# **Composition and Chemistry of the Mixed Higher Order Cuprates** $(PhMe_2Si)_m(CH_3)_nCu(CN)Li_{m+n}$

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Low-temperature <sup>28</sup>Si, <sup>13</sup>C, and <sup>1</sup>H NMR spectroscopic techniques were used to probe the nature of THF solutions of cuprates derived from PhMegSiLi, MeLi, and CuCN in the stoichiometric ratios 1:1:1, 2:1:1, and 1:2:1 (Si:Me:Cu). Unlike the corresponding mixed stannyl systems that yield R<sub>3</sub>Sn(R)<sub>2</sub>CuLi<sub>2</sub> when the ratio of stannyl anion:alkyl anion:cuprous ion is 1:2:1, these mixed silyl systems only form R<sub>3</sub>Si(R)Cu(CN)Li<sub>2</sub>. Solutions wherein the ratio of silyl anion and alkyl anion to cuprous ion is greater than 2:1 contain alkyllithium uncoordinated with cuprous ion. The most striking result is the preferential displacement of RLi when R<sub>3</sub>SiLi is added to solutions of R<sub>3</sub>Si(R)Cu(CN)Li<sub>2</sub> or R<sub>2</sub>Cu(CN)Li<sub>2</sub>. These mixed metallocuprate solutions preferentially transfer the PhMe<sub>2</sub>Si molety in reactions with  $\alpha,\beta$ -unsaturated enones and other unsaturated organic substrates. However, the mixed alkylsilylcuprate (PhMe<sub>2</sub>Si)(CH<sub>3</sub>)Cu(CN)Li<sub>2</sub> reacts with 1,2-epoxyoctane to afford up to 31% of the methylated alcohol. Frontier orbital analysis of both the predominant cuprates species and preferential ligand transfer provides a rationale for the observed behavior.

Lithium-based (trialkylsilyl)cuprates (R<sub>3</sub>Si)<sub>n</sub>CuLi<sub>n-1</sub>·LiX (n = 1 or 2, X = Br or CN) prepared from cuprous salts and R<sub>3</sub>SiLi are the most popular reagents for the transfer of  $R_3Si$  anions to organic substrates.<sup>1</sup> Reactions of these reagents occur under mild conditions and tolerate polar functional groups. Since in some reactions not all the metallo anions bound to copper are transferred, we recently undertook development of mixed metallocuprates, i.e.,  $R_3Si(R)CuLi\cdotLiX$  in which the alkyl anion serves as a nontransferrable ligand.<sup>2</sup> Spectroscopic evidence (<sup>29</sup>Si, <sup>13</sup>C, <sup>1</sup>H NMR) clearly showed that regardless of the method of preparation, THF solutions containing silyl anion:alkyl anion:cuprous ion (CuCN) in a 1:1:1 ratio reverted to  $R_3Si(R)Cu(CN)Li_2$ . It is obvious that these new reagents offer significant opportunities not only for selective transfer of the metallo anions bound to copper but in the event that R is chiral, this selective transfer should occur with chiral induction.

In the present study we have extended our studies of the mixed silvlcuprates to solutions containing silvl anion:alkyl anion:cuprous ion in ratios of 2:1:1 and 1:2:1. We found surprising differences between the mixed silyl and mixed stannyl cuprate systems.

#### **Results and Discussion**

<sup>13</sup>C, <sup>1</sup>H, and <sup>29</sup>Si NMR Studies of Mixed (Trialkylsilyl)cuprates. (Dimethylphenylsilyl)lithium (1) in THF was prepared by reaction of PhMe<sub>2</sub>SiCl and lithium metal (therefore contains LiCl).<sup>3a</sup> Solutions of this reagent at

#### Scheme I



1/3 PhMe2Si(Me)Cu(CN)Li2 + 1/3 (PhMe2Si)2CuLi2 + 1/3 (PhMe2Si)2Cu(CN)Li2 + 2/3 MeLi + 1/3 LiCN

-50 °C gave a <sup>29</sup>Si NMR signal at -28.5 ppm. Solutions of the mixed (trialkylsilyl)(methyl)cuprate,<sup>1b</sup>  $(PhMe_2Si)(Me)Cu(CN)Li_2$  (2) were prepared as described previously.<sup>2</sup> These solutions displayed a single <sup>29</sup>Si NMR signal at -20.6 ppm, indicating the presence of 2.

It has been shown<sup>2</sup> that the <sup>13</sup>C NMR spectrum of (PhMe<sub>2</sub>Si)(Me)Cu(CN)Li<sub>2</sub> (2) at -70 °C, prepared from a THF solution of MeCu(CN)Li (3) and PhMe<sub>2</sub>SiLi (1), consisted of seven lines: four in the phenyl region ( $\delta$  159.2, ipso; 135.3, ortho; 127.2, meta; 125.1, para), one nitrile ( $\delta$ 159.7), and two high field signals at  $\delta$  6.4 and -5.0. The latter two signals were assigned to a methyl bonded to silicon (6.4 ppm) and a methyl bonded to copper (-5.0 ppm), respectively.<sup>2,10</sup>

The <sup>13</sup>C, <sup>1</sup>H, and <sup>29</sup>Si NMR spectra of solutions containing 2 equiv of silyl anion and 1 equiv each of methyl anion and cuprous ion were next examined. Solutions generated by addition of 2 equiv of PhMe<sub>2</sub>SiLi (1) to solutions containing 1 equiv each of MeLi and CuCN or solutions generated by addition of 1 equiv of MeLi to solutions containing 2 equiv of PhMe<sub>2</sub>SiLi (1) and 1 equiv of CuCN would be expected to lead to the formation of one, or a combination, of several possible adduct mixtures. If the solutions composed of a 2:1:1 ratio of silyl anion to alkyl anion to cuprous ion were to display behavior analogous to alkylcuprates derived from CuCN,<sup>4a</sup> they would be expected to lead to the formation of an equivalent each of PhMe<sub>2</sub>Si(Me)Cu(CN)Li<sub>2</sub> (2) and PhMe<sub>2</sub>SiLi (1),

<sup>(1) (</sup>a) Fleming, I.; Newton, T. W. J. Chem. Soc., Perkin Trans. I 1984,
1805. (b) Fleming, I.; Newton, T. W.; Roessler, F. J. Chem. Soc., Perkin Trans. I 1981, 2527. (c) Fleming, I.; Roessler, F. J. Chem. Soc., Chem. Commun. 1980, 276. (d) Fleming, I.; Ager, D. J. J. Chem. Soc., Chem. Soc., Perkin Trans. I 1981, 2520.
(2) Oehlschlager, A. C.; Sharma, S. J. Org. Chem. In press.
(3) (a) Sharma, S.; Oehlschlager, A. C. Tetrahedron 1989, 45, 557. (b) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (c) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (d) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (e) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (d) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (e) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (b) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (c) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (c) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (d) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (e) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 45, 557. (d) Sharma, S.; Oehlschlager, A. C. J. Org. Chem. 1989, 54, 5383. (c) <sup>13</sup>C NMR values for (PhMe<sub>2</sub>Si)<sub>3</sub>CuLi<sub>2</sub> were recorded in THF at -70 °C. (d) (a) Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. J. Org. Chem. 1984, 49, 3943 and references cited therein. (b) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. Tetrahedron Lett. 1985, 5911.

<sup>lowski, J. A.; Breneman, C. M. Tetrahedron Lett. 1985, 5911.
(5) Ashby, A. C.; Watkins, John J. J. Am. Chem. Soc. 1977, 99, 5312.
(6) Gilman, H.; Cartledge, F. K.; See Yuen J. Organomet. Chem. 1963,</sup> 1, 8.

<sup>(7)</sup> Still, C. W.; Macdonald, T. L. Tetrahedron Lett. 1976, 2659.

<sup>(8) (</sup>a) Fleming, I. Frontier Orbitals and Organic Chemical Reactions; Wiley: London, 1976; Chapter 3. (b) Klopman, G. J. Am. Chem. Soc. 1968, 90, 223.

<sup>(9) (</sup>a) Pearson, R. G. J. Am. Chem. Soc. 1963, 85, 3533. (b) Pearson, R. G.; Songstad, J. J. Am. Chem. Soc. 1967, 89, 1827. (c) Pearson, R. G. Surv. Prog. Chem. 1969, 5, 1. (d) Pearson, R. G.; Ed. Hard and Soft Acids and Bases; Dowden, Hutchinson, and Ross: Stroudsberg, PA, 1973. (10) Note that these spectra were recorded at -35 °C and chemical shifts will vary somewhat from those reported for other spectra in ref 3a,b.



Figure 1. <sup>13</sup>C NMR spectra of (a)  $(PhMe_2Si)_2Cu(CN)Li_2$  (4) at -35 °C,<sup>11</sup> (b)  $(PhMe_2Si)_2Cu(CN)Li_2$  (4) + MeLi at -35 °C, (c)  $(PhMe_2Si)_2Cu(CN)Li_2$  (4) + excess MeLi at -35 °C, (d) Me\_2Cu-(CN)Li\_2 (8) at -35 °C, and (e) Me\_2Cu(CN)Li\_2 (8) + PhMe\_2SiLi (1) at -35 °C.

or an equivalent each of  $(PhMe_2Si)_2Cu(CN)Li_2$  (4) and MeLi. If the solutions containing a 2:1:1 ratio of silyl anion to alkyl anion to cuprous ion were to display behavior analogous to homo (trialkylsilyl)cuprates,<sup>3a,b</sup> they would be expected to lead to the formation of  $(PhMe_2Si)_2(Me)$ - $CuLi_2$  (5) and LiCN, or one half an equivalent each of  $PhMe_2Si(Me)_2CuLi_2$  (6) and  $(PhMe_2Si)_3CuLi_2$  (7) and 1 equiv of LiCN. It is also possible for solutions containing a 2:1:1 ratio of silv anion to alkyl anion to cuprous ion to simultaneously display behavior analogous to both alkylcuprates and homo (trialkylsilyl)cuprates. In this case the solutions would be expected to lead to any one, or a combination, of three possible mixtures (Scheme I): (1) one-half an equivalent each of PhMe<sub>2</sub>Si(Me)Cu(CN)Li<sub>2</sub> (2),  $(PhMe_2Si)_3CuLi_2$  (7), and MeLi and 1 equiv of LiCN; (2) one-third an equivalent each of  $Me_2Cu(CN)Li_2$  (8) and MeLi and two-thirds an equivalent each of  $(PhMe_2Si)_3CuLi_2$  (7) and LiCN; or (3) one-third an equivalent each of  $PhMe_2Si(Me)Cu(CN)Li_2$  (2),  $(PhMe_2Si)_3CuLi_2$  (7),  $(PhMe_2Si)_2Cu(CN)Li_2$  (4), and LiCN and two-thirds an equivalent of MeLi.

The <sup>13</sup>C NMR spectrum for the combination of 1 equiv of MeLi to preformed  $(PhMe_2Si)_2Cu(CN)Li_2$  (4) (Figure 1a) at -35 °C is shown in Figure 1b. Identical spectra were obtained for the 2:1 combination of PhMe<sub>2</sub>SiLi (1) and MeCu(CN)Li (3) at this temperature. These spectra exhibited five resonances of unequal intensity in the methyl region ( $\delta$  -14.6, -5.0, 6.0, 6.4, and 8.3) as well as signals in the phenyl region ( $\delta$  123.3, 125.4, 127.2, 135.3, 158.3, 159.7, 165.0), indicating the presence of more than one species. Addition of excess MeLi to either of the above solutions composed of a 2:1:1 ratio of silyl anion to methyl anion to cuprous ion resulted in an increase in intensity of the

Scheme II



resonance at  $\delta$  -14.6, while the intensities of the other peaks in the methyl region remained relatively unchanged (Figure 1c). The <sup>1</sup>H NMR spectrum of the combination of 1 equiv of MeLi to preformed (PhMe<sub>2</sub>Si)<sub>2</sub>Cu(CN)Li<sub>2</sub> (4) at -35 °C also exhibited five resonances of unequal intensity in the methyl region ( $\delta$  -2.0, -1.3, 0.08, 0.10, and 0.20) (for assignments see below) and sufficient multiplets in the aromatic region to indicate the presence of more than one species. Further addition of MeLi to this solution resulted in an increase of intensity of the resonance at  $\delta$ -2.0 while the intensity of the other peaks in the methyl region remained relatively unchanged. The <sup>29</sup>Si NMR spectrum of the combination of 1 equiv of  $PhMe_2SiLi$  (1) to preformed PhMe<sub>2</sub>Si(Me)Cu(CN)Li<sub>2</sub> (2) exhibited three resonances of unequal intensity in the methyl region ( $\delta$ -24.4, -20.6, -18.9), indicating the presence of three distinct species containing the silvl moiety.

In the <sup>13</sup>C spectrum for the solutions composed of a 2:1:1 ratio of silyl anion to alkyl anion to cuprous ion (Figure 1b) the signal at -5.0 ppm was assigned to the methyl group bonded to copper in PhMe<sub>2</sub>Si(Me)CuLi<sub>2</sub> (2) and the signal at 6.4 ppm is attributed to the methyl groups bonded to silicon in this species.<sup>2</sup> The signal at 6.0 ppm was assigned to the methyl groups bonded to silicon in (PhMe<sub>2</sub>Si)<sub>2</sub>Cu(CN)Li<sub>2</sub> (4)<sup>2</sup> and the signal at 8.3 ppm assigned to the methyl groups bonded to silicon in (PhMe<sub>2</sub>Si)<sub>3</sub>CuLi (7).<sup>3c</sup> The remaining signal at -14.6 ppm can be assigned to free MeLi and hence the stoichiometric ratio of the solution is maintained.

The signal at -1.3 ppm in the <sup>1</sup>H spectrum can be assigned to the methyl group bonded to copper in  $PhMe_2Si(Me)Cu(CN)Li_2$  (2) and the signal at 0.10 ppm can be assigned to the methyl groups bonded to silicon in this species. This signal at 0.08 ppm in the <sup>1</sup>H spectrum can be assigned to the methyl groups bonded to silicon in  $(PhMe_2Si)_2Cu(CN)Li_2$  (4), and the signal at 0.20 ppm can be assigned to the methyl groups bonded to silicon in  $(PhMe_2Si)_3CuLi_2$  (7). The signal at -2.0 ppm can be assigned to free MeLi<sup>5</sup> and the stoichiometric ratio is therefore maintained. The resonances observed in the <sup>29</sup>Si spectrum for the same solutions are attributed to  $(PhMe_2Si)_2Cu(CN)Li_2$  (4) ( $\delta$  -24.4)<sup>3a</sup> PhMe<sub>2</sub>Si(Me)Cu- $(CN)Li_2$  (6)  $(\delta - 20.6)$ ,<sup>2</sup> and  $(PhMe_2Si)_3CuLi_2$  (7)  $(\delta - 18.9)$ .<sup>3a</sup> A positive Gilman's test<sup>6</sup> for the solutions containing a 2:1:1 combination of silyl anion to alkyl anion to cuprous ion gives further evidence for the presence of free MeLi. A positive Gilman's test was observed even when less than 1 equiv of MeLi was used.

According to this analysis the mixed silyl(alkyl)cyanocuprates, wherein the silyl anion to alkyl anion to copper cation ratio is 2:1:1, exist in the dynamic equilibrium shown in Scheme II and contain 2, 4, 7, and MeLi. The observed equilibrium is consistent with those observed for alkylcyanocuprates<sup>4a</sup> in that when there is at least one alkyl

### Table I. Selectivity of Silyl Transfer in PhMe<sub>2</sub>Si(CH<sub>2</sub>)Cu(CN)Li<sub>2</sub> (2)

PhMe<sub>2</sub>Si(CH<sub>3</sub>)Cu(CN)Li<sub>2</sub> (2) + substrate  $\frac{\text{THF}}{-78 \, ^{\circ}\text{C}}$  products



<sup>a</sup>All methyl transfer products were detected by selected ion monitoring during mass spectral analysis (SIM-MS) and/or by coinjection with authentic sample.



group coordinated to copper with one other coordinated ligand, MeLi exchange is slow on the NMR time scale. The observed equilibrium is also consistent with those observed for homo(trialkylsilyl)cyanocuprates<sup>3a</sup> in that when there are two silyl groups coordinated with copper the third silyl ligand can coordinate to give species 7. Hence, solutions containing a 2:1:1 ratio of silyl anion to alkyl anion to cuprous anion display behavior analogous to both alkylcyanocuprates and homo(trialkylsilyl)cyanocuprates.

The <sup>13</sup>C NMR spectra of solutions containing 2 equiv of methyl anion and 1 equiv each of silyl anion and cuprous ion were next examined. The <sup>13</sup>C NMR spectrum of solutions generated from the combination of 1 equiv of PhMe<sub>2</sub>SiLi (1) to preformed Me<sub>2</sub>Cu(CN)Li<sub>2</sub> (8) (Figure 1d) at -35 °C displayed the presence of free MeLi in a similar fashion to those solutions composed of a 2:1:1 ratio of silyl anion to alkyl anion to cuprous ion (Figure 1b). Solutions generated from the combination of 2 equiv of MeLi to preformed PhMe<sub>2</sub>SiCu(CN)Li (5) gave a <sup>13</sup>C spectrum identical with that observed in Figure 1e. The <sup>13</sup>C spectrum for solutions containing PhMe<sub>2</sub>SiLi (1), MeLi, and CuCN in a 1:2:1 ratio show resonances in the methyl region consistent with the presence of  $PhMe_2Si(Me)Cu(CN)Li_2$ (2) and free MeLi. The signal at 6.4 ppm is attributed to the methyls bonded to silicon in 2 and the signal at -5.0ppm is attributed to the methyl bonded to copper in this species. The four signals in the phenyl region at 159.2, 135.3, 127.2, and 125.1 ppm can be attributed to the phenyl group on the silicon in 2, and the signal at 159.7 ppm can be attributed to the nitrile in  $2.^2$  The signal at -14.6 ppm can be attributed to free MeLi. These solutions gave a positive Gilman's test, confirming the presence of free MeLi. A positive Gilman's test was observed even when less than 2 equiv of MeLi was used.

According to this analysis the mixed silyl(alkyl)cyanocuprates, wherein the silyl anion to alkyl anion to copper cation ratio is 1:2:1, also exist in the dynamic equilibrium shown in Scheme III and contain 2 and MeLi. The absence of cuprates containing two or three silyl moieties in these solutions indicates that solutions containing an excess of alkyl anion tend to display behavior analogous to alkylcyanocuprates.<sup>4a</sup>

The  $^{13}$ C NMR spectrum of solutions generated by the addition of 3 equiv of PhMe<sub>2</sub>SiLi (1) to preformed MeCu(CN)Li (9) gave signals attributable to  $7^3$  and free MeLi. These solutions, wherein the silyl anion to alkyl anion to copper cation ratio is 3:1:1, exhibit behavior characteristic of the dynamic equilibrium shown in Scheme IV and contain 7 and MeLi. Absence of cuprates containing alkyl moieties in these solutions indicates that solutions containing a greater than twofold excess of silyl anion tend to display behavior analogous to homo(trialkylsilyl)cyanocuprates.

The appearance of free MeLi in solutions containing a 2:1:1 combination or a 1:2:1 combination of silyl anion to alkyl anion to cuprous ion indicates that the exchange of MeLi with cuprates 2 and 4 is slow on the NMR time scale. The presence of only  $(PhMe_2Si)_3CuLi$  (7) and MeLi in solutions containing a 3:1:1 combination of silyl anion to alkyl anion to cuprous ion indicates that the exchange of PhMe<sub>2</sub>SiLi (1) is fast on the NMR time scale.

The mixed reagents  $(PhMe_2Si)_m(CH_3)_nCu(CN)Li_{m+n}$ offer significant opportunities for conservation of the more valuable trialkylsilyl residues.  $(PhMe_2Si)(Me)Cu(CN)Li_2$ (2) efficiently transfers its silyl ligand to cyclohex-2-en-1one in a Michael addition<sup>1,7</sup> to the virtual exclusion of methyl transfer. Product yields are higher than for the classical homo(trialkylsilyl)cuprate<sup>1</sup> because of simplification in isolation procedures since methane is the hydrolysis product whereas  $R_3SiSiR_3$ ,  $R_3SiH$ , and  $R_3SiOH$ are the side products obtained on workup of homo(trialkylsilyl)cuprates. Likewise, solutions containing a silyl anion to methyl anion to cuprous ion ratio of 2:1:1 react with 2 equiv of cyclohex-2-en-1-one in a Michael addition to the exclusion of Me transfer. Similarly, solutions containing a 1:2:1 ratio of the same ions react with 1 equiv of

#### Mixed Higher Order Cuprate Chemistry

 $(PhMe_2Si)(CH_3)Cu(CN)Li_2$  (2) was reacted with a series of substrates under the same conditions as were used in the reaction of 2 with cyclohex-2-en-1-one to broaden the scope of synthetic utility of mixed (trialkylsilyl)cuprates already demonstrated by our lab<sup>2</sup> and others<sup>1,7</sup> (Table I). The cuprate 2 transfers the silyl moiety to a primary alkyl bromide in an  $S_N 2$  fashion to the virtual exclusion of methyl transfer. The products resulting from methyl transfer were detected in very small amounts (<5%), using selected ion monitoring for GC/MS analysis (SIM-MS). Surprisingly, cuprate 2 transferred the silyl moiety less preferentially over the methyl group when reacted with a terminal epoxide.

The above has shown preferential transfer of  $R_3Si$  to enones and other organic substrates. We have suggested that for mixed (trialkylsilyl)(alkyl)cuprates the ligand that migrates is the one which is least tenaciously bound to copper.<sup>2</sup> The preferential migration of the  $R_3Si$  ligands can thus be rationalized as being due a weaker Si–Cu bond. Although the cyanide anion is the least basic ligand in these mixed cuprates and hence would be expected to have a weak nitrile-copper bond, it is not transferred. It is possible that backbonding increases the relative strength of the nitrile-copper bond, making cyanide a nontransferrable ligand.

An alternative qualitative hypothesis can be derived from the HSAB principle and frontier orbital theory.<sup>8</sup> The methyl anion is harder and less polarizable than the phenyldimethylsilyl anion. The former will therefore have a HOMO that is low in energy in comparison with the HOMO of the latter.<sup>9</sup> The copper(I) cation is classified as a soft electrophile<sup>9</sup> and thus has a low-lying LUMO. Copper(I) will experience *less net stabilization* upon bond formation with the low-energy HOMO of the methyl anion than with the high-energy silyl anion HOMO. Methyl anion can therefore be ejected from higher order cuprates by silyl anion because of more orbital interaction between the HOMO of the silyl anion and the LUMO of the copper(I) cation.

This reasoning also explains the preferential transfer of the silvl moiety in reactions of (PhMe<sub>2</sub>Si)(CH<sub>3</sub>)Cu(CN)Li<sub>2</sub> (2) with organic substrates. Thus, the HOMO for the silicon-copper bond in 2 will be of higher energy than that for the carbon-copper bond. When cuprate 2 reacts with soft electrophiles such as enones, allylic halides, or alkylbromides that have low-energy LUMO's, the ligandcopper bond having the more orbital interaction with the LUMO of the substrate will be the ligand that is transferred. In this case the high-energy HOMO of the silicon-copper bond has more interaction with the low-energy LUMO of the substrate and the silvl moiety is transferred selectively. In the substitution reaction of cuprate 2 with the terminal carbon of an epoxide (classified as a hard electrophile and having a high-energy LUMO in comparison with unsaturated substrates) the low-energy HOMO of the carbon-copper bond has more interaction with the LUMO of the carbon-oxygen bond than it does with the LUMO of other more polarizable substrates. Hence, although the silyl moiety is still transferred preferentially, methyl is transferred to a significant extent in this reaction.

Likewise, it can be reasoned that  $R_3Sn(R)_2CuLi_2^{11}$  is formed upon combination in THF of a 1:2:1 ratio of stannyl anion:alkyl anion:cuprous ion whereas  $R_3Si(R)_2CuLi_2$  cannot be formed upon combination in THF of a 1:2:1 ratio of silyl anion:alkyl anion:cuprous ion. The formation of either of these cuprate complexes requires the displacement of the nitrile anion by the trialkylstannyl anion or the trialkylsilyl anion. Since the HOMO of the trialkylstannyl anion is higher lying than that of silyl anion, it is more likely to displace the nitrile anion due to more interaction with the LUMO of the  $R_2CuLi$  fragment. The  $R_3Si(R)_2CuLi_2$  species is difficult to form because the HOMO of the nitrile anion has more interaction with the LUMO of the  $R_2CuLi$  fragment than does the HOMO of the trialkylsilyl anion.

These hypotheses, while solely qualitative in nature, suggest study of reactions of cuprates containing a greater variety of ligands with electrophilic substrates of varying hardness would be of interest.

#### **Experimental Section**

General Methods. All glassware and syringes were dried in an oven overnight at 120 °C, and glassware was flame dried and flushed with argon immediately prior to use. Syringes were flushed with argon and kept under positive argon pressure until use. Transfer of reagents was performed by syringes equipped with stainless steel needles. Reactions were carried out under argon in round-bottom flasks equipped with septa and Teflon-coated magnetic stirring bars. Transfer of CuCN took place in a glovebag. All alkyllithiums were freshly titrated before use.<sup>7</sup> Tetrahydrofuran was freshly distilled over potassium benzophenone-ketyl. Unless otherwise stated, other chemicals obtained from commercial sources were used without further purification. Lowtemperature <sup>29</sup>Si NMR experiments were conducted on a Bruker WM-400 spectrometer with an operating frequency of 79.495 MHz. A typical set of parameters utilized a spectral width of 20000 Hz, 8K of memory, 2.44 H/data point, an acquisition time of 0.204 s, and a 15° pulse of 10  $\mu$ s. The decoupler was turned on during acquisition and off during the relaxation delay (4 s) in order to suppress the negative NOE of <sup>29</sup>Si. A line broadening of 20 Hz was applied to all spectra. Spectra were recorded in THF that contained Me<sub>4</sub>Si as internal reference. <sup>13</sup>C NMR spectra were obtained on a Bruker AMS-400 spectrometer with an operating frequency of 100.62 MHz. The spectra were recorded on THF solutions unless otherwise specified and were referenced to THF,  $\alpha = 26.7$  ppm,  $\beta = 68.6$  ppm. Low-temperature <sup>1</sup>H NMR spectra were recorded on a Bruker AMX400 spectrometer with an operating frequency of 400.13 MHz in THF. The peaks are referenced to THF,  $\alpha = 1.85$  ppm,  $\beta = 3.75$  ppm. A vacuum-jacketed, glass dewar measuring  $7.5 \times 16.0$  cm (i.d. 5.5 cm) was designed with tapering bottom to fit in the cup of the vortex mixer. All NMR samples were stirred while cooling at the indicated temperatures in this dewar.

**Preparation of PhMe<sub>2</sub>SiLi (1) in THF.** Dimethylphenylsilyl chloride was stirred with small pieces of lithium in THF (20 mL) at -5 °C in an ice/salt bath as described in ref 2. (Dimethylphenylsilyl)lithium was titrated according to the procedure of Fleming et al.<sup>1b</sup>

**Preparation of PhMe<sub>2</sub>Si(Me)Cu(CN)Li<sub>2</sub> (2). 2** was prepared as described in ref 2.

**Reaction of PhMe**<sub>2</sub>Si(Me)Cu(CN)Li<sub>2</sub> (2) and PhMe<sub>2</sub>SiLi (1). (Dimethylphenylsilyl)lithium (1) in THF (1.03 mL, 1.0 mmol) was added dropwise via syringe to a THF solution of PhMe<sub>2</sub>Si-(Me)Cu(CN)Li<sub>2</sub> (2) (1.0 mmol)<sup>2</sup> in a 10-mm NMR tube equipped with a septum under argon at -50 °C and vortex stirred at this temperature for 10 min before recording the <sup>29</sup>Si NMR spectrum.

Typical Procedure for Preparation of Solutions Containing a 2:1:1 or 1:2:1 Ratio of PhMe<sub>2</sub>SiLi (1), MeLi, and CuCN. To a round-bottom flask containing CuCN (0.269 g, 3.0 mmol) in 20.0 mL of THF at -50 °C was added PhMe<sub>2</sub>SiLi (6.19 mL, 6.0 mmol) dropwise via a syringe, and the solution was stirred 1 h under a positive pressure of argon. A 3.0-mL aliquot was removed via cooled syringe and placed in a 10-mm NMR sealed with a septum. The presence of (PhMe<sub>2</sub>Si)<sub>2</sub>Cu(CN)Li<sub>2</sub> was confirmed by NMR and the concentration calculated (3.0 mL × 0.115 M = 0.35 mmol) before adding MeLi in Et<sub>2</sub>O (0.25 mL, 0.35

<sup>(11)</sup> In a parallel study we found that mixing (trialkylstannyl)lithium, alkyllithium, and cuprous cyanide in a 1:1:1 ratio gave a new reagent,  $R_3Sn(R)Cu(CN)Li_2$ , and that when the ratio was changed to 1:2:1 a new reagent,  $R_3Sn(R)_2CuLi_2$ , was generated: S. Sharma, unpublished results.

mmol) to the NMR tube. The solution was vortex stirred for 10 min before recording the NMR spectra of the solution containing a 2:1:1 ratio of PhMe<sub>2</sub>SiLi, MeLi, and CuCN.

Typical Procedure for Reactions of PhMe<sub>2</sub>SiLi/MeLi/ CuCN Solutions with 2-Cyclohexen-1-one. PhMe<sub>2</sub>SiLi (3.00 mL, 3.0 mmol) was added dropwise at -78 °C to a solution of MeCu(CN)Li [(3.0 mmol, prepared from the addition of MeLi in Et<sub>2</sub>O (2.14 mL, 3.0 mmol) and CuCN (0.269 g, 3.0 mmol in THF (20 mL) at -50 °C)] in THF (22.14 mL) under argon. The resulting deep red solution was stirred for 0.5 h after which cyclohexenone (0.29 mL, 3.0 mmol) was added via a syringe. Reactions were stirred for a further 0.5 h and then guenched with 2 N HCl. Workup involved extraction of the organic phase with Et<sub>2</sub>O ( $3 \times 15$  mL). The combined extracts were dried over anhydrous MgSO<sub>4</sub> and concentrated in vacuo. Flash column chromatography (5:1 hexanes:EtOAc) yielded 3-(dimethylphenylsilyl)cyclohexanone in 82% isolated yield and >95% purity as judged by gas chromatographic analysis. The <sup>1</sup>H NMR and IR data for the 1.4-adduct matched those reported by Fleming et al.<sup>1</sup> for this compound:  ${}^{13}C$  (CDCl<sub>3</sub>)  $\delta$  212.5, 136.6, 133.8, 129.2, 127.8, 42.3, 41.8, 29.7, 27.5, 26.0, -5.4, -5.5; MS m/e (rel intensity) 232 (M<sup>+</sup>, 20), 217 (15), 189 (5), 156 (22), 135 (100).

Typical Procedure for Reactions of (PhMe<sub>2</sub>Si)(CH<sub>2</sub>)Cu-(CN)Li<sub>2</sub> (2) with Organic Substrates. PhMe<sub>2</sub>SiLi (3.00 mL, 3.0 mmol) was added dropwise at -78 °C to a solution of MeCu(CN)Li [prepared as above] in THF (22.14 mL) under argon. The resulting deep red solution was stirred for 0.5 h after which 3.0 mmol of the organic substrate dissolved in 5.0 mL of THF was added via cannula. Reactions were stirred for a further 1.5 h at -78 °C and then quenched with saturated NH<sub>4</sub>Cl. Workup involved extraction of the organic phase with  $Et_2O$  (3 × 15 mL). The combined extracts were dried over anhydrous MgSO4 and concentrated in vacuo. Compounds were purified by flash column chromatography (10:1 hexanes:EtOAc).

Reaction of (PhMe<sub>2</sub>Si)(CH<sub>3</sub>)Cu(CN)Li<sub>2</sub> (2) with 1,2-Epoxyoctane. Methyl transfer product (nonan-3-ol): <sup>1</sup>H NMR

(CDCl<sub>3</sub>) § 3.5 (m, 1 H, CHOH), 1.56-1.34 (m, 5 H, CH<sub>2</sub>), 1.28 (m, 7 H,  $CH_2$ ), 0.93 (t, J = 7.83 Hz, 3 H,  $CH_3$ ), 0.87 (t, J = 6.96 Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) § 73.23, 36.87, 31.74, 30.04, 29.28, 25.52, 22.50, 13.93, 9.72; GC/MS, m/e (rel intensity) 126 (M<sup>+</sup> -18, 6.4), 115 (30.6), 97 (76.1), 69 (20.6), 59 (100.0); HRMS m/e (M - 18) calcd 126.2412, obsd 126.1412 (96% pure by GC). Phenyldimethylsilyl transfer product (1-(phenyldimethylsilyl)octan-2-ol): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.58-7.32 (m, 5 H, Ar), 3.78 (m, 1 H, CHOH), 1.48-1.33 (m, 2 H, CH<sub>2</sub>), 1.33-1.16 (m, 8 H, CH<sub>2</sub>'s),  $1.16-1.02 \text{ (m, 2 H, CH}_2), 0.88 \text{ (t, } J = 8.00 \text{ Hz}, 3 \text{ H, CH}_3), 0.35 \text{ (s,}$ 6 H, SiCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 139.33, 133.55, 128.92, 127.82, 69.91, 40.86, 31.79, 29.19, 25.76, 25.63, 22.56, 14.03, -2.26; GC/MS m/e (rel intensity) 262 (M<sup>+</sup> - 2, 9.9), 247 (63.5), 185 (59.3), 137 (100.0), 101 (16.5); HRMS m/e (M - 2) calcd 262.4663, obsd 262.1762 (98% pure by GC).

Reaction of (PhMe<sub>2</sub>Si)(CH<sub>3</sub>)Cu(CN)Li<sub>2</sub> (2) with 2-Methyl-2-(3-bromopropyl)-5,5-dimethyl-1,3-dioxane. Phenyldimethylsilyl transfer product (2-methyl-2-(3-(phenyldimethylsilyl)propyl)-5,5-dimethyl-1,3-dioxane): <sup>1</sup>H NMR (CDCl<sub>2</sub>)  $\delta$  7.57-7.27 (m, 5 H, Ar), 3.52 (d,  $J_{gem} = 11.30$  Hz, 2 H, ring CH<sub>2</sub>), 3.41 (d,  $J_{\text{gem}} = 11.30$  Hz, 2 H, ring  $CH_2$ ), 1.72 (m, 2 H,  $CH_2$ ), 1.47 (m, 2 H,  $CH_2$ ), 1.33 (s, 3 H,  $CH_3$ ), 0.99 (s, 3 H,  $CH_3$ ), 0.90 (s, 3 H, CH<sub>3</sub>), 0.78 (m, 2 H, CH<sub>2</sub>), 0.28 (s, 6 H, SiCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) & 139.59, 133.54, 128.73, 127.69, 98.92, 70.30, 41.77, 29.93, 22.71, 20.45, 17.82, 16.10, -2.98; GC/MS m/e (rel intensity) 307 (M<sup>+</sup>, 70.1), 229 (13.9), 143 (100.0), 129 (20.1), 105 (14.0); HRMS m/e (M<sup>+</sup>) calcd 306.5193, obsd 306.2000 (90% pure by GC).

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## Photochemistry of Benzophenone-Capped $\beta$ -Cyclodextrin

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The photochemistry of  $6^{A}$ ,  $6^{C}$ -(3,3'-benzophenonedisulfonyl)- $\beta$ -cyclodextrin (1) is explored. Irradiation of 1 in H<sub>2</sub>O or aqueous CH<sub>3</sub>CN results in regioselective oxidation of a glucose C6 hydroxymethyl group, giving 2a and 2b via intramolecular H-abstraction by the excited benzophenone group. Molecular mechanics calculations suggest that the photooxidation occurs at the E and F glucose residues. In contrast, irradiation of 1 in aqueous *i*-PrOH gives rise to pinacol coupling products 3a-c.

#### Introduction

Cyclodextrins (CDs) are well-known host molecules that find extensive use in complexation and catalysis studies.<sup>1</sup> Their well-defined cavities, small size, and ease of functionalization make them ideal enzyme models.<sup>2</sup> A number of interesting catalysts have been synthesized from CDs.<sup>3</sup> Cyclodextrins also have been used to modify photochemical reactions;<sup>4</sup> however, only a few photochemically active, derivatized CDs have been created. Among the photoreactive groups attached to CDs are benzophenone, rose bengal, and porphyrin moieties.<sup>5-7</sup> We have recently reported the photochemistry of several anthraquinone-substituted  $\beta$ -CDs<sup>8</sup> and found that they undergo facile intramolecular H-abstraction upon irradiation. On the other hand, Tabushi and co-workers report that benzophenone-capped  $\beta$ -CD is an effective triplet sensitizer in frozen solutions.<sup>5</sup> Since photoexcited benzophenone also

<sup>(1)</sup> Bender, M. L.; Komiyama, M. Cyclodextrin Chemistry, Spring-er-Verlag: New York, 1978. Saenger, W. Angew Chem., Int. Ed. Engl. 1980, 19, 344-362.

<sup>(2)</sup> Breslow, R. Science 1982, 218, 532-537. Tabushi, I. Acc. Chem. Res. 1982, 15, 66-72. D'Souza, V. T.; Bender, M. L. Acc. Chem. Res. 1987, 20, 146-152.

Croft, A. P.; Bartsch, R. A. Tetrahedron 1983, 39, 1417–1474.
 Ramamurthy, V.; Eaton, D. F. Acc. Chem. Res. 1988, 21, 300–306. Ramamurthy, V. Tetrahedron 1986, 42, 5753-5839.

<sup>(5)</sup> Tabushi, I.; Fujita, K.; Yuan, L. C. Tetrahedron Lett. 1977, 2503-2506.

 <sup>(6)</sup> Neckers, D. C.; Paczkowski, J. J. Am. Chem. Soc. 1986, 108, 291-292. Neckers, D. C.; Paczkowski, J. Tetrahedron 1986, 2, 4671-4683.
 (7) Gonzalez, M. C.; McIntosh, A. R.; Bolton, J. R.; Weedon, A. C. J.

Chem. Soc., Chem. Commun. 1984, 1138-1140. (8) Aquino, A. M.; Abelt, C. J.; Berger, K. L.; Darragh, C. L.; Kelley, S. E.; Cossette, M. V. J. Am. Chem. Soc. 1990, 112, 5819-5824.