
$NaCuHyp_2$ (**5**)	av. 228.8	2	4	
$KCuHyp_2$ (**4**)	av 229.9	2	4	
$[(THF)_6K][CuHyp_2]$	av 229.3	2	4	16
$(toluene)_2Cs[CuHyp_2]$	229.1	2	4	16
$[Li_7(OtBu)_6][Cu_2Hyp_3]$	av 231.4, av 238.7	2	4 (2 ×), 5 (1 ×)	7
$LiCu_2Hyp_3$	av 232.9, av 240.0	2	4 (2 ×)[b], 5 (1 ×)	7
$[(THF)_4Li][Cu_5Cl_4Hyp_2]$	av 233.4/av 234.8	3	5	5
$[(THF)_3Li][Cu_2BrHyp_2]$	226.6/240.6	2	4/5	4
$[(THF)_2Na][CuSup_2]$	236.1 (2 ×)	2	4	8
$[(THF)_4Na][CuSup_2]$	231.1 (2 ×)	2	4	8

[a] Ar = C_6H_3-2,6-Mes_2; Mes = C_6H_2-1,3,5-Me.

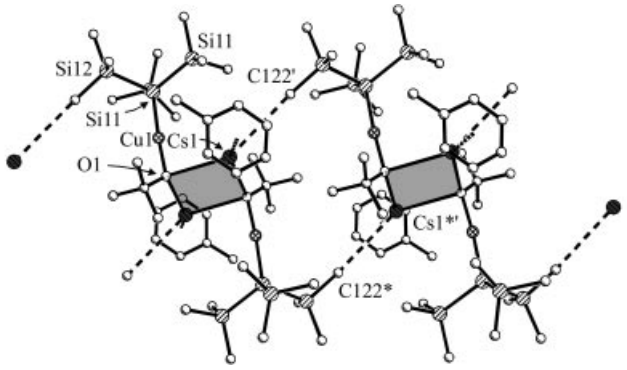

Figure 2. Molecular and crystal structure of heterocuprate **3**; intermolecular contacts are symbolized as dashed lines; atoms are represented by spheres of arbitrary radii; selected structural parameters are given in Table 2

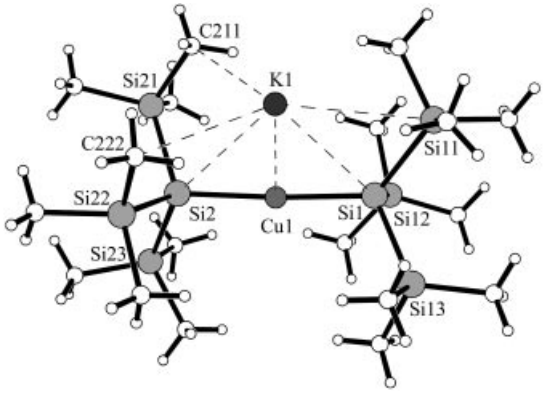

Figure 3. Molecular structure of potassium di(hypersilyl)cuprate (**4**); atoms are represented by spheres of arbitrary radii; dashed lines are used to symbolize interatomic distances markedly smaller than the sum of the corresponding van der Waals radii; selected structural parameters are given in Table 2

At first we investigated the reaction of unsolvated lithium hypersilanide with toluene solutions of the heterocuprates **1**−**3**. In the course of all these reactions the heterocuprates are fully consumed and one very soluble compound, probably unsolvated lithium *tert*-butoxide, is detected as a major product. The ^1H NMR spectra of the non-volatile products reveal the presence of at least one novel species present in all three reaction mixtures, in each case giving a resonance near $\delta = 0.38$ ppm (C_6D_6). The same resonances are found if pure hypersilylcopper is reacted with solvated or unsolvated lithium or potassium hypersilanide in a 1:1 molar ratio. Only for potassium has the respective product — potassium di(hypersilyl)cuprate $K[CuHyp_2]$ (**4**) — been isolated almost pure and in high yields after crystallization from pentane/toluene mixtures [according to Equation (6) with X = Hyp] as a colorless crystalline compound that could be fully characterized by X-ray diffraction (Table 1 and 4; Figure 3 and 4) and NMR spectroscopy.

The colorless solid material from the reaction of heterocuprate **2** contains at least three different compounds. Beside the desired $Na[CuHyp_2]$ (**5**), which again could be structurally characterized, varying amounts of crystalline sodium hypersilanide and one further unidentified product are present in the recrystallized material; from the reaction of cesium derivative **3**, solid mixtures of the desired $Cs[CuHyp_2]$ (**6**), cesium hypersilanide, hypersilylcopper, $Si(SiMe_3)_4$ and at least one other unidentified product are obtained. We concentrate here on the discussion of solid-state structures for the di(hypersilyl)cuprates **4** and **5** which could be determined from single crystals. A thorough comparison of molecular structures and spectroscopic data for all three dihypersilyl cuprates **4**−**6** will be discussed in a later paper, since only during the writing of the present report were we able to isolate the di(hypersilyl)cuprates **5** and **6** as pure compounds from direct reactions of hypersilylcopper and the appropriate alkali metal hypersilanide.[14]

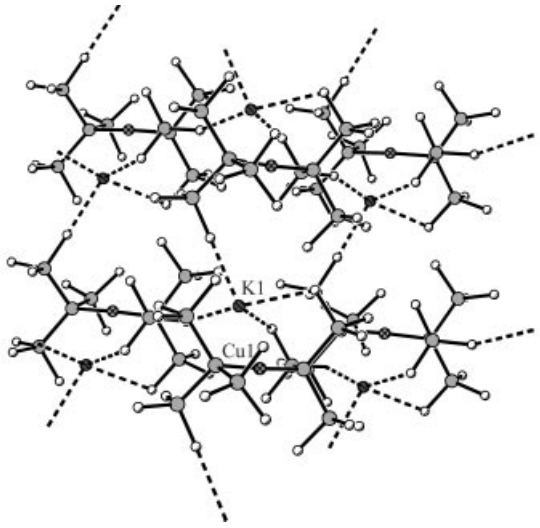

Figure 4. View parallel to [001] of the puckered two-dimensional coordination polymer of cuprate **4**; dashed lines indicate agostic-type intermolecular K···C contacts

The colorless crystal needles of potassium di(hypersilyl)-cuprate (**4**) comprise discrete molecules (Figure 3) interlinked weakly by agostic-type interactions (Figure 4). The potassium ion is located above the center of the dumbbell-like di(hypersilyl)cuprate fragment, thus giving short K−Si distances to the central silicon atoms of the hypersilyl groups of nearly equal length (380 pm), and a short K−Cu distance of 305 pm. The copper atom is slightly bent away from the potassium atom giving a Si−Cu−Si angle of about 176.4°. We assume the most adequate description of the molecule to be as an intimate ion-pair with a predominantly ionic binding mode between the K^+ cation and the cuprate anion. The anion is isoelectronic with di(hypersilyl)-zinc and, in spite of the additional K^+ ion present in **4**, adopts an almost ideal staggered conformation (approximate local D_{3d} symmetry) and has similar structural parameters.[15] According to the somewhat larger atomic radius of zinc the Cu−Si bonds found in the cuprate **4** (2 × 230 pm) are slightly shorter (by 4 pm) than the corresponding Zn−Si bonds in di(hypersilyl)zinc (2 × 234 pm).

The only structural differences between the cuprate anion and di(hypersilyl)zinc worth mentioning are markedly widened Cu−Si−Si angles to those trimethylsilyl groups in the neighborhood of the intruding K^+ cation (Table 4). The electrostatic bond between the K^+ cation and $[Hyp_2Cu]^-$ anion is further amended by agostic-type interaction to two methyl groups within the molecular unit [K···CH_3: 331.2(6) and 336.0(5) pm]. Two further, but intermolecular, K···CH_3 contacts of 321.8(5) and 342.1(5) pm complete the coordination of the K^+ cation, leading to puckered infinite two-dimensional coordination polymers (Figure 4).

The structural parameters of the related sodium di(hypersilyl)cuprate (**5**) are very similar (Table 4). Significant differences occur only for the location and coordination of the markedly smaller Na^+ cation. Other than the K^+ ion in compound **5**, which is located above the center of the dumbbell anion, the Na^+ ion is statistically disordered about two positions. The sites are located on opposite sites of the $CuSi_2$ dumbbell and slightly displaced from the center of the dumbbell in opposite directions (Figure 5). Again, due to the smaller ionic radius of Na^+, the sodium derivative **5** does not form coordination polymers but only dimers, as illustrated in Figure 6.

Very recently the synthesis of related sodium di(supersilyl)cuprates Na[Cu(Si*t*Bu$_3$)$_2$] was reported by Lerner et al.[8] They were obtained as THF solvates from CuCl and sodium supersilanide in tetrahydrofuran at −78 °C. However, similar to the findings of Stalke the overall yields were relatively low (47%), perhaps again due to the presence of halide. Interestingly two *different* solvates were isolated from the reaction mixture. The first, [Na(THF)$_4$][Cu(Si*t*Bu$_3$)$_2$], consists of separated ions, whereas the second, [Na(THF)$_2$][Cu(Si*t*Bu$_3$)$_2$], displays similar structural features to potassium di(hypersilyl)cuprate, i.e. contact ion-pairs, but now with two additional THF molecules coordinated to the sodium cation.

Unexpectedly, the Cu−Si bonds shorten markedly from ca. 236 pm to 231 pm on going from the contact ion-pair to

Table 4. Selected bond lengths [pm] and angles [°] in M^I[HypCuHyp] [M^I = K (**4**), Na (**5**)]

	4	**5**
Cu1−Si1	229.88(13)	228.09(14)
Cu1−Si2	230.01(13)	228.63(14)
Si−Si (range)	232.6(2) −234.2(2)	232.5(2) −233.7(2)
M^I−Si1	379.9(2)	305.3(7) *(Na1)*
M^I−Si2	380.3(2)	323.1(5) *(Na2)*
M^I···Cu1	305.18(13)	267.9(4) *(Na1)*; 252.2(7) *(Na2)*
Si1−Cu1−Si2	176.44(4)	177.45(6)
Cu1−Si1−Si11	123.69(5)	114.45(7)
Cu1−Si1−Si12	108.77(6)	111.59(7)
Cu1−Si1−Si13	103.06(6)	106.00(7)
Cu1−Si2−Si21	109.57(5)	113.70(6)
Cu1−Si2−Si22	115.19(6)	109.69(7)
Cu1−Si2−Si23	108.40(6)	111.07(7)
Si−Si−Si (range)	106.26(6)−109.42(7)	104.70(7) −109.92(8)

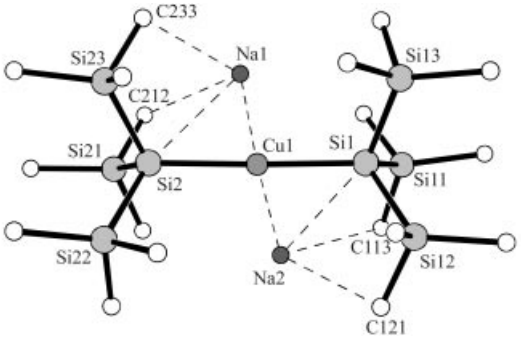

Figure 5. Molecular structures of sodium di(hypersilyl)cuprate (**5**), atoms are represented by spheres of arbitrary radii; dashed lines are used to symbolize interatomic distances markedly smaller than the sum of the corresponding van der Waals radii; the sodium atoms are statistically disordered about the sites Na1 and Na2; selected structural parameters are given in Table 3

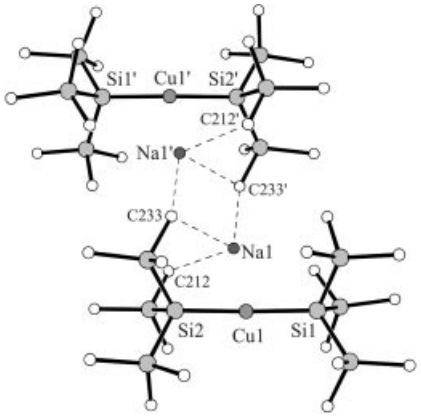

Figure 6. Coordination dimer of cuprate **5**; dashed lines indicate intra- and intermolecular agostic-type Na···C contacts

the separated anion, although we do not see a comparable shortening of the Cu−Si bonds on going from the contact ion-pair in cuprate **4** to separated ions in $[K(THF)_6][CuHyp_2]$, which is obtained by reaction of potassium hypersilanide with copper *tert*-butoxide in tetrahydrofuran (Table 3).[16]

It should be noted, finally, that a mixture of lithium hypersilanide and other lithium silanides may be used as a reactant in the reaction with the heterocuprates **1**−**3**, leading to cuprates with two different silyl ligands. In some cases mixed bis(silyl)cuprates may be isolated, whereas in other cases ligand redistribution takes place and the two symmetric species are formed. Detailed investigations are currently in progress.

Finally, we report a rational synthesis of large amounts of pure hypersilylcopper[6] — a compound ideal for the study of prototypic reactions of the Cu−Si bond towards organic or inorganic substrates — and for which no straightforward synthesis is known to date. Since the cuprates **1**, **2**, and **3** in turn are very easily accessible, we looked for a possible transformation of those cuprates into the neutral silylcopper complex. We finally succeeded with the reaction of the cuprates with chlorotrimethylsilane in toluene or pentane at low temperatures [Equation (7)].

$$\underset{(\mathbf{1})}{[K(\text{toluene})][t\text{BuOCuHyp}]} + Me_3SiCl \longrightarrow CuHyp + KCl + Me_3SiO t\text{Bu} + \text{toluene} \quad (7)$$

At ambient temperature both nucleophiles — the *tert*-butoxide and the hypersilanide anion — are stripped simultaneously from the heterocuprate anion leading to mixtures of hypersilylcopper and undesired non-volatile side-products such as copper *tert*-butoxide, the mixed tetramers $Cu_4Hyp_2(OtBu)_2$ (**7**) and $Cu_4Hyp_3(OtBu)$ (**8**) as well as tetrakis(trimethylsilyl)silane [Equation (8) and (9)]. At temperatures below −20 °C solutions of almost pure hypersilylcopper are obtained, however, from which crystalline material is obtained after removing all volatile components in vacuo and subsequent crystallization of the residue from toluene. To get very clean hypersilylcopper the cuprate **1** should be recrystallized before use and the ratio of the reactants should be as close as possible to 1:1. The mixed tetramers **7** and **8**, which are found as major side-products if the temperature chosen is too high, represent the first *heteroleptic* neutral Cu^I species bearing silyl substituents. A rational synthesis, spectroscopic data and structural details will be discussed in a subsequent paper.

$$\underset{(\mathbf{1})}{[K(\text{toluene})][t\text{BuOCuHyp}]} + Me_3SiCl \longrightarrow CuOtBu + KCl + Me_3SiHyp + \text{toluene} \quad (8)$$

$$x\ CuOtBu + y\ CuHyp \longrightarrow Cu_4(OtBu)_xHyp_y \quad [x = 2, y = 2\ (\mathbf{7}); x = 1, y = 3\ (\mathbf{8})] \quad (9)$$

Conclusion

We have shown that copper *tert*-butoxide reacts with the hypersilanides of the heavier alkali metals Na, K, and Cs in toluene solution to yield heterocuprates of the type $M^I[t$-BuOCuHyp] (**1**−**3**). They form dimers in the solid state and contain the shortest Cu−Si bond ever determined for molecular compounds. These cuprates can be used as valuable sources for the parent hypersilylcopper complex and other silylcopper reagents. Due to the fact that Li^+ cations bind to the *tert*-butoxide anion very strongly, reactions of cuprates **1**−**3** with lithium salts often leads to a replacement of the *tert*-butoxide anion for the counteranion of the employed salt. Therefore di(hypersilyl)cuprates, or even unsymmetrically substituted bis(silyl)cuprates, are obtained if the heterocuprates **1**−**3** are treated with a mixture of lithium hypersilanide and other lithium silanides. If the *tert*-butoxide anion is completely removed from the heterocuprate anion pure hypersilylcopper is obtained.

Experimental Section

General Remarks: All experiments were carried out under dry oxygen-free argon using standard Schlenk techniques. Solvents were freshly distilled under Ar from $LiAlH_4$ prior to use. NMR: Bruker AM 200 and AC 250 instruments and referenced to solvent resonances.

$[M^I(C_7H_8)][t$BuOCuSi(SiMe$_3$)$_3$] [M^I = K (1), Na (2), Cs(3)]: In a typical experiment unsolvated $M^ISi(SiMe_3)_3$ (2 mmol) dissolved in toluene (10 mL) was slowly added to a well-stirred solution of CuO*t*Bu (0.27 g, 2 mmol) in toluene (20 mL) at −20 °C. The reaction mixture was stirred for 30 min at −20 °C and then rapidly heated for a few minutes to about 40 °C. After filtration from small amounts of copper powder the now pale-yellow solution was concentrated under dynamic vacuum to a volume of about 20 mL and cooled to −60 °C for 24 h. The cuprates **1**−**3** were obtained as colorless (**1** and **2**) or pale-yellow (**3**) crystalline toluene solvates. Some more crystalline material was obtained after subsequent concentration and crystallization at −60 °C. Typical yields lie between 85 and 96%.

1: $C_{40}H_{88}Cu_2K_2O_2Si_8$ (1031.10): calcd. C 46.59, H 8.6; found C 46.23, H 8.52. ^{1}H NMR (C_6D_6): δ = 0.49 (s, 27 H, $SiMe_3$) 1.12 [s, 9 H, Me (O*t*Bu)] ppm. ^{13}C NMR (C_6D_6): δ = 5.53 ($SiMe_3$, $^1J_{C,Si}$ = 42.1 Hz), 37.4 [C(*C*H$_3$)], 70.1 [*C*(CH$_3$)] ppm. ^{29}Si NMR: δ = −7.40 [Si(*Si*Me$_3$)$_3$], 141.2 [*Si*(SiMe$_3$)$_3$] ppm.

2: $C_{40}H_{88}Cu_2Na_2O_2Si_8$ (998.88): calcd. C 48.09, H 8.88; found C 47.92, H 8.91. ^{1}H NMR (C_6D_6): δ = 0.49 (s, 27 H, $SiMe_3$) 1.06 [s, 9 H, Me (O*t*Bu)] ppm. ^{13}C NMR (C_6D_6): δ = 5.43 ($SiMe_3$, $^1J_{C,Si}$ = 42.0 Hz), 37.4 [C(*C*H$_3$)], 69.8 [*C*(CH$_3$)] ppm. ^{29}Si NMR: δ = −7.60 [Si(*Si*Me$_3$)$_3$, $^1J_{Si,Si}$ = 47.3 Hz), 139.6 [*Si*(SiMe$_3$)$_3$] ppm.

3: $C_{40}H_{88}Cu_2Cs_2O_2Si_8$ (1218.72): calcd. C 39.42, H 7.28; found C 39.12, H 7.24. ^{1}H NMR (C_6D_6): δ = 0.48 (s, 27 H, $SiMe_3$) 1.13 [s, 9 H, Me (O*t*Bu)] ppm. ^{13}C NMR (C_6D_6): δ = 6.20 ($SiMe_3$, $^1J_{C,Si}$ = 41.4 Hz), 36.5 [C(*C*H$_3$)], 70.4 [*C*(CH$_3$)] ppm. ^{29}Si NMR: δ = −7.40 [Si(*Si*Me$_3$)$_3$], 141.5 [*Si*(SiMe$_3$)$_3$] ppm.

KCu[Si(SiMe$_3$)$_3$]$_2$ (4): Unsolvated lithium hypersilanide (2.5 g, 9.82 mmol) dissolved in toluene (10 mL) was added to a solution of cuprate **1** [5.06 g, 4.91 mmol (dimer)] in toluene (20 mL) at −20 °C and stirred for 30 min at this temperature, then warmed to room temperature and stirred for another 20 min. The volatiles were removed at 25 °C/10^{-2} Torr and the oily residue extracted with 3 × 10 mL of *n*-pentane. The pentane solution was concentrated under dynamic vacuum at 20 °C until a few colorless crystals appeared and then placed at −60 °C for 24 h. The cuprate **4** was obtained in 65% yield as colorless crystal blocks. $C_{18}H_{54}CuKSi_8$ (597.97): calcd. C 36.15, H 9.10; found C 35.95, H 9.13. ^{1}H NMR (C_6D_6): δ = 0.38 (s, 27 H, $SiMe_3$) ppm. ^{13}C NMR (C_6D_6): δ = 6.1 ($SiMe_3$, $^1J_{C,Si}$ = 41.6 Hz) ppm. ^{29}Si NMR: δ = −7.5 [Si(*Si*Me$_3$)$_3$], 147.5 [*Si*(SiMe$_3$)$_3$].

NaCu[Si(SiMe$_3$)$_3$]$_2$ (5): Unsolvated lithium hypersilanide (2.5 g, 9.82 mmol) dissolved toluene (10 mL) was added to a solution of cuprate **2** [4.90 g, 4.91 mmol (dimer)] in toluene (20 mL) at −20 °C and stirred for 30 min at this temperature, then warmed to room temperature and stirred for another 20 min. The volatiles were removed at 25 °C/10^{-2} Torr and the oily residue extracted with 3 × 10 mL of *n*-pentane. The pentane solution was concentrated to 5 mL and then placed at −60 °C for several days. The cuprate **5** was obtained as a solid mixture with sodium hypersilanide and one unidentified product. ^{1}H NMR (C_6D_6): δ = 0.38 (s, 27 H, $SiMe_3$) ppm. ^{13}C NMR (C_6D_6): δ = 5.9 ($SiMe_3$, $^1J_{C,Si}$ = 41.7 Hz) ppm. ^{29}Si NMR: δ = −7.3 [Si(*Si*Me$_3$)$_3$], 147.3 [*Si*(SiMe$_3$)$_3$] ppm.

Synthesis of Hypersilylcopper [CuSi(SiMe$_3$)$_3$] from [K(C$_7$H$_8$)][*t*BuOCuSi(SiMe$_3$)$_3$] (1): A solution of Me_3SiCl (0.466 g, 4.29 mmol) in toluene (20 mL) was added dropwise to a stirred solution of cuprate **1** [2.21 g, 2.14 mmol (dimer)] in the same solvent (15 mL) at −20 °C. The solution was slowly warmed to room temperature and stirred for 0.5 h. Then all volatiles were removed at 25 °C/10^{-2} Torr. After addition of 25 mL of *n*-pentane to the residue, the resulting suspension was filtered through a glass filter. The solution was concentrated in dynamic vacuum to approximately 5 mL and cooled to −30 °C for 24 h. Hypersilylcopper was obtained as colorless crystal plates or needles in about 80% yield. The yield may be improved by another 5−10% by subsequent cooling of the mother liquor to −60 °C for several days. The identity and purity of the product were verified by comparison with published NMR spectroscopic data.

X-ray Crystallographic Study: Diffraction data for compounds **1**−**5** were collected on a Siemens P4 four-circle diffractometer using monochromated Mo-K_α radiation (λ = 0.71073 Å) at 173 K. Crystals were covered with nujol, placed on the tip of a glass fiber and mounted on the diffractometer under a stream of cold nitrogen gas. The cell dimensions were determined from the positions of 35−52 selected reflections ($20 < 2\theta < 25°$). The structures were solved by direct methods and refined against all F^2 using the SHELXTL-PC 5.03 program package on a local PC. Anisotropic thermal parameters were included for all non-hydrogen atoms. Hydrogen atoms were placed at ideal positions using appropriate HFIX procedures and refined with riding models. The isotropic displacement parameters were constrained to 1.5 (aliphatic) or 1.2 (aromatic) times the U_{eq} of the connected carbon atom. Further details can be found in Table 1.

CCDC-213800 (**1**), -213801 (**2**), -213802 (**3**), -213803 (**4**), and -213804 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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