aryl-substituted homocuprates $[R_2Cu]Li$, the copper atom of **2** exhibits a linear geometry, and the Cu–C distance in **2** (1.940 (6) Å) compares favorably with those found in $[CuMe_2]^-$ (1.935 (8) Å), $[CuPh_2]^-$ (1.925 (10) Å av), and $[Cu(Br)CH(SiMe_3)_2]^-$ (1.920 (6) Å).[4c,9] However, one important difference between the structure of **2** and those of the homocuprates is that the lithium is bound to the heteroatom (P). The approximately tetrahedral geometries at phosphorus and lithium of **2** are similar to those in $[Cu(t\text{-}Bu_2P)_2][Li(THF)_2]$ (**6**).[5] However, in **6** each lithium is bonded to two phosphorus atoms rather than one as in the case of **2**, and this is reflected in the different number of THF molecules. A further consequence of this difference in ligation is that the Li–P interaction is considerably stronger in **2** (2.54 (1) Å) than in **6** (2.837 (7) Å). This parameter may be compared to that found in $[Li(DME)(PH_2)]_\infty$ (DME = 1,2-dimethoxyethane) (2.574 (8) Å av)[10] and $[Li(THF)_2PPh_2]_\infty$ (2.63 (2) Å)[11] in which the Li atoms also have distorted tetrahedral geometries. An additional interesting structural feature is that the Cu–P bond distance in **2** (2.217 (2) Å) is shorter than that in **6** (2.256 (5) Å av).

The results of the reactions of these novel phosphido(alkyl)cuprates **2–5** with a variety of electrophiles are summarized in Table I,[12] and several general comments are appropriate. As evidenced by a comparison of reaction times, a preliminary survey has revealed that the phosphido(*n*-butyl)cuprate **3** was only slightly less reactive in conjugate additions to enones than lithium dibutylcuprate or the corresponding higher order cuprate derived from copper cyanide.[2c] Although **3** readily effected the displacement of primary iodides and bromides, it did not undergo reaction with secondary iodides. Furthermore, whereas **3** added readily to disubstituted epoxides, trisubstituted epoxides were unreactive, perhaps because of the steric bulk of **3**. Finally, α- and β-monosubstituted unsaturated esters underwent smooth conjugate addition upon reaction with **3**, but this reagent did not add in the desired 1,4-sense to either α,β- or β,β-disubstituted enoate systems. Thus, these new phosphido(alkyl)cuprates $[RCuP(t\text{-}Bu)_2Li]$ exhibit reactivity profiles that are comparable with other related phosphido(alkyl)cuprates $[RCuPPh_2Li]$ (**7**) and $[RCu(c\text{-}C_6H_{11})_2PLi]$ (**8**),[3b-d] but they do not appear to be as reactive as the higher order cyanocuprates $[(R_2CuCN)Li_2]$.[2c,e]

On the other hand, a significant difference between the thermal stability of the previously described phosphido(alkyl)cuprates **7** and **8**[3b-d] and these new phosphido(alkyl)cuprates **3–5** was observed. For example, the heterocuprates **3–5** are extremely stable in THF retaining >96% of their activity after 4 h at room temperature,[12] whereas the corresponding cuprates **7** and **8** began to decompose at room temperature in THF after only 30 min. Indeed, the phosphido(*n*-butyl)cuprate **3** in THF suffered less than 15% decomposition after 24 h at room temperature or 4 h at reflux. As expected, these phosphido(alkyl)cuprates were slightly less stable when dissolved in diethyl ether. The enhanced thermal stability of these and related phosphido(alkyl)cuprates should prove advantageous in reactions with less reactive electrophiles.

In summary, our initial investigations of the structurally novel phosphido(alkyl)cuprates **2–5** have revealed that these thermally stable organocopper reagents react as "normal" organocuprates in a number of synthetically important transformations, including conjugate addition, halide displacement, and epoxide opening. Future work will be directed toward the study of other related phosphidocuprates with the goal of developing superior reagents for carbon–carbon bond constructions. The results of these studies will be reported in due course.

Acknowledgment. We thank the National Institutes of Health (CA 37929), the Robert A. Welch Foundation, and the National Science Foundation for generous financial support of this research. We are also grateful to the NSF (CHE8305785) and the NIH (RR01912) for NMR facilities.

Supplementary Material Available: Experimental details for the generation of **2–5** and their subsequent reactions with electrophiles; experimental details for the stability studies of **3–5**; and tables of bond lengths, angles, positional parameters, and thermal parameters for **2** (8 pages); table of observed and calculated structure factors for **2** (16 pages). Ordering information is given on any current masthead page.

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[9] As noted previously,[4b,c] the somewhat long Cu–C distance observed for $[Cu\{C(SiMe_3)_3\}_2]^-$ (2.027 (7) Å) may be due to disorder problems.

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[11] Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243.

[12] See Supplementary Material for experimental details.

The Reactions of Diorganosilylenes with Carbon Monoxide

Mary-Ann Pearsall and Robert West*

Department of Chemistry
University of Wisconsin-Madison
Madison, Wisconsin 53706

Received June 30, 1988

There has been much interest recently in the Lewis acid behavior of divalent silicon, particularly of diorganosilylenes which have been shown to form stable acid–base complexes with low-temperature matrix isolation techniques.[1-4] We now report our studies of the interactions of diorganosilylenes with carbon monoxide in frozen hydrocarbon matrices at 77 K.[5,6]

Solutions of the appropriate silylene precursor $RR'Si(SiMe_3)_2$ (**1a–c**) or $(Me_2Si)_6$ (**1d**) in the hydrocarbon were saturated with carbon monoxide (900 Torr) at room temperature. The solutions were cooled to 77 K, and silylenes (**2a–d**) were then generated by irradiation of the matrix at 254 nm.[7] The interaction of silylenes with CO was monitored by observing the UV–vis spectrum of the reaction mixture, both at 77 K and upon warming.

$$\underset{\mathbf{1}}{\mathrm{(Mes(R)Si(SiMe_3)_2}} \xrightarrow[77\ K]{h\nu} \underset{\mathbf{2a-c}}{\mathrm{Mes(R)Si:}} \xrightarrow{CO}$$

1a, R = mesityl
b, R = 2,6-diisopropylphenoxy
c, R = *tert*-butyl

$$\underset{\mathbf{3a-c}}{\mathrm{Mes(R)Si{:}CO}} \longrightarrow \underset{\mathbf{4a-c}}{\mathrm{MesRSi{=}SiRMes}} \qquad (1)$$

$$\underset{\mathbf{1d}}{\mathrm{(Me_2Si)_6}} \xrightarrow{h\nu} \underset{\mathbf{2d}}{\mathrm{Me_2Si:}} \longrightarrow \underset{\mathbf{3d}}{\mathrm{Me_2Si{:}CO}} \qquad (2)$$

In 3-methylpentane (3-MP), which forms a rigid matrix at 77 K, **1a** and **1b** gave silylenes **2a** and **2b**, identified by their characteristic visible absorption bands (Figure 1). Annealing of the matrix resulted in disappearance of those bands and growth of a new band at shorter wavelength (Table I), which we attribute to the silylene–CO complex, **3a** or **3b**. (Similar absorptions are observed for other silylene acid–base complexes.)[1,4] Upon further

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[4] Gillette, G. R.; Noren, G. H.; West, R. *Organometallics*, in press.

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[6] A recent communication reports that no reaction takes place between SiH_2 and CO in the gas phase. See: Chu, J. O.; Beach, D. B.; Estes, R. D.; Jasinski, J. M. *Chem. Phys. Lett.* **1988**, *143*, 135.

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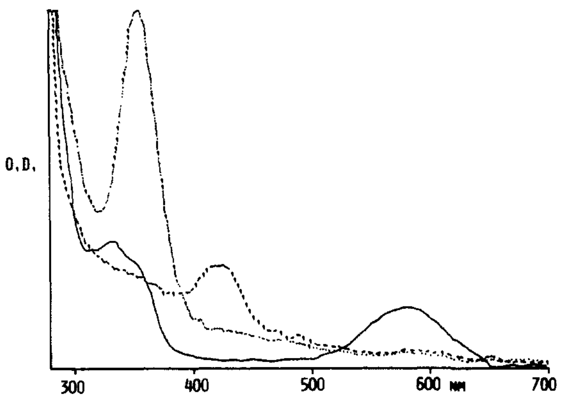


Figure 1. Reaction of Mes_2Si: with CO in rigid matrix: (—), after photolysis at 77 K, showing silylene absorptions; (···), after annealing, band at 354 is assigned to CO complex; (---), further warming, showing disilene spectrum.

Table I

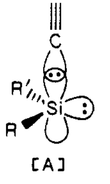
R, R′	RR′Si:	RR′Si:CO	RR′Si=SiRR′
mes, mes	580, 330	354, 284	420
mes, *t*-Bu	505, 290	338, 290	330
Me, Me	454	345	not obsd
mes, OAr	398	328	380, 342

warming the new band disappeared as absorptions for the disilenes **4a** and **4b** grew in.

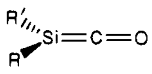
With precursors **1c** and **1d**, photolysis in 3-MP gave not only the absorption bands for silylenes **2c**,**2d** but also an absorption attributed to the complex **3c**,**3d**. On standing for several hours the complex band grew more intense, while the silylene band decreased. Annealing of the matrix led to complete disappearance of the silylene band and a simultaneous large increase of the absorption band near 350 nm attributed to the complex. Further warming gave the stable disilene **4c** from **3c**. In the dimethylsilylene case further warming gave products with no absorption longer than 300 nm.

Photolysis of **1a–d** was also carried out in a 4:1 2-methylbutane:3-methylpentane mixture, which forms a soft matrix at 77 K.[8] Under these conditions only the absorption bands attributed to the silylene–CO complex were observed. Annealing of the matrix led again to the disilenes **4a–c** but not **4d**.

Carbon monoxide might react with silylenes to give a nonplanar complex (A) or might combine to form a silaketene (B). Silylene–CO complexes **3a–c** behave similarly to other acid–base complexes of silylenes **2a–c** with donor molecules in that they produce disilenes (**4a–c**) when the matrix is melted.[1,4] These results are consistent with formulation of the CO adducts as acid–base complexes (A) rather than silaketenes (B), which would not be expected to dissociate readily. Recent theoretical calculations also indicate that A is more stable than B.[9]



[A]



[B]

Weak absorption bands at longer wavelength were also observed in matrices containing large amounts of **3b**, **3c**, and **3d**, at 425 (sh), 610, and 590 nm, respectively (Figure 2). Observation of these additional bands was easier in the soft matrices, where photogeneration of the silylene–CO complex was most efficient. These bands also disappear upon melting of the matrix, but at present it is not certain whether they arise from the silylene–CO complexes **3b–d** or from some other species generated simultaneously.[10]

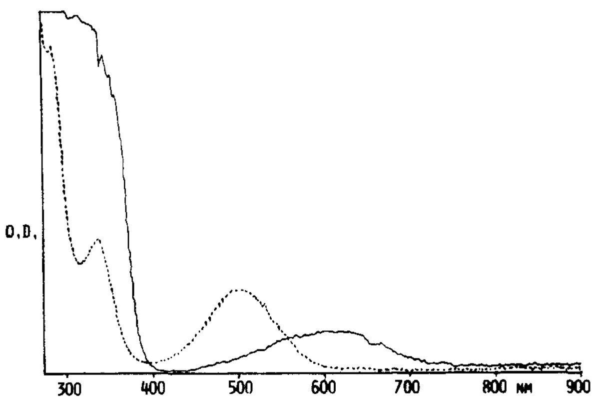


Figure 2. Interaction of Mes(*t*Bu)Si: with CO at 77 K: (---), irradiation in 3-MP; band at 505 is due to silylene, band at 338 is assigned to CO complex; (—), irradiation in soft matrix showing bands at 338 and 610.

Formation of the CO complexes **3c** and **3d** from silylenes **2c** and **2d** in 3-MP at 77 K requires that CO migrate through the rigid 3-MP matrix at this temperature. Silylene complexes **3a** and **3b** however were observed in 3-MP only when the matrix is annealed. Tentatively, we suggest that conformational effects prevent the formation of the complexes from **2a** and **2b** in the rigid matrix. Warming of the matrix may allow relaxation of the silylenes to conformations which can react with CO to give the observed complexes.

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF under Contract no. F49620-86-0010 and National Science Foundation Grant no. CHE-8318820-02.

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(10) The long wavelength absorptions might possibly be due to $R_2Si{:}O{\equiv}C$ complexes in which the carbonyl oxygen serves as the electron donor. Complexes between the ketone, tetramethylindanone, and silylenes have been reported to absorb near 600 nm (see ref 4). The long wavelength band was not observed for **3a**, probably because of the difficulty in generating high concentrations of silylene **2a** in hydrocarbon matrices.

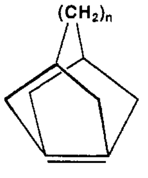
Synthesis of Homocub-4(5)-ene: Confirmation of a Computational Prediction

David A. Hrovat and Weston Thatcher Borden*

Department of Chemistry, University of Washington
Seattle, Washington 98195

Received June 6, 1988

We have reported the synthesis of the $n = 1$[1] and $n = 2$[2] members of a homologous series of pyramidalized alkenes (**1**),



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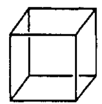

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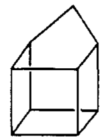

3

and we have also published the synthesis and X-ray crystal structure of the 10-methylselenonium derivative of the $n = 3$ hydrocarbon.[3] More recently, we have reported the results of

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