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# CHEMICAL AND SPECTROSCOPIC INVESTIGATIONS OF TRIALKYLSILYLCUPRATES DERIVED FROM CuCN.

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**Abstract:** We disclose that in THF addition of increasing amounts of $\Phi Me_2SiLi$ (with LiCl) to CuCN gives sequentially $\Phi Me_2SiCu(CN)Li$ (1:1), $(\Phi Me_2Si)_2Cu(CN)Li_2$ (2:1) and $(\Phi Me_2Si)_3CuLi_2$ (3:1). The formation of the latter species is corroborated with chemical tests on both $\alpha,\beta$-enones and 1-alkynes, as well as Gilman tests.

## INTRODUCTION

Recent advances in the development of organometallic reagents have been accelerated by an improved understanding of the species and mechanisms involved in reactions of these reagents.[1] No where is this more apparent than in the organic chemistry of copper which has emerged as the most heralded among the transition metals in organic synthesis. The pivotal role played by copper-complexes containing transferable ligands is attested to by the frequent reviews[2] which strive to keep organic chemists abreast of the rapidly expanding methodological advances and applications of copper based reagents.

The "ate" complexes of copper developed in the years since Gilman's initial report[3] of the formation of $Me_2CuLi$ are as varied as their chemistry. Reactivity of these reagents can be changed by altering several parameters: the source of Cu(I)X (where X = halide, nitrile etc.);[2,4] the ratio of CuX to R-M (being either stoichiometric or catalytic in CuX);[2] the gegenion involved (usually M = MgX or Li and more recently Na and Zn);[5] the presence of additives such as sulfides, phosphines or Lewis acids that solubilize, stabilize or activate;[2,6] and lastly, the choice of solvent.

More recently, silylcopper, $[(R_3Si)_nCuLi_{n-1}\bullet LiX]$ and stannylcopper $[(R_3Sn)_nCuLi_{n-1}\bullet LiX]$ reagents have begun to receive a significant share of the attention afforded to cuprates by synthetic organic chemists.[7] An appreciation of their considerable synthetic utility can quickly be gained from inspection of the numerous reactions that these reagents effect. The range of substitution reactions encompass primary alkyl and acyl centers.[7,8] Displacements following $S_N2'$ pathways occur in propargylic and allylic systems. Additions to unconjugated acetylenes,[9] allenes[10] and Michael acceptors[11] such as enones, enoates or ynoates comprise a second major reaction type. As initially with alkylcuprates, the structures of these silyl- and stannylcopper reagents proposed to date have been based solely on the stoichiometry of the solutions generated to achieve the desired chemistry.

Until the recent elegant studies of Lipshutz *et al.* on Cu(I) halide and CuCN derived alkylcuprates *via* $^7Li$ and $^1H$ NMR this was also the case for alkylcuprates.[12] A detailed examination of the $^1H$ and $^7Li$ NMR of solutions containing a 1:1 ratio of MeLi and MeCu (halide free) led this group to conclude that in THF these reagents exist as an equilibrium mixture of free MeLi, $Me_3Cu_2Li$ and $Me_4Cu_2Li_2$.[12a,b] Introduction of a further equivalent of MeLi to such solutions generated a high proportion of free MeLi and shifted the relative concentrations of $Me_3Cu_2Li$ and $Me_4Cu_2Li_2$ toward the latter. The postulated equilibrium (equation 1) and existence of free alkyl lithium in these solutions was supported by chemical reactivity studies. In contrast, in the presence of lithium salts, only signals due to $Me_4Cu_2Li_2$ were observed.[12a]

$$Me_4Cu_2Li_2 \underset{K_{eq} = 10 \pm 3}{\rightleftarrows} Me_3Cu_2Li + MeLi \qquad (1)$$

Similarly, a solution composed of $\Phi Li$ and $\Phi_2CuLi$ (prepared from $\Phi Li$ and CuI) in THF did not afford

$\Phi_3CuLi_2$ but contained free ΦLi and the "lower order" (LO) cuprate, $\Phi_2CuLi{\cdot}LiI$.[12e] Whereas, the combination of ΦLi and $\Phi_2CuLi{\cdot}LiX$ (X = Br or I), in dimethyl sulfide (DMS) gave a "higher order" (HO) cuprate, $\Phi_3CuLi_2$.[12e]

When organocuprates were derived from MeLi and CuCN in THF, no equilibrium among HO [i.e., $Me_2Cu(CN)Li_2$], the LO reagent, MeCu(CN)Li and free MeLi (equation 2) was evident.[12f] Thus, when equimolar amounts of MeLi and CuCN were mixed in THF at -30°C a $^1H$ signal attributed to MeCu(CN)Li was observed. Introduction of a further equivalent of MeLi to solutions containing MeCu(CN)Li produced a signal assigned to $Me_2Cu(CN)Li_2$. Addition of MeLi to solutions of $Me_2Cu(CN)Li_2$ resulted in formation of no new species but gave solutions exhibiting signals attributable to both free MeLi and $Me_2Cu(CN)Li_2$.[12f]

$$2MeLi + CuCN \longrightarrow Me_2Cu(CN)Li_2 \qquad (2)$$

## RESULTS AND DISCUSSION

We now present preliminary studies employing low-temperature $^{29}Si$, $^{13}C$, $^1H$ and $^7Li$ nuclear magnetic resonance spectroscopy to probe the composition of solutions generated by mixing dimethylphenylsilyl lithium (**1**) with CuCN. Species likely to be formed in these experiments are lower and higher order silylcuprates, **2** and **3** respectively.[12] These species are differentiated on the basis of formal charge associated with the copper-containing center; hence, LO cuprates are monoanionic, while HO cuprates are Cu(I) dianions.[12a]

| | |
|---|---|
| Lower Order Silyl Cuprates | **2a** $(\Phi Me_2Si)Cu(CN)Li$<br>**2b** $(\Phi Me_2Si)_2CuLi$ |
| Higher Order Silyl Cuprates | **3a** $(\Phi Me_2Si)_2Cu(CN)Li_2$<br>**3b** $(\Phi Me_2Si)_3CuLi_2$ |

**Silicon-29[13] NMR investigations:** Dimethylphenylsilyl lithium (**1**) in THF was prepared by reaction of $\Phi Me_2SiCl$[14a] or $(\Phi Me_2Si)_2$[14b] and lithium metal. Preparations were conducted at -5°C in THF and both sources of **1** gave $^{29}Si$ signals at -28.5 ppm (Figure 1a). Solutions of silylcuprates[7b] were generated by addition of **1** (prepared from $\Phi Me_2SiCl$ and Li metal) to THF solutions of copper(I) cyanide at -50°C. When the ratio of **1** to CuCN was 1:1 a major singlet at -25.5 ppm accompanied by a minor signal due to **1** (-28.5 ppm) was observed (Figure 1b). The major peak is attributed to $\Phi Me_2SiCu(CN)Li$ (**2a**). Corroborating evidence for this formulation comes from infrared analysis of these solutions which show a bound nitrile ($\upsilon_{CN}$= 2111 $cm^{-1}$)[12f,15] but no free LiCN.

As the ratio of **1** to CuCN increased from 1:1 to 2:1 (>0.5 but <1.0 equiv.), a new peak at -24.7 ppm gradually increased in intensity at the expense of the signal at -25.5 ppm (Figure 1c). When the ratio of $\Phi Me_2SiLi$ to CuCN reached 2:1, the major signal was that at -24.4 ppm and a minor signal at -18.8 ppm was visible (Figure 1d). The signal at -24.4 ppm is assigned to $(\Phi Me_2Si)_2Cu(CN)Li_2$ (**3a**) and not **2b** again based on the absence of free cyanide in the solution as judged by infrared ($\upsilon_{CN}$= 2123 $cm^{-1}$) and $^{13}C$ chemical shifts (*vide infra*). Alternative species possessing stoichiometries of $\Phi Me_2Si$ to Cu(I) of other than 2:1 or disproportionation of **3a** would generate either free **1** or free CuCN neither of which is observed by NMR (δ -28.5) or IR ($\upsilon_{CN}$= 2148 $cm^{-1}$).[15c]

Addition of an equivalent of **1** to the above sample (Figure 1d) would be expected to generate free $\Phi Me_2SiLi$ (δ -28.5) by analogy with CuCN based alkylcuprates. Contrary to these expectations, only a minor signal attributable to **1** was observed in this experiment (Figure 1e). What was observed in solutions containing **1** and CuCN in a 3:1 ratio was a significant signal at -18.9 ppm as well as a small signal assigned to **3a** (-24.4 ppm). The appearance of signals for both **3a** and **1** in the $^{29}Si$ spectrum of this solution indicates that chemical exchange between these three species is slow on the NMR time scale.

An attractive formulation for the species exhibiting a $^{29}Si$ signal at -18.9 ppm is $(\Phi Me_2Si)_3CuLi_2$ (**3b**).[12] This composition is supported by the infrared of this solution which exhibits an absorption of free LiCN ($\upsilon_{CN}$= 2085 $cm^{-1}$). The formation of a species in which three $\Phi Me_2Si$ groups are directly associated with the copper center requires a nitrile to be displaced. Secondly, addition of an equivalent of CuCN to the solution whose $^{29}Si$ NMR spectrum is shown in Figure 1e results in the regeneration of $(\Phi Me_2Si)_2Cu(CN)Li_2$ (Figure 1d). Further introduction of CuCN to this solution results in the regeneration of the spectrum shown in Figure 1b. Thirdly, solutions of 3:1,

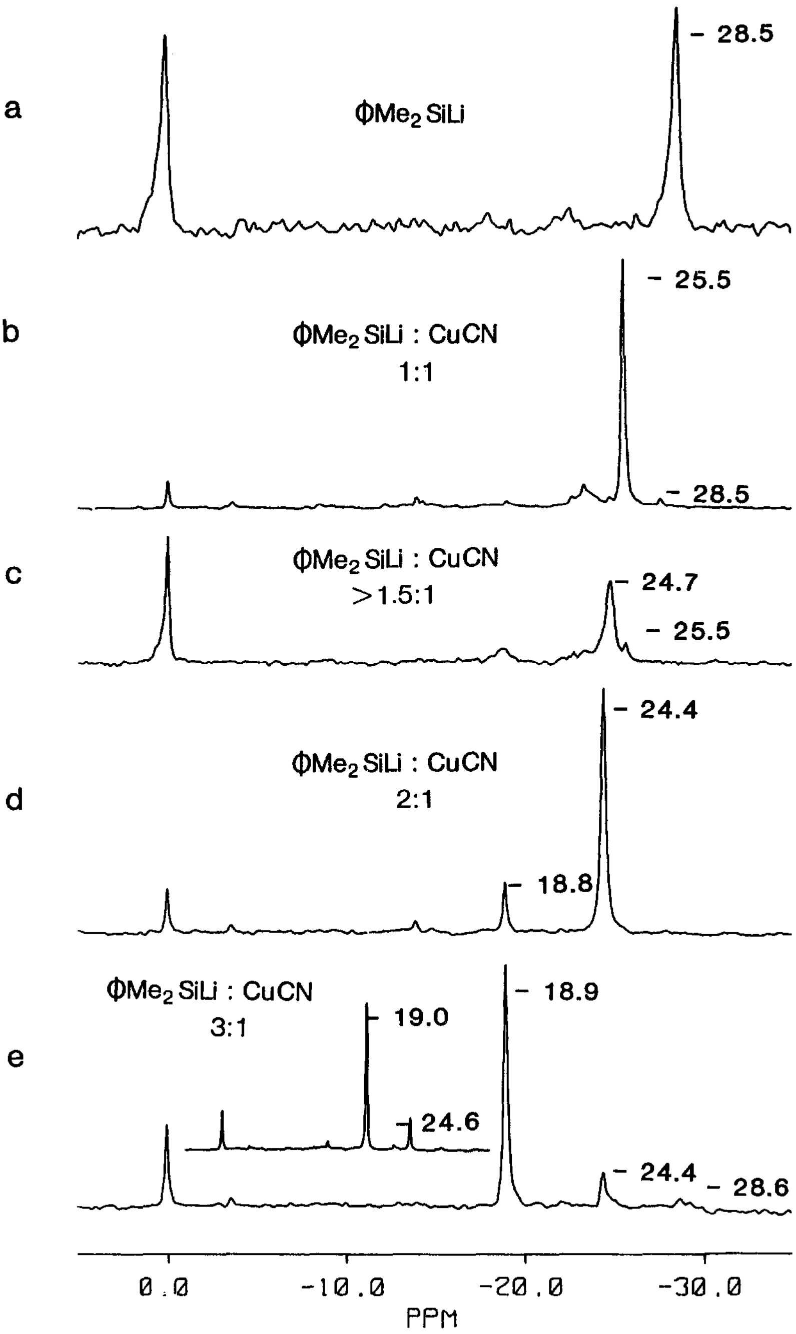


**Figure 1.** $^{29}$Si NMR spectra of (a) $\Phi Me_2SiLi$ (prepared from $\Phi Me_2SiCl$ + Li); (b) $\Phi Me_2SiLi$:CuCN, 1:1; (c) $\Phi Me_2SiLi$:CuCN, >1.5:1; (d) $\Phi Me_2SiLi$:CuCN, 2:1; (e) $\Phi Me_2SiLi$:CuCN, 3:1; (inset 1e) $\Phi Me_2SiLi$:CuBr•$Me_2S$, 3:1; all spectra except 1c (-70°C) were recorded at -50°C.

$\Phi Me_2SiLi{:}CuBr{\bullet}Me_2S$ exhibited $^{29}Si$ spectra with signals at -19.0 ppm and -24.6 ppm (Figure 1e inset, but again no free **1**) which are very close to those assigned to **3b** and **3a** respectively.[16a] The species exhibiting signals at -25.5, -24.4 and -18.9 ppm are thus in dynamic exchange as represented by equation 3.

$$\begin{tikzcd}[column sep=huge, row sep=huge]
\underset{\mathbf{1}}{\Phi Me_2SiLi + CuCN} \arrow[r, shift left, "k_1"] & \underset{\mathbf{2a}}{\Phi Me_2SiCu(CN)Li} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift right, swap, "\Phi Me_2SiLi\quad k_2"] \\
\underset{\mathbf{3b}}{LiCN + (\Phi Me_2Si)_3CuLi_2} \arrow[r, shift right, swap, "K_3 = 34\pm10"] & \underset{\mathbf{3a}}{(\Phi Me_2Si)_2Cu(CN)Li_2} \arrow[l, shift right, swap, "\Phi Me_2SiLi"] \arrow[u, shift right, swap, "k_{-2}"]
\end{tikzcd} \qquad (3)$$

The relative intensities of the $^{29}Si$ signals attributed to contributing species in solutions whose spectra are shown in Figure 1, allow estimation of the position of the equilibria shown in equation 3.[16b] The equilibrium between $\Phi Me_2SiLi$ (**1**), CuCN and $\Phi Me_2SiCu(CN)Li$ (**2a**) lies significantly on the side of **2a** ($k_1 >> k_{-1}$). Likewise, in solutions containing **1** and CuCN in a 2:1 ratio, $(\Phi Me_2Si)_2Cu(CN)Li_2$ (**3a**) is favored ($k_2 >>> k_{-2}$) to the spectroscopic exclusion of $\Phi Me_2SiCu(CN)Li$ (**2a**). In solutions comprised of 3:1, $\Phi Me_2SiLi{:}CuCN$, $(\Phi Me_2Si)_3CuLi_2$ (**3b**) predominates over $(\Phi Me_2Si)_2Cu(CN)Li_2$ by ~4:1. This leads to the calculation of an equilibrium constant $K_3$.[16] The values of $K_3$ and the errors[17] reported were calculated by averaging three determinations.

It is interesting that the chemical shift change observed when LO silylcyanocuprates are converted to HO silylcyanocuprates is opposite to what would be expected from simple arguments based on electronegativity. Addition of electron-rich $\Phi Me_2SiLi$ to $\Phi Me_2SiCu(CN)Li$ should increase the electron density at a coordinating copper and hence at both silicons in the resultant HO species. The $^{29}Si$ resonance in the HO species would therefore be expected to be upfield of that in the LO reagents, not downfield as found. This anomolous pattern of shielding for nuclei like carbon[18a] and silicon[13] compared to $^1H$ has recently been explained through semiempirical calculations of p-orbital "imbalance" and its contribution to the paramagnetic term of nuclear shielding.[18b]

The observation that the $^{29}Si$ signals of HO silylcyanocuprates are downfield to those of LO silylcyanocuprates has a parallel in $^{13}C$ NMR spectroscopy. Deshielding of the carbonyl carbon of transition metal carbonyls increases with increased metal to carbonyl π back-donation as evidenced by an inverse linear relationship between the CO stretching constants and the $^{13}C$ chemical shifts of such carbonyls.[18c] Increased metal to carbonyl π back-donation has been attributed to a decrease in the magnitude of the separation between the ground state and the lowest lying excited states of these bonds.[18d] The observation that the $^{29}Si$ chemical shifts change in the same manner as the $^{13}C$ chemical shifts of the carbonyls, suggests that as in the M-CO bond there is a significant π bonding in the Cu-Si bond. This need not involve the 3d orbitals of silicon but rather the $\sigma^*$ orbitals, as recently proposed for phosphines.[18e]

**Carbon-13 NMR Studies:** The chemical shifts of the $^{13}C$ resonances for the silylcuprates and their precursors are summarized in Table I. Specific peak assignments were made with the aid of proton decoupled as well as proton-coupled spectra. The major trends apparent in Table I are that the formation of silylanions from neutral silyl derivatives causes both the *ipso* and methyl carbons to be strongly deshielded and the *para* carbons to be shielded with the maximum effect observed in the case of $\Phi Me_2SiLi$. This effect is expected by extension of the Cu-Si π bonding arguments advanced above to Si-C bonds. Such π bonding would be predicted to be more significant for $Si\text{-}C_{sp2}$ than for $Si\text{-}C_{sp3}$. As expected the *ipso* carbons of $\Phi Me_2SiLi$ experience larger deshielding than the methyl carbons compared to $\Phi Me_2SiCl$.[13c,19] Similar reasoning can be used to explain the chemical shift changes observed for the $^{13}C$ resonance of the *ipso* carbon upon the successive addition of the electron-releasing ligand ($\Phi Me_2SiLi$) to solutions of Cu(I) salts. Thus as one progresses in the series $\Phi Me_2SiCu(CN)Li$ => $(\Phi Me_2Si)_2CuLi$ => $(\Phi Me_2Si)_2Cu(CN)Li_2$ the *ipso* carbon is progressively deshielded (150 => 156 => 157.4 ppm, Table I).

**Table I.** $^{13}C$ Chemical Shifts of Silyl Anions and Related Species in THF[a]

| | Ipso | Ortho | Meta | Para | Me | Other C |
|---|---|---|---|---|---|---|
| $\Phi Me_2SiCl$ | 136.3 | 133.1 | 128.1 | 130.3 | 2.0 | |
| $(\Phi Me_2Si)_2$ | 139.1 | 133.8 | 128.4 | 127.7 | -3.9 | |
| $\Phi Me_2SiLi$ | 166.0 | 133.6 | 126.3 | 122.5 | 7.5 | |
| $(\Phi Me_2Si)_2Cu(CN)Li_2$ | 157.4 | 134.9 | 126.5 | 124.7 | 5.1 | 156.7(CN) |
| $(\Phi Me_2Si)_2CuLi$ | 156.0 | 134.0 | 126.0 | 123.9 | 6.0 | 17.8($Me_2S$) |
| $\Phi Me_2SiCu(CN)Li$ | 150.0 | 135.0 | 126.0 | 124.6 | 6.3 | 155.0(CN) |

[a] The spectra were recorded at 0°C at which temperature the species are equilibrating more rapidly than the time constant of the NMR measurements.[17] The chemical shifts reported are therefore weighted average of the equilibrating species.

**Hydrogen-1 NMR Studies:** The ease with which we were able to study the HO silylcuprates derived from CuCN, by $^{29}Si$ NMR spectroscopic techniques, encouraged us to study the formation of these species using $^{1}H$ and $^{7}Li$ NMR. The $^{1}H$ nuclear magnetic resonance spectra were recorded at -85°C at 300 MHz in the region between 1.0 ppm and -2.0 ppm with the specific goal of observation of the resonances due to the methyl hydrogens. Solutions of **1** exhibited a singlet at 0.10 ppm whereas solutions containing **1**:CuCN in a 1:1 ratio showed a major signal at 0.22 ppm which we attributed to **2a**. As the ratio of **1** to CuCN increased from 1:1 to 2:1, a new signal at 0.02 ppm was visible. When the ratio was precisely 2:1, the major signal observed was at 0.02 ppm; this signal was assigned to **3a**. Solutions containing 2:1, **1**:CuCN to which one or more equivalents of $\Phi Me_2SiLi$ had been added revealed only one major $^{1}H$ signal with a chemical shift close to that assigned to **3a**. We assume from the $^{29}Si$ NMR studies (*vide supra*) that the chemical shifts of the methyl hydrogens attached to silicon for the presumed species **3a** and **3b** are very similar.

**Lithium-7[20] NMR Studies:** Dimethylphenylsilyl lithium, **1**, (LiCl free) was prepared from $(\Phi Me_2Si)_2$[14b] and lithium metal. Initial $^{7}Li$ NMR studies were conducted on $(\Phi Me_2Si)_2Cu(CN)Li_2$ (**3a**) at -70°C. Addition of two equivalents of $\Phi Me_2SiLi$, **1**, ($\delta$ -1.69) to one equivalent of CuCN produced a solution exhibiting a major $^{7}Li$ signal[20b] at -3.33 ppm which was assigned to $(\Phi Me_2Si)_2Cu(CN)Li_2$, **3a**, along with a peak for **1**. This is expected as the absence of LiCl in the reaction mixture would result in decreased solublity of the CuCN as evidenced by the heterogeneous nature of the solution. Addition of LiCl to this sample resulted in the disappearance of the signal due to **1** and resulted in the appearance of single peak at -1.84 ppm. We interpret these observations to indicate that in the absence of LiCl, exchange between **1** and **3a** is slow on NMR time scale whereas, in the presence of LiCl exchange between various lithium containing species is rapid. In agreement with these interpretations, a positive Gilman test was obtained for **3a** (LiCl free) and a negative test when LiCl was added to the above solution.

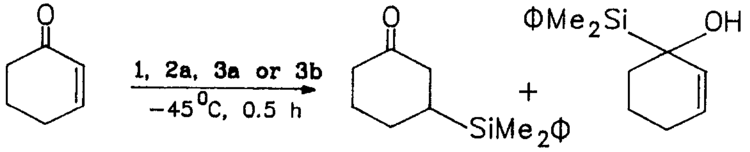
Sequential addition of **1** (LiCl free, 1.0 equiv) to **3a** resulted in the appearance of no new peak but the signal at -3.3 ppm gradually increased in intensity. Lowering the temperature to -80°C did not result in the appearance of additional signals. These observations suggest that the proposed components, *vide supra*, have similar $^{7}Li$ chemical shifts or that averaging of signals due to exchange between **3a** and **3b** is rapid.[20c-f] This is well-precedented for alkylcuprates[12a] and other organometallics.[20g,h] Experiments to study the effect of LiCl on HO silylcuprates are currently in progress.

Observation of an average signal in the case of $^{1}H$ and $^{7}Li$ spectral analysis but not in the case of $^{29}Si$ is a function of the frequency of the measurements and the chemical shift differences of the exchanging species. Thus for $^{29}Si$, the chemical shift differences for **2a**, **3a** and **3b** are at least 1.0 ppm and the measurement is carried out at 79.5 MHz. If the equilibration between the species is faster than 79 Hz, an averaging of signals will be observed in the $^{29}Si$ spectrum. For $^{1}H$ assuming a separation of the methyl $^{1}H$ signals of **2a**, **3a** and **3b** of ~0.1 ppm and a measurement frequency of 300 MHz the averaged signals observed require exchange to be faster than 30 Hz. Thus at -50°C the species equilibrate with a rate constant between 30 and 79 Hz.

## CHEMICAL TESTS

Perhaps, the single most intriguing question which arises from $^{29}Si$ NMR studies relates to the composition of solutions attributed to **3b**. If the species **3b** is not as postulated but rather is composed of free **1** in rapid equilibrium with silylcyanocuprates containing a Si:Cu ratio of <3:1, then the "free" $\Phi Me_2SiLi$ would be expected to participate along with the silylcyanocuprates in their reactions. To test this concept, side-by-side reactions were conducted on two substrates, cyclohex-2-en-1-one and 1-octyne, each being treated with **1**, **2a**, **3a**, **3b** and **3b** + **1**. The results are summarized in Schemes I and II.

**Scheme I.** Addition reactions of "$\Phi Me_2SiCu$" reagents to cyclohex-2-en-1-one.

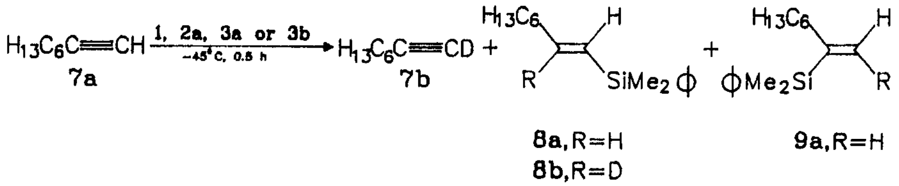


| 4 | | 5 | 6 |
|---|---|---|---|
| **1** | $\Phi Me_2SiLi$ | - | 62% |
| **2a** | $\Phi Me_2SiCu(CN)Li$ | 58% | - |
| **3a** | $(\Phi Me_2Si)_2Cu(CN)Li_2$ | 65% | - |
| **3b** | $(\Phi Me_2Si)_3CuLi_2$ | 70% | - |
| | $(\Phi Me_2Si)_3CuLi_2$ + **1** | 67% | - |

We found that solutions of both **3a** and **3b** deliver a $\Phi Me_2Si$ group exclusively *via* the 1,4-addition to cyclohex-2-en-1-one. This is consistent with the absence of **1** in these solutions as judged by $^{29}Si$ and $^1H$ NMR analysis (*vide supra*). Remarkably, solutions composed of **3b** + **1** and where only 10% CuCN was present compared to $\Phi Me_2SiLi$ also added to **4** in a 1,4-manner. These tests suggest that 1,4-additions of "$\Phi Me_2SiCu$" reagents to α,β-enones takes place with an increased propensity over 1,2-additions.[21] It is also clear that $\Phi Me_2SiLi$ (if any present) is no longer "free" in solutions of **3b**:**1** (>1:1), otherwise a substantial increase in the amount of **6** would have been observed in the above reactions. Perhaps, under catalytic conditions the "extra" $\Phi Me_2SiLi$ serves to rapidly convert the LO cuprate back to the HO cuprate.

We next focused attention on silylcuprations of 1-octyne (**7a**). In agreement with existing reports,[7b] we found that **2a** added to **7a** to yield a mixture of **8a** and **9a** in a 60 to 40 ratio whereas, addition reactions of **3a**, **3b** and **3b** + **1** gave exclusively **8a** in ~90% isolated yields. Under similar conditions **1** abstracted the acetylenic hydrogen of **7a** to give **7b** as judged by GC-MS (70% incorporation of $^2H$ in 1-octyne). No addition products were observed (capillary g.c. analysis). That "free" $\Phi Me_2SiLi$ is not present in the solutions of silylcuprates was confirmed by the absence of incorporation of two $^2H$ in the vinyl products when quenched with $^2H_2O$.

**Scheme II.** Silylcupration of 1-alkynes



| | | 7b | 8 | 9 | %yield |
|---|---|---|---|---|---|
| **1** | $\Phi Me_2SiLi$ | 100 | - | - | 72 |
| **2a** | $\Phi Me_2SiCu(CN)Li$ | | 60 | 40 | 62 |
| **3a** | $(\Phi Me_2Si)_2Cu(CN)Li_2$ | - | >98 | <2 | 92 |
| **3b** | $(\Phi Me_2Si)_3CuLi_2$ | - | >98 | <2 | 90 |
| | $(\Phi Me_2Si)_3CuLi_2$ + **1** | - | >98 | <2 | 87 |

**Gilman Tests:** Corroboration of our interpretation of the $^{29}Si$ and $^{1}H$ NMR data and the propensity of all solutions of **1** and CuCN studied (1:1 => 4:1) to undergo addition reactions to **4** and **7a** was obtained from the results of Gilman tests on THF solutions containing **1** and CuCN.[22] Thus, a positive Gilman test was obtained for **1** in THF while a negative test was obtained for all solutions of **1** containing CuCN including those where these reagents are present in a 3:1 ratio. A slight green coloration was observed for 4:1, **1**:CuCN case indicating the presence of minute quantites of free $\Phi Me_2SiLi$ (Table II).

**Table II.** Gilman Test on CuCN-Derived Silylcuprates

| Reagents | Results |
|---|---|
| $\Phi Me_2SiLi$ | positive |
| $\Phi Me_2SiCu(CN)Li$ | negative |
| $(\Phi Me_2Si)_2Cu(CN)Li_2$ | negative |
| $(\Phi Me_2Si)_3CuLi_2$ | negative |

## CONCLUSION

Comparison of the present silylcyanocuprate system with that of the methylcyanocuprate system studied by Lipshutz *et al.*[12f] reveals several interesting features. In both of these systems, when the ratio of RLi (R=$\Phi Me_2Si$ or Me) to Cu(I)CN is unity, a nitrile containing monoanionic cuprate is formed. In neither system does this species appear to be in significant equilibrium with other species or free RLi. As the proportion of anion is increased from RLi:Cu ratio of 1:1 to 2:1 a new species, still containing a bonded nitrile, is formed in both cases. In the case of HO, $Me_2Cu(CN)Li_2$, association of alkyl residues with copper beyond this stoichiometry does not occur and further addition of MeLi beyond this point gives solutions containing free alkyllithium. In the case of HO, $(\Phi Me_2Si)_2Cu(CN)Li_2$, addition of further silyllithium gives solutions which contain negligible free silyl anion and whose $^{29}Si$ spectra support the association of three silyl residues with the copper accompanied by displacement of the nitrile. Chemical studies on two different substrate types, as well as Gilman tests for the presence of free RLi, are fully consistent with the spectroscopic data.

## EXPERIMENTAL

All glassware and syringes were dried in an oven overnight at 120°C, and glassware was flame dried under vacuum and flushed with Argon immediately prior to use. Syringes were flushed with Argon and kept under positive Argon pressure while cooling until use. Transfer of reagents was performed by using Hamilton syringes equipped with stainless steel needles. Reactions were carried out in a three necked round bottom flasks equipped with filtration units and teflon-coated magnetic stirring bars. Storage and transfer of CuCN and $CuBr{\cdot}Me_2S$ took place in a glove bag.

THF was freshly distilled from potassium/benzophenone ketyl. All other chemicals (Aldrich) were used as received.

Low-temperature $^{29}Si$ NMR experiments were conducted on a Bruker WM-400 spectrometer at a frequency of 79.495 MHz. A typical set of parameters utilized a spectral width of 20000 Hz (251.6 ppm), 8K of memory, 2.44 Hz/data point, an acquisition time of 0.204 s and a 15° pulse of 10 μs. The decoupler was turned on during acquisition and off during the relaxation delay (4 s) in order to supress the negative nOe of $^{29}Si$. A line broadening of 20 Hz was applied to all spectra. Spectra were recorded in THF that contained $Me_4Si$ as internal reference.

$^{13}C$ NMR spectra were also conducted on Bruker WM-400 spectrometer at a frequency of 100.61 MHz. Parameters for the $^{13}C$ spectral acquisition typically involved a spectral width of 250 ppm, 32K of memory, 1.32 Hz/data point, an acquisition time of 0.75 s and a 13.5° pulse of 9 μs. The spectra were recorded on THF solutions unless otherwise specified and were referenced to THF, $\alpha$ = 26.0 ppm, $\beta$ = 68.2 ppm. Inverse-gated decoupling was employed.

Low-temperature $^{7}Li$ NMR spectra were conducted on a Varian XL-300 spectrometer at a frequency of 116.6 MHz using a sweep width of 20000 Hz, 16K of memory, 1.25 Hz/data point, an acquisition time of 0.4 s and a 55°

pulse of 12 µs. A line broadening of 10 Hz was applied to all spectra. $^7$Li chemical shifts are calculated with respect to 0.5M LiCl/CD$_3$OD (δ 0 ppm) in a capillary insert.

Low-temperature $^1$H NMR spectra were recorded on a Varian XL-300 spectrometer in THF-d$_8$. The peaks are referenced to acetone.

Infrared (IR) spectra were recorded in THF solutions using Perkin-Elmer Model 283 spectrophotometer. Gas liquid chromatographic analysis were obtained on an HP 5880A or 5890A gas chromatogram fitted with a capillary inlet systems, flame-ionization detectors and WCOT columns (30 m x 0.25 id) of glass or fused silica gel. The columns were coated with OV-101 or DB-1 liquid phases. Chromatographic purifications were carried out with E.M. Merck silica gel (60, particle size 0.040-0.063 mm). Low resolution mass spectra were obtained with an HP 5985B GC-MS system using electron-impact ionization at 70 eV while the high resolution mass spectra were obtained on a Kratos MS50 RFA mass spectrometer.

**Preparation of $\Phi$Me$_2$SiLi/THF (with LiCl):** Dimethylphenylsilyl chloride (3.6 g, 21 mmol) was stirred with small pieces of lithium (0.450 g, 64 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 stirred overnight at -5°C. Dimethylphenylsilyl lithium was titrated according to the procedure of Fleming *et al.*[7b]

**Preparation of $\Phi$Me$_2$SiCu(CN)Li (with LiCl):** CuCN (0.18 g, 2 mmol) was placed in a 10 mm NMR tube, equipped with an argon inlet. The tube was repeatedly (3x) evacuated (vacuum pump) and purged with argon. Me$_4$Si (0.5 mL) was injected, the reaction was cooled to -50°C and dimethylphenysilyl lithium in THF (1.8 mL, 2 mmol) added dropwise. The solution was stirred on a vortex mixer at -50°C in a custom built dewar for 20 min. The spectrum was then immediately recorded.

**Preparation of ($\Phi$Me$_2$Si)$_2$Cu(CN)Li$_2$ (with LiCl):** A THF solution of $\Phi$Me$_2$SiLi (1.8 mL, 2 mmol) was added to a 10 mm NMR tube containing a THF solution of $\Phi$Me$_2$SiCu(CN)Li (*vide supra*) at -50°C. The deep red colored solution was stirred for 20 min at -50°C prior to examination by NMR and IR.

**Preparation of ($\Phi$Me$_2$Si)$_3$CuLi$_2$ (with LiCl):** To a THF solution of ($\Phi$Me$_2$Si)$_2$Cu(CN)Li$_2$ (2 mmol) prepared as outlined above was added a THF solution of $\Phi$Me$_2$SiLi (1.8 mL, 2 mmol) at -50°C. The reaction was stirred for 20 min at -50°C before examination by NMR and IR. Mixture of $\Phi$Me$_2$SiLi ($\Phi$Me$_2$SiCl + Li) (3 mmol) and CuBr•Me$_2$S (1 mmol) at -50°C resulted in the same species.

**Regeneration of ($\Phi$Me$_2$Si)$_2$Cu(CN)Li$_2$:** CuCN (0.18 g, 2 mmol) was added to the above solution. The reaction was stirred for 20 min at -50°C before examination by NMR.

**Regeneration of $\Phi$Me$_2$SiCu(CN)Li:** CuCN (0.18 g, 2 mmol) was added to the NMR tube containing HO silylcyanocuprate, **3a**. The reaction was stirred for 20 min at -50°C and then examined by NMR.

**Preparation of LiCl Free $\Phi$Me$_2$SiLi:** According to the procedure of Gilman,[14a] to a solution of 1,2-diphenyl-1,1,2,2-tetramethyldisilane (prepared according to the procedure of Gilman[14b]) (4.6 g, 17 mmol) in THF (10 mL), was added small pieces of lithium (24 mg, 34 mmol). The reaction was initiated in a sonicator bath for 30 min and then stirred overnight at -5°C. The resultant green solution showed a negative halogen test.

**Preparation of 2a, 3a and 3b (no LiCl):** These were all prepared precisely as described above by substituting LiCl free **1** for $\Phi$Me$_2$SiLi. All the solutions except for **2a** were green in colour. Addition of LiCl resulted in the familiar red silylcuprates.

**Typical procedure for preparation of $^1$H and $^{13}$C NMR samples (with LiCl):** According to the procedure of Knochel *et al.*[5c], THF-d$_8$ (11 mL) was added to a mixture of CuCN (0.99 g, 11 mmol) and LiCl (0.95 g, 22 mmol) in a round bottomed flask under argon. A clear faint yellow solution was obtained after 0.5 h of stirring. This solution was used as the Cu(I)CN source for all the samples. CuCN (0.5 mL, 0.5 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-d$_8$ (0.6 mL, 0.5 mmol) added dropwise. The solution was stirred on a vortex mixer in a custom built dewar for 20 min. The spectra were recorded immediately.

**Typical Procedure for Reactions of $\Phi$Me$_2$SiLi/CuCN Solutions with 4:** $\Phi$Me$_2$SiLi (1.25 mL, 1.0 mmol) was added dropwise at -45°C to CuCN (0.089 g, 1 mmol) in THF (2 mL) under argon. The resulting deep red solution was stirred for 0.5 h after which **4** (0.08 mL, 0.82 mmol) was added *via* a syringe. All reactions were stirred for a further 0.5 h and then quenched with sat'd. NH$_4$Cl/10% NH$_4$OH. The usual workup involved extraction of the organic phase with Et$_2$O (2 x 2 mL) and washing with brine (2 x 2 mL). The combined extracts were dried over anhyd. MgSO$_4$ and concetrated *in vacuo*. Column chromatography (4:1 hexanes:EtOAc) yielded 3-(dimethylphenylsilyl)-cyclohexanone (**5**). The ratios of 1,2- *vs* 1,4-addition products and the overall yields are reported in Scheme I. The $^1$H NMR and IR data for **5** matched that reported by Fleming *et al.*[11c] for this compound. $^{13}$C{$^{1}$H} ($\mathrm{CDCl_3}$) δ 212.5 ($\mathrm{\underline{C}{=}O}$), 136.6 (*ipso*), 133.8, 129.2, 127.8, 42.3, 41.8, 29.7, 27.5, 26.0, -5.4 ($\mathrm{Si\underline{C}H_3}$), -5.5 ($\mathrm{Si\underline{C}H_3}$); MS m/e (rel. intensity) 232 ($\mathrm{M^+}$, 20), 217 (15), 189 (5), 156 (22), 135 (100); Anal. calc. $\mathrm{C_{14}H_{20}OSi}$ 232.1283 found 232.1282.

**Preparation of 1-(Dimethylphenylsilyl)-cyclohex-2-en-1-ol (6):** Cyclohex-2-en-1-one (0.08 mL, 0.82 mmol) was added dropwise to a solution of $\mathrm{\Phi Me_2SiLi}$ (1.25 mL, 1 mmol) at -45°C in THF (2 mL) under argon. The solution turned yellow upon completion of addition. The reaction was stirred for 0.5 h and then quenched with sat'd. $\mathrm{NH_4Cl}$/10% $\mathrm{NH_4OH}$. The usual workup followed by column chromatography (4:1 hexanes:EtOAc) gave 62% of **6** as a colorless oil. IR (NaCl) 3460 (OH), 1440 ($\mathrm{\Phi\underline{Me_2}Si}$) $\mathrm{cm^{-1}}$; 400 MHz $^{1}$H NMR ($\mathrm{CDCl_3}$) δ 7.2-7.7 (m, 5H, Ph), 5.9 (ddd, J = 10, 5, 3 Hz, 1H, $\mathrm{CH_2\underline{H}C{=}C}$), 5.7 (dt, J = 10, 3 Hz, 1H, $\mathrm{C{=}C\underline{H}}$), 1.4-2.1 (m, 6H, ring $\mathrm{C\underline{H_2}}$), 1.18 (bs, 1H, $\mathrm{O\underline{H}}$), 0.38 (s, 3H, $\mathrm{SiC\underline{H_3}}$), 0.36 (s, 3H, $\mathrm{SiC\underline{H_3}}$); $^{13}$C{$^{1}$H} ($\mathrm{CDCl_3}$) δ 136.4 (*ipso*), 134.6, 130.4, 130.2, 129.2, 127.7, 64.2 ($\mathrm{\underline{C}OH}$), 32.7, 25.2, 17.5, -5.8 ($\mathrm{Si\underline{C}H_3}$), -6.0 ($\mathrm{Si\underline{C}H_3}$); MS m/e (rel. intensity) 232 ($\mathrm{M^+}$, 5), 214 ($\mathrm{M^+}$-18, 20), 199 (15), 135 (100); Anal. calc. $\mathrm{C_{14}H_{20}OSi}$ 232.1284 found 232.1286.

**Reaction of $\mathrm{\Phi Me_2SiLi}$ with 7a:** 1-octyne (0.24 g, 2.2 mmol) was added dropwise to a solution of $\mathrm{\Phi Me_2SiLi}$ (2.6 mL, 2.2 mmol) at -45°C in THF (3 mL) under argon. The reaction was stirred for 0.5 h and then quenched with $\mathrm{^2H_2O}$ (5 mL). It was gradually warmed to room temperature. The usual workup yielded octyne-d (70% incorporation as calculated from GC-MS analysis). For **7a**: MS m/e (rel. intensity) 95 ($\mathrm{M^+}$-15, 30), 81 (100), 67 (52). For **7b**: MS m/e (rel. intensity) 96 ($\mathrm{M^+}$-15, 25), 95 (17.5), 82 (100), 81 (28), 68 (40).

**Typical Procedure for silylcupration of "$\mathrm{\Phi Me_2SiCu}$":** According to the procedure of Fleming *et al.*[7b] $\mathrm{\Phi Me_2SiLi}$ (2.6 mL, 2.2 mmol) was added dropwise at -45°C to CuCN (0.197 g, 2.2 mmol) in THF (3 mL) under argon. The resulting deep red solution was stirred for 0.5 h after which **7a** (0.24 g, 2.2 mmol) was added *via* a syringe. All reactions were stirred for an additional 0.5 h and then quenched with $\mathrm{^2H_2O}$ (5 mL). The reactions were warmed gradually to room temperature. The usual workup followed by column chromatography (hexanes) yielded the vinyl products which were analyzed by $^{1}$H NMR and GC-MS analysis to determine the amount of $^{2}$H incorporated. The ratios of **8** to **9** and the overall yields are reported in Scheme II.

For **8a**: IR (NaCl) 1620, 1440, 1250, 1120, 995 $\mathrm{cm^{-1}}$; 400 MHz $^{1}$H NMR ($\mathrm{CDCl_3}$) δ 7.1-7.5 (m, 5H, Ph), 6.17 (dt, J = 18, 6 Hz, 1H, $\mathrm{\underline{H}C{=}CSi}$), 5.85 (dt, J = 18, 1.5 Hz, 1H, $\mathrm{C{=}C\underline{H}Si}$), 2.7 (tdd, J = 7, 6, 1.5 Hz, 2H, allylic), 1.2-1.42 (m, 8H, $\mathrm{C\underline{H_2}}$), 0.95 (t, J = 7 Hz, 3H, $\mathrm{CH_3}$), 0.3 (s, 6H, $\mathrm{SiC\underline{H_3}}$); $^{13}$C{$^{1}$H} ($\mathrm{CDCl_3}$) δ 149.5 ($\mathrm{\underline{C}{=}CSi}$), 139.4 ($\mathrm{C{=}\underline{C}Si}$), 133.8 (*ipso*), 128.7, 127.6, 127.2, 36.8, 36.7, 31.7, 28.8, 28.6, 22.5, 13.9 ($\mathrm{Si\underline{C}H_3}$); MS m/e (rel. intensity) 246 ($\mathrm{M^+}$, 9), 231 (70), 161 (35), 135 (50), 121 (100); Anal. calc. $\mathrm{C_{16}H_{26}Si}$ 246.1803 found 246.1809. For **8b**: 400 MHz $^{1}$H NMR ($\mathrm{CDCl_3}$) δ 7.1-7.5 (m, 5H, Ph), 5.85 (brt J = 1.5 Hz, 1H, $\mathrm{C{=}C\underline{H}Si}$), 2.7 (td, J = 7, 1.5 Hz, 2H, allylic), 1.2-1.42 (m, 8H, $\mathrm{C\underline{H_2}}$), 0.95 (t, J = 7 Hz, 3H, $\mathrm{CH_3}$), 0.3 (s, 6H, $\mathrm{SiC\underline{H_3}}$); MS m/e (rel. intensity) 247 ($\mathrm{M^+}$, 12), 232 (100), 162 (80), 148 (40), 135 (60), 122 (80), 121 (80); Anal. calc. $\mathrm{C_{16}H_{25}DSi}$ 247.1866 found 247.1874. For **9a**: 400 MHz $^{1}$H NMR ($\mathrm{CDCl_3}$) δ 5.9 (dt, J = 7, 1.5 Hz, 2H, vinyl); MS m/e (rel. intensity) 246 ($\mathrm{M^+}$, 45), 231 (45), 161 (35), 135 (100), 121 (35).

**Gilman Tests.** All cuprates used in these tests were prepared in a 10 mm NMR tube as described above. An equal volume of Michler's ketone (1% solution) in dry benzene was added to the cuprate at 0°C. $\mathrm{H_2O}$ (1 mL) was introduced after 10 min and the reaction was allowed to warm to room temperature. After vigorous stirring, a 2% solution of $\mathrm{I_2}$ in glacial acetic acid was added dropwise. A persistent blue color in the organic layer is considered a positive test (confirmation of free RLi).[22]

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$$2Me_3CuLi_2 \leftrightarrows Me_4Cu_2Li_2 + 2MeLi \tag{4}$$

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$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\Phi Me_2SiCu(CN)Li]}{[\Phi Me_2SiLi]\,[CuCN]}$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[(\Phi Me_2Si)_2Cu(CN)Li_2]}{[\Phi Me_2SiCu(CN)Li]\,[\Phi Me_2SiLi]}$$

$$K_3 = \frac{k_3}{k_{-3}} = \frac{[(\Phi Me_2Si)_3CuLi_2]\,[LiCN]}{[(\Phi Me_2Si)_2Cu(CN)Li_2]\,[\Phi Me_2SiLi]} = 34 \pm 10$$

The concentrations of silicon containing species were calculated using the integral ratio for **1**, **2a**, **3a** and **3b** and the initial concentration of **1** corrected for the number of $\Phi Me_2Si$ groups in each species. The concentration of LiCN was calculated from the initial concentration of CuCN and the concentration of **2a** calculated from the $^{29}Si$ spectrum.

[17] Some uncertainty in the measurement of equilibria from $^{29}Si$ signal intensities comes from the negative gyromagnetic ratio[13b] of $^{29}Si$. Under the conditions of broad-band $^1H$ decoupling the $^{29}Si$ resonance will suffer a negative nuclear Overhauser effect if the $^{29}Si$ nucleus is in close proximity (<3 °A) to a $^1H$ nucleus. To surpress the negative nOe of $^{29}Si$ the decoupler was turned on during the acquisition and off during the relaxation delay. Another source of uncertainty in calculations of equilibrium constant could arise from the differential $T_1$'s of the equilibrating species. Since the proposed species are equilibrating with a rate constant between 30 and 79 Hz which is ~10x faster than the acquisition time (0.2 s, *vide infra*) for $^{29}Si$ NMR experiments, the effective $T_1$'s of the equilibrating species would be equivalent under these conditions.

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