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2-bromooctane (**16**),[12] and 3β-OMs-5α-cholestane (**17**)[13] are prepared as described.

Preparation of $P^+[F^-, 1.5HF]$ (1d). Wet commercial resin in the chloride form Amberlyst A 26 or Amberlite IRA 900 (50 g, ca. 0.1 molar equiv), packed in a polyethylene column, were washed with an aqueous solution of 2 M NaOH until elimination of chloride ions ($AgNO_3$ test) and then with water until neutrality, and 220 mL of a 1 M HF aqueous solution were passed through the column. The resin was washed with acetone (50 mL) followed by diethyl ether (50 mL) and then poured into 400 mL of benzene, and a further dehydration was achieved by distilling the azeotrope water–benzene. The resin was filtered and dried in the air. Titration by sodium hydroxide gave the acidity of the resin, approximately 6 mequiv g^{-1} as H^+, which corresponds to the formula $P^+[F^-, 1.5\ HF]$.

Preparation of the Fluoride P^+F^- (1a). The wet form $P^+[F^-, 1.5HF]$ (**1d**) obtained as above after the reaction of 1 M HF was washed with water until neutrality. Then the resin was washed with acetone (50 mL) followed by diethyl ether (50 mL), and an additional dehydration performed by distilling the azeotrope water–benzene in the same conditions as with **1d** leads to the dried form P^+F^- (**1a**).

Preparation of the Hydrogen Difluoride $P^+HF_2^-$ (1b). Dried $P^+H_2F_3^-$ (**1c**) (see ref 3b) (5.2 g, ca. 0.02 molar equiv) was stirred in 8 mL of 0.2 M NaOH (0.017 mol) at room temperature for 20 min. Then the resin was filtered and washed with acetone (10 mL) followed by diethyl ether (10 mL), and an additional dehydration was achieved by distilling the azeotrope water–benzene from 80 mL of benzene. The resin was filtered and dried in the air, and the titration with NaOH gave an average acidity of 3.8–4.6 mequiv g^{-1} (H^+), which corresponds respectively to $P^+[F^-, 0.9HF]$ and $P^+[F^-, 1.1HF]$.

The same procedure can be used from dried **1d** with convenient amounts of sodium hydroxide.

General Procedure for the Reactions of the Reagents 1a–c with the Bromo Ketones 2–4. To 0.01 mol of bromo ketone **2–4** dissolved in CCl_4 (30 mL) was added the reagent **1a** (10 g, ~0.04 mol F^-), or **1b** (5 g, ~0.02 mol HF_2^-), or **1c** (5.5 g, ~0.02 mol $H_2F_3^-$). The reaction mixture, contained in a 50-mL round-bottomed flask equipped with a reflux condenser and a $CaCl_2$ tube, was heated under stirring (for the temperature and the reaction times, see Table I). After cooling to room temperature, the resin was filtered off and washed with dry diethyl ether (50 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated; then the crude reaction mixture was analyzed by ^1H and ^{19}F NMR. The obtained products were identified unambiguously by comparison with data from literature and if necessary by high-resolution mass spectrometry.

2-Fluoro-1-phenylethanone (5). ^1H NMR: CH_2F 5.53 (d, $^2J_{HF} = 47$) [lit.[2e] 5.4, $^2J_{HF} = 48$]. ^{19}F NMR: −230.3 (t, $^2J_{HF} = 47$) [lit.[14] −231.9, $^2J_{HF} = 47$].

2-Hydroxy-1-phenylethanone (6). ^1H NMR: CH_2 4.83 (s), OH 3.4 (s) [lit.[15] CH_2 4.85 (s), OH 3.1 (s)].

2-Chloro-1-phenylethanone (7). ^1H NMR: CH_2 4.72 (s) [lit.[16] 4.75 (s)].

2-Fluoro-1-phenylpropanone (8). ^1H NMR: 1.58 (dd, 3 H), 5.6 (dq, 1 H), $^2J_{HF} = 48.7$, $^3J_{HF} = 24$, $^3J_{HH} = 6.8$ [lit.[17] 1.61 (dd, 3 H), 5.48 (dq, 1 H), $^2J_{HF} = 48.7$, $^3J_{HF} = 23.5$, $^3J_{HH} = 6.7$]. ^{19}F NMR: −180.5 (sext), $^2J_{HF} = 48.2$, $^3J_{HF} = 24.1$.

2-Hydroxy-1-phenyl-1-propanone (9). ^1H NMR: CH_3 1.35 (d, $J = 7$), OH 4.9 (s) [lit.[15] CH_3 1.35 (d), CH 4.97 (q, $J = 7$), OH 4.95 (s)]. Note: the CH signal, centered at ca. $\delta = 5$, is not well resolved as it is mixed with one of the two quadruplets provided by the CHF group in **8** and with the OH signal.

2-Chloro-1-phenyl-1-propanone (10). ^1H NMR: CH_3 1.68 (d, $J = 7$) [lit.[18] 1.65].

2-Fluoro-2-methyl-1-phenyl-1-propanone (11). ^1H NMR: CH_3 1.68 (d, 6 H), $^3J_{HF} = 21.8$. ^{19}F NMR: −142.1 (hept), $^3J_{HF} = 21.6$ [lit.[19] −144, $^3J_{HF} = 22$].

2-Methyl-1-phenyl-2-propen-1-one (12). ^1H NMR: 2.07 (dd, 3 H, $J \sim 1.3$), 5.63 (m, 1 H), 5.92 (m, 1 H, $J \sim 1.3$). HRMS: m/e (M^+) calcd for $C_{10}H_{10}O$: 146.073, found 146.075.

2-Hydroxy-2-methyl-1-phenyl-1-propanone (13). ^1H NMR: 1.53 (s, 6 H), 3.75 (s, 1 H) [lit.[19] 1.5 (s, 6 H), 3.85 (s, 1 H)].

2-Chloro-2-methyl-1-phenyl-1-propanone (14). ^1H NMR: CH_3 1.9 (s) [lit.[20] 1.9 (s)].

General Procedure for the Reactions of the Reagents 1a–c with the Compounds 15–17. **1a** (10 g, ~0.04 mol F^-), **1b** (5 g, ~0.02 mol HF_2^-), or **1c** (5.5 g, ~0.02 mol $H_2F_3^-$) was added into a 50-mL round-bottomed flask equipped with a reflux condenser and a $CaCl_2$ tube to 0.01 mol of compound **15–17** dissolved in 30 mL of solvent (CCl_4 or *n*-dodecane for compounds **15** and **16**, *n*-octane for compound **17**, see below), and the reaction mixture was heated under stirring (for the temperature and the reaction times, see Table II). The analyses of the reaction products were carried out as follows.

The reactions with compounds **15** and **16** were followed by ^1H NMR when CCl_4 was used, that which allows to determine the overall yield of transformation and to estimate the relative yields of 2-fluorooctane (**18**) and octenes. *n*-Dodecane as a solvent was used for an accurate analysis of the obtained products by GLC (oven temperature 70 °C).

The reaction of compound **17** in *n*-octane was followed by ^1H NMR. The usual workup after the reaction gave a crude reaction mixture of 3α-fluoro-5α-cholestane (**19**) and 2-cholestene (**20**) which was analyzed by ^1H and ^{19}F NMR.

2-Fluorooctane (18). ^1H NMR: CHF 4.55 (dm, 1 H, $^2J_{HF} = 48$) [lit.[2e] 4.57, $^2J_{HF} = 49$]. ^{19}F NMR: −170.8, $^2J_{HF} = 49$ [lit.[2m] −172.5, $^2J_{HF} = 46$].

3α-Fluoro-5α-cholestane (19). ^1H NMR: CHF 4.8 (dm, 1 H, $^2J_{HF} = 48$). ^{19}F NMR: −179.4 (dm, $^2J_{HF} = 47$) [lit.[2f] ^1H 4.8; ^{19}F −181; $^2J_{HF} = 47.9$]. The epimer 3β-fluoro-5α-cholestane was detected in the ^{19}F spectrum as a very small doublet with $\delta = -166$ [lit.[2f] −167.6].

2-Cholestene (20). ^1H NMR: CH═CH 5.6 (m) [lit.[21] 5.6 (m)].

Acknowledgment. We are indebted to Professor A. Gorgues for valuable discussions during this work.

Registry No. **2**, 70-11-1; **3**, 2114-00-3; **4**, 10409-54-8; **5**, 450-95-3; **6**, 582-24-1; **7**, 532-27-4; **8**, 21120-36-5; **9**, 5650-40-8; **10**, 6084-17-9; **11**, 71057-10-8; **12**, 769-60-8; **13**, 7473-98-5; **14**, 7473-99-6; **15**, 924-80-1; **16**, 557-35-7; **17**, 3381-51-9; **18**, 407-95-4; **19**, 3856-83-5; [F, 1.5HF], 100830-75-9; F^-, 16984-48-8; HF_2^-, 18130-74-0; $H_2F_3^-$, 12260-12-7; amberlyst A 261, 39339-85-0; amerlite IRA 900, 9050-97-9; 2-octene, 111-67-1; 1-octene, 111-66-0.

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Chemistry and Composition of (Trialkylsilyl)cuprates Derived from Cuprous Halides

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Since the discovery of R_2CuLi by Gilman[1] in 1952, most organocuprate chemistry has favored alkyl-based reagents which are known to exist as both lower order[2] and higher

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0022-3263/89/1954-5383$01.50/0

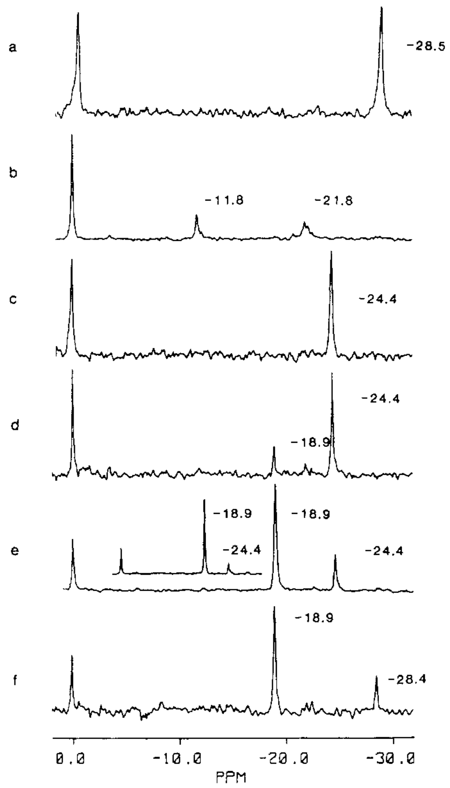

Figure 1. ^{29}Si NMR spectra in THF of (a) $PhMe_2SiLi$, (b) $PhMe_2SiLi$:CuBr, 1:1, (c) $PhMe_2SiLi$:CuBr, 1.5:1, (d) $PhMe_2SiLi$:CuBr, 2:1, (e) $PhMe_2SiLi$:CuBr, 3:1 (inset 1e), $PhMe_2SiLi$:CuCN, 3:1 (f) $PhMe_2SiLi$:CuBr, 4:1, the spectra were run at −50 °C.

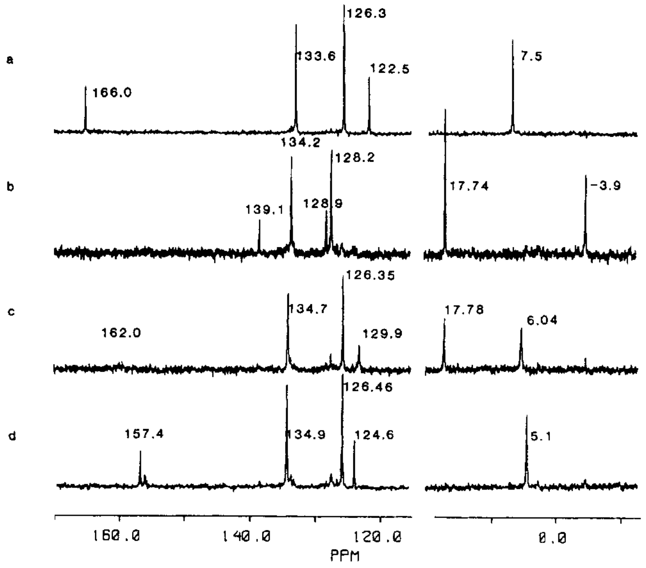

Figure 2. ^{13}C NMR spectra in THF at 0 °C of (a) $PhMe_2SiLi$, (b) $PhMe_2SiLi$:CuBr·Me_2S, 1:1, (c) $PhMe_2SiLi$:CuBr·Me_2S, 2:1, (d) $PhMe_2SiLi$:CuCN, 2:1.

order[3] species. Recently, silylcuprates $[(R_3Si)_nCuLi_{n-1}\cdot LiX]$[4] and stannylcuprates $[(R_3Sn)_nCuLi_{n-1}\cdot LiX]$[5] have joined the alkylcuprates at the forefront of synthetic methodology. The propensity of these mixed metallocuprates to participate in an impressive number of synthetic elaborations accounts for their increasing popularity among organic chemists.[6] And yet, the structures of $[(R_3Si)_nCuLi_{n-1}\cdot LiX]$ and $[(R_3Sn)_nCuLi_{n-1}\cdot LiX]$ proposed to date have been based solely on the stoichiometries of the solutions generated from mixtures of their precursors.

In the course of our study on the nature[7] and synthetic potential of higher order metallocuprates, $(R_3Si)_2Cu(CN)Li_2$, it has been demonstrated, not unexpectedly, that in their preparation the Cu–CN moiety remained intact as shown by infrared spectroscopy. This lack of simple metal–metal exchange (i.e., $R_3SiLi + CuCN \not\rightarrow R_3SiCu + LiCN$) can be attributed to the likelihood of dπ backbonding between the copper and nitrile ligand.[8] More remarkable was the observation that the addition of 3 equiv of R_3SiLi, **1** (R = $PhMe_2$), to CuCN resulted in the unprecedented formation of $(PhMe_2Si)_3CuLi_2$,[7] **2**, rather than $(PhMe_2Si)_2Cu(CN)Li_2$, **3**, and free $PhMe_2SiLi$ as was found in the case of alkylcuprates derived from CuCN.[9] This unusual stability was also attributed to significant π bonding between silicon and copper in these species.[7]

Whether such an equilibrium exists in the case of copper halide derived silylcuprates, however, remained to be elucidated. In this paper we present ^{29}Si,[10] ^{13}C,[11] and ^{7}Li,[12] NMR spectroscopic investigations of the composition of silylcuprates derived from (dimethylphenylsilyl)lithium (**1**) and CuX (where X = Br or I). We also discuss the effect of the halide salts on the nature of these cuprates.

Results and Discussion

Reaction of $PhMe_2SiCl$ with lithium metal in THF gave a LiCl-containing solution of **1**.[13] Preparations were conducted at −5 °C in THF and **1** gave a ^{29}Si signal at −28.5 ppm (Figure 1a). Solutions of silylcuprates[4] were generated by addition of THF solutions of **1** to CuBr·Me_2S at −50 °C. The combination of equimolar amounts of **1** and CuBr·Me_2S yielded a suspension in which most of the ^{29}Si signal was lost (Figure 1b). The resulting ^{29}Si spectrum contained several signals in the −10 to −25 ppm region which were attributed to polymeric "$PhMe_2SiCu$" (**5**). In agreement with the observations made using ^{29}Si NMR, most ^{13}C signal was also lost in solutions containing equimolar amounts of **1** (Figure 2a) and CuBr·Me_2S. The signals that were visible were due to $(PhMe_2Si)_2$ (Figure 2b).

The combination of **1** and CuBr·Me_2S in a 1.5:1 molar ratio gave a nearly homogeneous solution exhibiting a ^{29}Si

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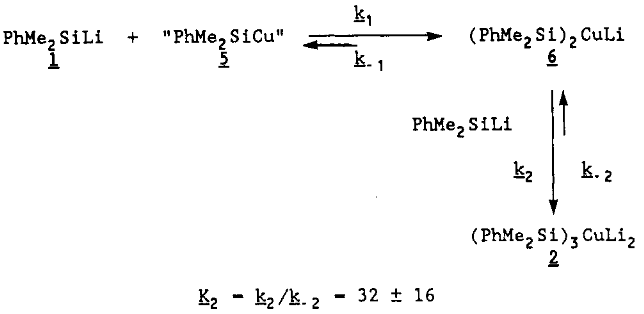
(12) ^{7}Li has natural abundance of 92.58%, NMR receptivity compared to ^{13}C of 1540, and a gyromagnetic ratio of 10.396.

(13) George, M. V.; Paterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1960**, *82*, 403.

Scheme I



signal at −24.4 ppm attributed to $(\mathrm{PhMe_2Si})_2\mathrm{CuLi}$, **6** (Figure 1c). The assignment of this signal to **6** was facilitated by the observation that at a 2:1 ratio of **1** to $\mathrm{CuBr{\cdot}Me_2S}$ the signal at −24.4 ppm remained intense while a minor signal at −18.9 ppm appeared (Figure 1d). A signal at −24.4 ppm has previously been observed for $(\mathrm{PhMe_2Si})_2\mathrm{Cu(CN)Li_2}$ (**3**) produced by the reaction of 2 equiv of **1** and CuCN.[7] That $(\mathrm{PhMe_2Si})_2\mathrm{CuLi}$ (**6**) and $(\mathrm{PhMe_2Si})_2\mathrm{Cu(CN)Li_2}$ (**3**) are different species is confirmed by ^{13}C NMR spectral analysis (compare Figure 2c with Figure 2d). The ^{13}C NMR spectrum of **6** consists of four resonances in the phenyl region (δ 162.0, ipso; 134.7, ortho; 126.3, meta; 123.9, para), one due to DMS (17.8 ppm), and a methyl signal at 6.04 ppm (Figure 2c) whereas **3** exhibited resonances at 157.4 ppm, ipso; 134.9 ppm, ortho; 126.5 ppm, meta; 124.6 ppm, para; a nitrile carbon at 156.7 ppm; and a methyl signal at 5.1 ppm (Figure 2d). As previously reported, evidence for the formulation of **3** came from the infrared analysis of this solution which shows a bound nitrile ($\nu_{\mathrm{CN}} = 2123$ cm^{-1}) but no free LiCN.[7] The coincidence of the ^{29}Si chemical shifts of **3** and **6** is attributed to the narrow chemical shift window of this nucleus and suggests a similar electronic environment for silicon in **3** and **6**.

Solutions containing **1** and $\mathrm{CuBr{\cdot}Me_2S}$ in a 3:1 ratio exhibited a significant signal at −18.9 ppm as well as a small signal assigned to **6** (−24.4 ppm, Figure 1e). An attractive formulation for the species exhibiting a ^{29}Si signal at −18.9 ppm is $(\mathrm{PhMe_2Si})_3\mathrm{CuLi_2}$ (**2**).[7,14] The chemical shift of this species is identical with that previously observed for $(\mathrm{PhMe_2Si})_3\mathrm{CuLi_2}$[7] (prepared from 3 equiv of **1** and CuCN, Figure 1e inset). Secondly, the ^{13}C NMR spectra at −70 °C of the two solutions exhibited identical chemical shifts for silyl-bound methyl and phenyl signals (δ 163.3, ipso; 133.5, ortho; 125.0, meta; 121.8, para; and a methyl signal at 6.7 ppm).

That the conversions of **5** to **6** and **6** to **2** are reversible were shown by addition of $\mathrm{CuBr{\cdot}Me_2S}$ to **2** whose ^{29}Si NMR spectrum is shown in Figure 1e. Addition of 0.5 equiv resulted in the regeneration of $(\mathrm{PhMe_2Si})_2\mathrm{CuLi}$ (**6**). Further introduction of 1 equivalent $\mathrm{CuBr{\cdot}Me_2S}$ to **6** resulted in the regeneration of "$\mathrm{PhMe_2SiCu}$" (**5**).

While no $\mathrm{PhMe_2SiLi}$ (**1**) was detectable in solutions containing **1** and $\mathrm{CuBr{\cdot}Me_2S}$ in a 3:1 ratio, a substantial amount of **1** appeared in the spectrum of solutions where this ratio was 4:1 (Figure 1f).

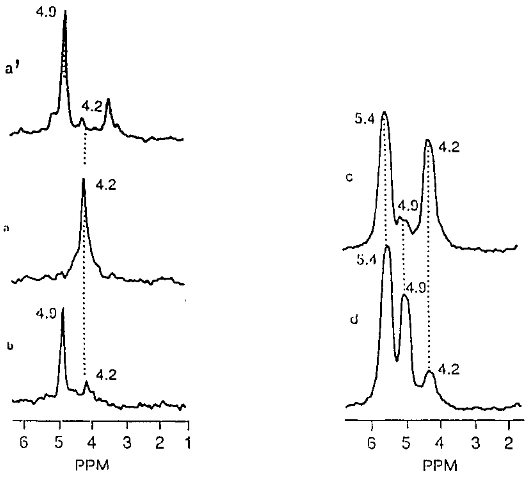


Figure 3. ^{13}C NMR spectra in DMS at −85 °C of (a) $\mathrm{PhMe_2SiLi{:}CuBr{\cdot}Me_2S}$, 2:1, (a′) $\mathrm{PhMe_2SiLi{:}CuBr{\cdot}Me_2S}$, 2:1, in THF, (b) $\mathrm{PhMe_2SiLi{:}CuI}$, 2:1, (c) $\mathrm{PhMe_2SiLi{:}CuBr{\cdot}Me_2S}$, 3:1, (d) $\mathrm{PhMe_2SiLi{:}CuI}$, 3:1.

This interpretation was reinforced by a positive Gilman test[15] for **1** in THF and a negative test for all solutions of **1** containing $\mathrm{CuBr{\cdot}Me_2S}$, including those where these reagents were present in a 3:1 ratio. A slight green coloration was observed for solutions composed of 4:1 $\mathrm{1{:}CuBr{\cdot}Me_2S}$, indicating small quantities of $\mathrm{PhMe_2SiLi}$.

The relative intensities of the ^{29}Si signals, attributed to contributing species in solutions whose spectra are shown in Figure 1, suggest the equilibrium between $\mathrm{PhMe_2SiLi}$ (**1**), "$\mathrm{PhMe_2SiCu}$" (**5**), and $(\mathrm{PhMe_2Si})_2\mathrm{CuLi}$ (**6**) lies significantly on the side of **6** (i.e., $k_1 \gg k_{-1}$, Scheme I). In solutions comprised of 3:1 $\mathrm{PhMe_2SiLi{:}CuBr{\cdot}Me_2S}$, $(\mathrm{PhMe_2Si})_3\mathrm{CuLi_2}$ (**2**) predominates over $(\mathrm{PhMe_2Si})_2\mathrm{CuLi}$ by ~4:1 (Scheme I). The values of K_2[16] and the errors[17] reported were calculated by averaging three determinations.

The ease with which we were able to differentiate between the higher order silylcuprates derived from CuCN and the lower order reagents prepared from $\mathrm{CuBr{\cdot}Me_2S}$ by ^{13}C NMR encouraged us to undertake a study of the complexation of LiX with these reagents. Specifically, we constructed solutions containing $(\mathrm{PhMe_2Si})_2\mathrm{CuLi}$ using $\mathrm{CuBr{\cdot}Me_2S}$ or CuI in DMS or THF. The ^{13}C NMR spectra were recorded in the region between 0 and 10.0 ppm with the goal of observing the resonances due to the silicon methyl carbons.

At −85 °C in DMS, the ^{13}C NMR spectrum (Figure 3a) of $(\mathrm{PhMe_2Si})_2\mathrm{CuLi}$, prepared from $\mathrm{CuBr{\cdot}Me_2S}$ and 2 equiv of $\mathrm{PhMe_2SiLi}$, **1** (prepared from $(\mathrm{PhMe_2Si})_2$ and Li metal),[13] consisted (in the 0–10 ppm region) of a singlet at 4.2

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[14] The combination of PhLi and $\mathrm{Ph_2CuLi}$, in dimethyl sulfide, gave a higher order cuprate, $\mathrm{Ph_3CuLi_2}$.[14a,b] (a) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668. (b) Bertz, S. H.; Dabbagh, G. *Tetrahedron, symposia-in-print on organocopper chemistry* **1989**, *45*, 425. (c) Similarly, on the basis of ^{1}H NMR analysis, Ashby[14d,e] proposed that in solutions containing a 2:1 ratio of MeLi and MeCu an equilibrium existed between the higher order species $\mathrm{Me_3CuLi_2}$, the lower order species, $\mathrm{Me_2CuLi}$, and free MeLi. (d) Ashby, E. J.; Watkins, J. J. *J. Chem. Soc., Chem. Commun.* **1976**, 784. (e) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312.

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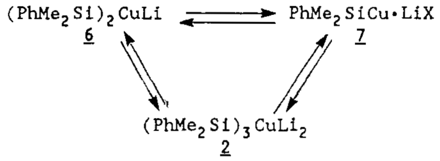
[16] K_2 was estimated using the expression:

$$K_2 = \frac{[(\mathrm{PhMe_2Si})_3\mathrm{CuLi_2}]}{[(\mathrm{PhMe_2Si})_2\mathrm{CuLi}]\,[\mathrm{PhMe_2SiLi}]} = 32 \pm 16 \qquad (1)$$

The concentrations of silicon-containing species were calculated using the integral ratio for **1**, **2**, and **6** and the initial concentration of **1** corrected for the number of $\mathrm{PhMe_2Si}$ groups in each species. The concentration of LiBr was calculated from the initial concentration of CuBr and the concentration of **6** calculated from the ^{29}Si spectrum.

[17] Some uncertainty in the measurement of equilibria from ^{29}Si signal intensities could arise from the differential T_1's of the equilibrating species. It can be estimated from the observation of coalesced ^{7}Li (116.6 MHz, $\Delta\delta = 0.1$ ppm and ^{1}H (300 MHz, $\Delta\delta = 0.1$ ppm) but not the ^{29}Si (79.495 MHz) spectra that the silicon species are equilibrating with a rate constant between 30 and 79 Hz which is ~10 times faster than the acquisition time (0.2 s) for ^{29}Si NMR experiments; therefore, the effective T_1's of the equilibrating species would be equivalent under these conditions.

Scheme II



ppm. This was attributed to halide-free $(PhMe_2Si)_2CuLi$ (**6**) due to the precipitation of LiBr from DMS. Substitution of CuI for $CuBr\cdot Me_2S$ exhibited two signals: one major (δ 4.9) and a minor one at 4.2 ppm due to different methyl groups (Figure 3b). These were assigned to $(PhMe_2Si)_2CuLi\cdot LiI$, **7**, and $(PhMe_2Si)_2CuLi$, **6**, respectively, since the resonance of the methyl in the ^{13}C NMR spectrum of the latter was at the same position (δ 4.2) as the methyl resonance of $(PhMe_2Si)_2CuLi$ derived from CuBr.

The ^7Li NMR spectra of $(PhMe_2Si)_2CuLi$ prepared from CuI and CuBr were in harmony with the ^{13}C NMR results. At −70 °C in DMS, the ^7Li spectrum of the reagent prepared from $PhMe_2SiLi$ and $CuBr\cdot Me_2S$ (minus LiBr) showed a single resonance at 0.43 ppm, which is assigned to the halide-free species, **6**. Under the same conditions the ^7Li NMR spectrum of CuI-derived $(PhMe_2Si)_2CuLi$ consisted of two signals, the major one at δ 0.77 was assigned to the LiI-complexed copper cluster (**7**), while the minor one (δ 0.58) was attributed to the halide-free complex (**6**).

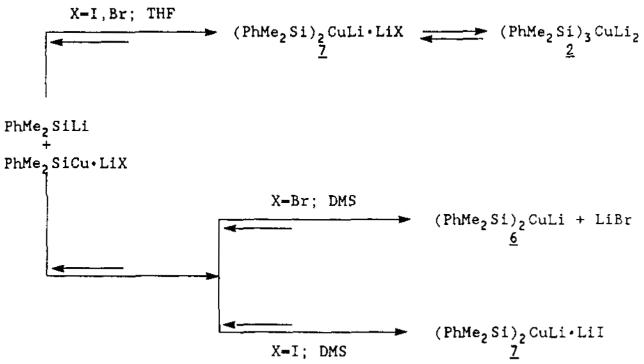
The ^{13}C NMR spectrum of $(PhMe_2Si)_3CuLi_2$, prepared by the addition of LiCl-free **1** to LiBr-free $(PhMe_2Si)_2CuLi$ (**6**), exhibited signals corresponding to LiBr-free lower order cuprate, $(PhMe_2Si)_2CuLi$, **6** (δ 4.2), and the LiBr-free higher order species **2** (δ 5.4, Figure 3c). Similarly, $(PhMe_2Si)_3CuLi_3$ (**2**) prepared from CuI exhibited two major high-field methyl resonances at δ 4.9 and 5.4 ppm which were attributed to $(PhMe_2Si)_2CuLi\cdot LiI$ (**7**) and $(PhMe_2Si)_3CuLi_2$ (**2**), respectively, along with a minor peak at δ 4.2 ppm which was earlier assigned to $(PhMe_2Si)_2CuLi$ (**6**) (Figure 3d).

In agreement with the above results, the ^7Li NMR spectrum of $CuBr\cdot Me_2S$ derived $(PhMe_2Si)_3CuLi_2$ in DMS exhibited signals at 0.55 and 0.21 ppm attributable to **6** and **2**, respectively, while $(PhMe_2Si)_3CuLi_2$ prepared from CuI consisted of a broad multiplet spanning the region assigned to LiI-containing lower order species (0.76 ppm) and halide-free $(PhMe_2Si)_3CuLi_2$ (**2**, ~0.29 ppm). The presence of broad signals in these spectra indicate that rate of exchange between the various lithium-containing species is near the NMR time scale, an observation with literature precedent.[18,19]

In DMS **7** and **6** are in dynamic equilibria with **2** as represented in Scheme II. Reversible interconversion between $(PhMe_2Si)_2CuLi$ and $(PhMe_2Si)_2CuLi\cdot LiX$ was established by observation that the silyl methyl signals in these species coalesce to a single peak as the temperature is increased from −85 °C to 0 °C, and upon cooling to −85 °C, the same two-signal pattern reappears.

That LiBr is also associated with (trialkylsilyl)cuprates in THF was evident from ^{13}C NMR spectroscopy of $(PhMe_2Si)_2CuLi$ (prepared from 2 equiv of LiCl-free $PhMe_2SiLi$[13] and $CuBr\cdot Me_2S$ at −85 °C). The ^{13}C NMR spectrum of this solution (Figure 3a′) showed two methyl signals, the major one at 4.9 ppm and a minor at 4.2 ppm which are very close to analogous methyl resonances assigned to $(PhMe_2Si)_2CuLi\cdot LiI$ (**7**) and $(PhMe_2Si)_2CuLi$ (**6**), respectively, in DMS (Figure 3b).

Scheme III



It appears that the lower order silylcuprate $(PhMe_2Si)_2CuLi$ is a more complex species than its straightforward preparation indicates. In DMS, when it is prepared with CuI, this reagent consists mostly of the LiI-associated copper species, $(PhMe_2Si)_2CuLi\cdot LiI$ (**7**), but when it is derived from $CuBr\cdot Me_2S$, it is free of LiBr. In THF, when $CuBr\cdot Me_2S$ is used in the preparation of this reagent exists primarily as LiX-associated copper species **7** and should be represented as $(PhMe_2Si)_2CuLi\cdot LiX$ (Scheme III). One would expect the degree of association of LiX with lower order silylcuprates to vary with the nature of the silyl substitution. We suspect the trends discovered in this study wherein LiX association is high in solvents such as THF in which the LiX salts are soluble to be general.

The proposed formation of $(PhMe_2Si)_2CuLi\cdot LiX$ in THF provides an explanation for the observation that **6** exhibited a ^{29}Si NMR chemical shift (Figure 1d) similar to that assigned to $(PhMe_2Si)_2Cu(CN)Li_2$, **3**. Thus, if the former existed primarily complexed with LiBr, the only structural difference between **3** and **6** is the substitution of a CN by a Br.

Treatment of cyclohex-2-en-1-one, **8**, with **1** at −45 °C yielded 62% of 1,2-addition product, 1-(dimethylphenylsilyl)cyclohex-2-en-1-ol, whereas reaction of this substrate with **6**, **3**, **2** or solutions of **1** and $CuBr\cdot Me_2S$ in ratios between >3:1 and 10:1 gave exclusive 1,4-addition product, 3-(dimethylphenylsilyl)cyclohexanone. These results show that silylcuprates **2**, **3**, and **6** behave in a fashion analogous to alkylcuprates in delivery of their anionic ligands in a 1,4-fashion even when copper is present only in catalytic concentrations.[20] Thus 1,4-addition of silylanions bound to copper must be faster than 1,2-addition of the unbound species. These observations also suggest that under catalytic conditions, $PhMe_2SiLi$ serves to rapidly convert lower order cuprate formed as a result of silyl transfer back to a higher order cuprate.

Summary

Comparison of the present silylcuprate system with that of the methylcuprate[18] system reveals several differences. When the ratio of RLi (R = $PhMe_2Si$ or Me) to CuX (X = I or Br) is 2:1, a new species, $(PhMe_2Si)_2CuLi\cdot LiX$, is

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formed in the case of silylcuprates, whereas, in the case of alkylcuprates, solutions prepared from 2 equiv of MeLi and CuX are composed of an equilibrium mixture of MeLi plus Me_3Cu_2Li and Me_2CuLi. In the case of lower order, Me_2CuLi, association of alkyl residues with copper beyond this stoichiometry does not occur, and further addition of MeLi beyond this point gives solutions containing free MeLi.[18]

In the case of lower order, $(PhMe_2Si)_2CuLi{\cdot}LiX$, addition of further silyllithium gives solutions which contain negligible free silyl anion and whose ^{29}Si NMR spectra support the association of three silyl residues with the copper. In THF the novel species, $(PhMe_2Si)_3CuLi_2$ is formed regardless of which copper(I) salt is employed.[7]

In DMS, analogous to phenylcuprates,[14a] $(PhMe_2Si)_2CuLi$ (derived from CuI) exists as an equilibrium mixture of halide-containing $(PhMe_2Si)_2CuLi{\cdot}LiI$ (**7**), and halide-free, $(PhMe_2Si)_2CuLi$ (**6**), species whereas CuBr-derived lower order silylcuprates are primarily devoid of LiBr because of the insolubility of this salt in this solvent.

Experimental Section

The ^{29}Si, ^{13}C, and ^{7}Li NMR parameters as well as general experimental procedures were reported earlier.[7] A vacuum jacketed, glass dewar measuring 7.5 × 16.0 cm (i.d. 5.5 cm) was designed with tapering a bottom to fit in the cup of a vortex mixer and was used to mix samples at subambient temperatures. $CuBr{\cdot}Me_2S$ was recrystallized by the procedure of House.[21]

Preparation of $PhMe_2SiLi$/THF, 1. (Dimethylphenylsilyl)lithium was prepared as previously described[7] and titrated according to the procedure of Fleming et al.[4]

Preparation of $PhMe_2SiCu$, 5. $CuBr{\cdot}Me_2S$ (0.41 g, 2.0 mmol) was placed in a 10-mm NMR tube, equipped with an argon inlet. The tube was repeatedly (3×) evacuated (vacuum pump) and purged with argon. Me_4Si (0.5 mL) was injected, the tube was cooled to −50 °C, and (dimethylphenysilyl)lithium in THF (1.8 mL, 2.0 mmol) was added dropwise. The solution was vortexed at −50 °C (vide supra) before recording the spectrum.

Preparation of $(PhMe_2Si)_2CuLi$, 6. A THF solution of $PhMe_2SiLi$ (1.8 mL, 2.0 mmol) was added to a 10-mm NMR tube containing a THF solution of "$PhMe_2SiCu$" (vide supra) at −50 °C. The deep red solution was stirred for 20 min at −50 °C prior to examination by NMR.

Preparation of $(PhMe_2Si)_3CuLi_2$, 2. To a THF solution of $(PhMe_2Si)_2CuLi$ (2.0 mmol) prepared as outlined above was added a THF solution of $PhMe_2SiLi$ (1.8 mL, 2.0 mmol) at −50 °C. The reaction mixture was stirred for 20 min before examination by NMR.

Preparation of $(PhMe_2Si)_3CuLi_2$, 2, from CuCN. The preparation of this solution is described elsewhere.[7]

Regeneration of $(PhMe_2Si)_2CuLi$. $CuBr{\cdot}Me_2S$ (0.205 g, 1.0 mmol) was added to the solution generated by mixing $PhMe_2SiLi$ and $CuBr{\cdot}Me_2S$ in a 3:1 ratio. The reaction mixture was stirred for 20 min before examination by NMR. This mixture gave the same NMR signals as **6**.

Regeneration of $PhMe_2SiCu$. $CuBr{\cdot}Me_2S$ (0.41 g, 2.0 mmol) was added to the NMR tube containing lower order silylcuprate, **6**. The reaction mixture was stirred for 20 min at −50 °C and then examined by NMR.

Preparation of $(PhMe_2Si)_2CuLi$ for ^{13}C NMR Analysis. $CuBr{\cdot}Me_2S$ (0.154 g 0.75 mmol) was added to a 5-mm NMR tube, equipped with an argon inlet. The reaction was cooled to −78 °C, and (dimethylphenylsilyl)lithium in THF (1.7 mL, 1.50 mmol) was added dropwise. The solution was stirred on a vortex mixer (vide supra). The spectra were recorded immediately at 0 °C.

Preparation of $(PhMe_2Si)_2Cu(CN)Li_2$ for ^{13}C NMR Analysis. This solution was prepared as described earlier.[7]

Preparation of $PhMe_2SiLi$ in DMS, 1. Tetramethyldiphenyldisilane (3.6 g, 21 mmol) was stirred with small pieces of lithium (0.450 g, 64.0 mmol) in THF (20 mL) at −5 °C in an ice/salt bath. The reaction was initiated by immersion of the reaction flask in a sonicator for 30 min, and then the mixture was stirred overnight at −5 °C. THF was removed under vacuum and replaced with equal volume of DMS. This procedure was repeated three times. (Dimethylphenylsilyl)lithium was titrated according to the procedure of Fleming et al.[4]

Preparation of $(PhMe_2Si)_2CuLi$ from $CuBr{\cdot}Me_2S$ in DMS for ^{13}C and ^{7}Li NMR Analyses. $CuBr{\cdot}Me_2S$ (0.154 g 0.75 mmol) was added to a 5-mm NMR tube, equipped with an argon inlet. The reaction was cooled to −78 °C, and (dimethylphenylsilyl)lithium in DMS (1.7 mL, 1.50 mmol) was added dropwise. The solution was stirred on a vortex mixer (vide supra). The spectra were recorded at −85 °C immediately.

Preparation of $(PhMe_2Si)_2CuLi$ from CuI in DMS for ^{13}C and ^{7}Li NMR Analyses. $(PhMe_2Si)_2CuLi$ was prepared as above except for the substitution of CuI (0.143 g 0.75 mmol) for $CuBr{\cdot}Me_2S$.

Preparation of 1-(Dimethylphenylsilyl)cyclohex-2-en-1-ol. This reaction was conducted as reported previously.[7]

Typical Procedure for Reactions of Silylcuprates with 8. $PhMe_2SiLi$ (1.25 mL, 1.0 mmol) was added dropwise at −45 °C to $CuBr{\cdot}Me_2S$ (0.10 g, 0.5 mmol) in THF (2 mL) under argon. The resulting deep red solution was stirred for 0.5 h after which **8** (0.04 mL, 0.41 mmol) was added via a syringe. All reactions were stirred for a further 0.5 h and then quenched with saturated NH_4Cl/10% NH_4OH. Standard workup and the spectral data are already reported.[7,22]

Gilman Tests. Cuprates used in the ^{29}Si NMR studies were subjected to Gilman tests as described previously.[7,15]

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Registry No. 1, 3839-31-4; 2, 122343-28-6; 3, 110769-32-9; 5, 122470-45-5; 6, 75583-57-2; 7, 122470-46-6; 8, 822-67-3; $CuBr{\cdot}Me_2S$, 54678-23-8; CuCN, 544-92-3; CuI, 7681-65-4; tetramethyldiphenyldisilane, 1145-98-8; 1-(dimethylphenylsilyl)cyclohex-2-en-1-ol, 104066-67-3.

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Ultrasound in Oxochromium(VI)-Amine-Mediated Oxidations-Modifications of the Corey-Suggs Oxidation for the Facile Conversion of Alcohols to Carbonyl Compounds[†]

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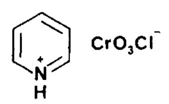
The use of oxochromium(VI)-amine reagents in oxidative transformations is of fundamental importance in organic synthesis. These reagents have been engaged for the general oxidation of alcohols to carbonyl compounds, the selective oxidation of allylic and benzylic alcohols, the oxidation of organometallics, oxidative transpositions, oxidative cleavages, allylic and benzylic oxidations, and oxidative cyclizations.[2] Pyridinium chlorochromate (PCC, 1), commonly known as the Corey-Suggs reagent,[3] leads



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[†] Dedicated to the memory of Dr. Charles M. Apt.

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