**Table I.** Relative Integrated Intensities of $\nu_3$ for $N_3^-$ Isotopomers

| | $^{14}N^{14}N^{14}N^-$ | $^{14}N^{14}N^{15}N^-$ | $^{15}N^{14}N^{15}N^-$ | $^{14}N^{15}N^{14}N^-$ | $^{14}N^{15}N^{15}N^-$ | $^{15}N^{15}N^{15}N^-$ |
|---|---|---|---|---|---|---|
| $^{14}N^{15}N$:$^{14}N_2$ (10:1) | | | | | | |
| obsd | 0.0 | 1.2 | 0.7 | 0.7 | 1.0 | 0.0 |
| calcd scrambled | 0.2 | 1.3 | 0.5 | 0.7 | 1.0 | 0.0 |
| calcd end-on | 0.2 | 1.4 | 1.0 | 1.2 | 1.0 | 0.0 |
| calcd scrambled +20% end-on | 0.2 | 1.3 | 0.6 | 0.8 | 1.0 | 0.0 |
| $^{15}N_2$:$^{14}N_2$ (1:1.4) | | | | | | |
| obsd | 1.6 | 1.1 | 0.3 | 0.4 | 0.9 | 1.0 |
| calcd scrambled | 2.0 | 0.9 | 0.5 | 0.5 | 0.9 | 1.0 |
| calcd end-on | 2.0 | 1.4 | 0.0 | 0.0 | 1.4 | 1.0 |
| calcd scrambled +20% end-on | 2.0 | 1.0 | 0.4 | 0.4 | 1.0 | 1.0 |

**Table II.** SCF[a] Optimized Geometries for the $N_3^-$ Anion

| state | symmetry | en[b] (au) | rel en,[b] (kcal/mol) | $R_{NN}$ (Å) | harmonic freq (cm$^{-1}$) |
|---|---|---|---|---|---|
| $^1\Sigma_g^+$ | $D_{\infty h}$ | −163.31968 | 0 | 1.151[c] | 2190 ($\sigma_u$),[d-f] 1553 ($\sigma_g$),[e,f] 706 ($\pi_u$)[e] |
| $^3B_2$ | $C_{2v}$ | −163.28132 | 24.0 | 1.240 | 1423 ($a_1$), 1181 ($b_2$), 708 ($a_1$) |
| $^3A'_2$ | $D_{3h}$ | −163.25148 | 42.7 | 1.362 | 1567 ($a'_1$), 1025 ($e'$) |

[a] 6-311+G* (5 d components). Restricted HF for singlet, unrestricted HF for triplets. [b] Not corrected for zero-point energies. [c] Observed,[19] 1.1884 Å. [d] Observed in gas phase,[19] 1986.4672 cm$^{-1}$, for free $N_3^-$ in $N_2$ matrix:[2] 2003.5 cm$^{-1}$. [e] Frequencies observed in $KN_3$ crystal:[20] 2036.4, 1344, 642.4 cm$^{-1}$. [f] Best available ab initio results:[23] 1950, 1295 cm$^{-1}$.

ceivable antiaromatic triplet ions should then be the $D_{3h}$ symmetry triatomics $N_3^-$, $P_3^-$, $O_3^{2+}$, $S_3^{2+}$, etc. Our data constitute evidence for the transient existence of the singlet or triplet form of the first one of these.

In order to establish whether cyclic $N_3^-$ of $D_{3h}$ symmetry represents a bound chemical entity with a triplet ground state, we have performed ab initio calculations. Results of initial SCF optimizations are collected in Table II. We find that a cyclic ($D_{3h}$) $N_3^-$ indeed is a bona fide isomer of the usual linear azide anion, with a triplet ground state. The ordinary bent triplet $N_3^-$ is 18.7 kcal/mol lower on the same $T_1$ surface, separated by a barrier. The geometrical distortion from the optimal cyclic triplet $N_3^-$ ($D_{3h}$) to the optimal bent acyclic triplet $N_3^-$ ($C_{2v}$) stabilizes the lowest singlet state strongly and brings it below the lowest triplet. The optimized linear ground-state singlet lies 42.7 kcal/mol below the optimized $D_{3h}$ triplet.

Our best value for the vertical triplet–singlet splitting in cyclic $N_3^-$ at the SCF-optimized geometry is 39 kcal/mol, from 6-311+G* CI calculations starting with ROHF triplet orbitals and including up to quadruple excitations in the $\sigma$ and $\pi$ spaces until the T–S difference coverged (up to ~25 000 configurations, degeneracy of the singlet satisfied to within 0.3 kcal/mol). This type of calculation is notoriously difficult,[21] and the value should be viewed as an upper limit, but there is no doubt that the $^3A_2'$ triplet lies below the $^1E'$ singlet at this geometry, as it does in $C_3H_3^-$ and $N_3H_3^{2+}$,[21] and that triplet cyclic $N_3^-$ is a metastable isomer of ordinary linear singlet $N_3^-$. Unlike $C_3H_3^-$ and $N_3H_3^{2+}$, the antiaromatic singlet cyclic $N_3^-$ is not able to ease its misery by out-of-plane distortion.

The theoretical results suggest that an involvement of cyclic $N_3^-$ triplet in the formation of isotopically scrambled $N_3^-$ in our matrix experiments is plausible. One can expect the metastable cyclic triplet $N_3^-$ to be relatively short-lived, and the cyclic triplet $P_3^-$, very recently calculated[22] to have a $D_{3h}$ equilibrium geometry as well, is a more promising candidate for direct observation.

**Acknowledgment.** This work was supported by the National Science Foundation (CHE 8796257). We are grateful to Professor Colin Marsden for sharing with us the results of his unpublished calculations on $P_3^-$.

---

(14) $C_5H_5^{+}$[15] and $C_6Cl_6^{2+}$[16] indeed are ground-state triplets, while $C_4H_4$ is a ground-state singlet,[17] distorted by the pseudo-Jahn–Teller effect and rapidly tunneling between two $D_{2h}$ minima.[18]

(15) Saunders, M.; Beyer, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M.; Perchonok, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017. Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1979**, *101*, 3771.

(16) Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965.

(17) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343.

(18) Orendt, A. M.; Arnold, B. R.; Radziszewski, J. G.; Facelli, J. C.; Malsch, K. D.; Strub, H.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 2648, and references therein.

(19) Polak, M.; Gruebele, M.; Saykally, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2884.

(20) Lamoureux, R. T.; Dows, D. A. *Spectrochim. Acta* **1075**, *31A*, 1945.

(21) Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1980**, *102*, 5302.

(22) Burdett, J. K.; Marsden, C. J. *Nouv. J. Chim.*, in press.

(23) Botschwina, P. *J. Chem. Phys.* **1986**, *85*, 4591.

---

## Structure and Reactivity of Novel Lithium Di-*tert*-butylphosphido(alkyl)cuprates

Stephen F. Martin,*[,1a] Jeffrey R. Fishpaugh, John M. Power, Dean M. Giolando, Richard A. Jones,*[,1b] Christine M. Nunn, and Alan H. Cowley*

*Department of Chemistry*
*The University of Texas at Austin*
*Austin, Texas 78712*

*Received April 19, 1988*

Organocopper reagents have been extensively exploited in organic synthesis as nucleophilic reagents for the formation of new carbon–carbon bonds.[2] Of the various organocuprates available, heterocuprates, RCuXLi (X = heteroatom ligand),[3] play one particularly important role in that they prevent the waste of precious alkyl groups (R) that is inherent in the use of homocuprates, $R_2CuLi$. However, with the notable exception of those heterocuprates based upon certain phosphido and amido ligands,[3b-d] the utility of heterocuprates may be restricted by their thermal instability. Although limited structural information is available for homocuprates $R_2CuLi$,[4] heterocuprate reagents have

---

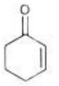
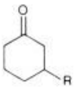
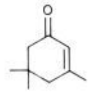
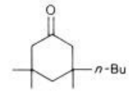
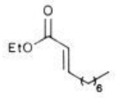
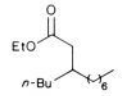
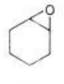
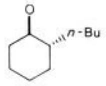
(1) (a) Recipient of a National Institutes of Health (National Cancer Institute) Research Career Development Award, 1980–1985. (b) Fellow of the Alfred P. Sloan Foundation, 1985–1989.

(2) For some general reviews, see: (a) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; John Wiley and Sons: New York, NY, 1980. (b) Normant, J. F. *J. Organomet. Chem. Lib.* **1976**, *1*, 219. (c) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005. (d) Taylor, R. J. K. *Synthesis* **1985**, 364. (e) Lipshutz, B. H. *Synthesis* **1987**, 325.

(3) (a) Posner, G. H.; Whitten, C. E.; Stirling, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 7788. (b) Bertz, S.; Dabbagh, G. *J. Chem. Soc., Chem. Commun.* **1982**, 1030. (c) Bertz, S.; Dabbagh, G.; Villacorta, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5824. (d) Bertz, S.; Dabbagh, G. *J. Org. Chem.* **1984**, *49*, 1119.

0002-7863/88/1510-7226$01.50/0

**Table I.** Reactions of Phosphidocuprates **2**–**5** with Electrophiles

| substrate | phosphidocuprate | reaction conditions | product | yield[a] |
|---|---|---|---|---|
|  | **2** | Et$_2$O, −78 °C, 30 min |  | 88 (R = Me) |
|  | **3** | Et$_2$O, −78 °C, 30 min |  | 84 (R = *n*-Bu) |
|  | **4** | Et$_2$O, −78 °C, 40 min |  | 77 (R = *sec*-Bu) |
|  | **5** | Et$_2$O, −78 °C, 30 min |  | 81 (R = *t*-Bu) |
|  | **3** | Et$_2$O, −78 °C, 60 min |  | 65 |
|  | **3** | Et$_2$O, −50 °C, 60 min |  | 72 |
|  | **3** | THF, 0 °C, 4 h |  | 63 |
| 1-bromooctane | **3** | THF, −23 °C, 3 h | dodecane | 80[b] |
| 1-iodooctane | **3** | THF, −23 °C, 3 h |  | 69[b] |
| 4-iodobutyrate | **3** | Et$_2$O, 0 °C, 2 h | ethyl octanoate | 67[b] |

[a] Isolated yields unless noted. [b] GC yield with undecane as internal standard.

not been structurally characterized previously. We now report the synthesis and single-crystal X-ray structure of a novel heterocuprate, [MeCu$\overline{\mathrm{P}(t\text{-Bu})_2\{\mathrm{Li}}$(THF)$_3$}] (**2**). Furthermore, we have discovered that phosphido(alkyl)cuprates of the general type [RCuP($t$-Bu)$_2$Li] (R = alkyl) are more stable than known heterocuprate reagents, yet they maintain significant reactivity toward common electrophiles. A preliminary survey of the stability and reactivity of these new heterocuprate reagents is also reported herein.

The neutral tetrameric copper(I) phosphide **1** was recently prepared in high yield from (trimethylsilyl)di-*tert*-butylphosphine and copper(I) chloride,[5,13] and it occurred to us that it might be utilized for the generation of novel mixed phosphido(alkyl)cuprates that might possess interesting structural and chemical properties (eq 1). In initial studies it was evident from both $^7$Li and $^{31}$P

$$[\mathrm{CuP}(t\text{-Bu})_2]_4 + 4\mathrm{RLi} \longrightarrow 4[\mathrm{RCuP}(t\text{-Bu})_2\mathrm{Li}] \qquad (1)$$

**1**

**2**, R = Me
**3**, R = *n*-Bu
**4**, R = *sec*-Bu
**5**, R = *t*-Bu

NMR assays indicated that the reaction of **1** with halide-free methyllithium (4 equiv) in THF (−78 °C) to produce **2** was incomplete. On the other hand, when **1** was allowed to react with a methyllithium/lithium bromide complex (4 equiv), the formation of **2** was virtually quantitative. Interestingly, in the reactions of **1** with *n*-BuLi, *sec*-BuLi, and *t*-BuLi it was not necessary to use alkyllithium/lithium bromide complexes to obtain complete conversion into **3**–**5**, respectively.[6]

Crystals of **2** of X-ray quality were grown from mixtures (5:1) of hexane/THF at −20 °C. It has been suggested previously that diphenylphosphido(alkyl)cuprates are dimeric in solution,[3d] but interestingly the X-ray analysis of **2**[8] reveals that this phosphidocuprate is monomeric in the solid state (Figure 1). This phenomenon is presumably a consequence of the increased steric demands of the *t*-Bu groups. As observed for the alkyl- and

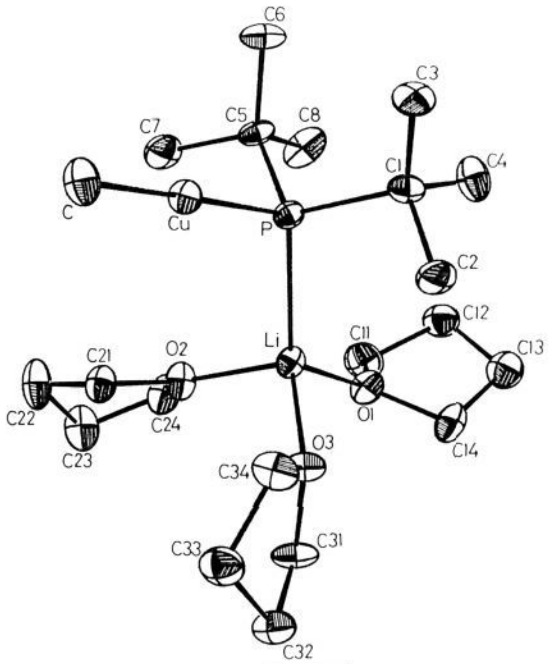


**Figure 1.** View (ORTEP) of [MeCu$\overline{\mathrm{P}(t\text{-Bu})_2\{\mathrm{Li}}$(THF)$_3$}] (**2**) showing the atom numbering scheme. Important parameters are as follows: Cu–C 1.940 (4), Cu–P 2.217 (2), P–Li 2.54 (1), P–C (1) 1.890 (7), P–C (5) 1.904 (7) Å, C–Cu–P 179.0 (3), Cu–P–C (1) 106.8 (2), Cu–P–C (5) 105.3 (2), C(1)–P–C (5) 111.2 (3)°.

---

(4) (a) Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240. (b) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23. (c) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337.

(5) Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 208. **Note Added in Proof.** For other examples of copper phosphido complexes see: Gol, F.; Knüppel, P. C.; Stelzer, O.; Sheldrick, W. S. *Angew. Chem.* **1988**, *100*, 1008. Brauer, D. J.; Knüppel, P. C.; Stelzer, O. *J. Chem. Soc., Chem. Commun.* **1988**, 551.

(6) The presence of LiX (X = Br, I) has been shown to increase the yields in certain organocuprate reactions, while its presence appears to have a negligible effect upon the rate of conjugate addition.[3d,7]

(7) (a) Whitesides, G. M.; Fischer, W. F., Jr.; San Filippo, J., Jr.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. (b) House, H. O.; Fischer, W. F. *J. Org. Chem.* **1968**, *33*, 949.

(8) Crystal data for **2**: $C_{21}H_{45}CuLiO_3P$, monoclinic, $C2/c$ (no. 15), $a$ = 18.487 (5) Å, $b$ = 14.331 (7) Å, $c$ = 20.295 (7) Å, $\beta$ = 111.54 (2)°, $V$ = 5001.6 Å$^3$, $Z$ = 8, $D$(calcd) = 1.187 g cm$^{-3}$, $\mu$ (Mo K$\alpha$) = 9.53 cm$^{-1}$. Colorless, highly air-sensitive prismatic crystals of **2** were coated with a hydrocarbon oil and placed in the cold stream (130 K) of an Enraf-Nonius CAD-4 diffractometer. Because of decay (>30%), it was necessary to use three different crystals for data collection; each crystal was removed when the check reflection intensities dropped to 70%. The three data sets were combined with an anisotropic decay correction. A total of 4502 unique reflections were collected over the range $3.0 \le 2\theta \le 50.0°$ using the $\theta/2\theta$ scan mode. Of these, 3192 were considered to be observed [$I > 3\sigma(I)$]. The data were corrected for Lorentz, polarization, decay, and absorption. The absorption correction was done with the empirical method (azimuthal scans) measured for the third crystal. There was no decay due to X-rays. The structure was solved by direct methods. Refinement (full matrix least squares) afforded the final residuals $R$ = 0.0685 and $R_w$ = 0.0825. See paragraph at end of text for Supplementary Material which is available.

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($t$-$Bu_2P$)$_2$][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)$_2$$PPh_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, $\alpha$- and $\beta$-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 $\alpha,\beta$- or $\beta,\beta$-disubstituted enoate systems. Thus, these new phosphido(alkyl)cuprates [RCuP($t$-Bu)$_2$Li] exhibit reactivity profiles that are comparable with other related phosphido(alkyl)cuprates [$RCuPPh_2Li$] (**7**) and [RCu($c$-$C_6H_{11}$)$_2$PLi] (**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.

---

(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.

(10) Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Inorg. Chem.* **1987**, *26*, 3610.

(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

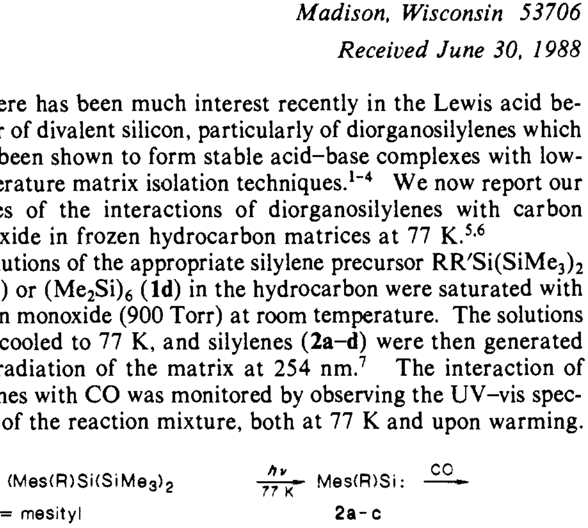
Mary-Ann Pearsall and Robert West*

*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.



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

---

(1) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1987**, *6*, 2617.

(2) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270.

(3) Ando, W.; Hagiwara, K.; Sekiguchi, A.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558.

(4) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics*, in press.

(5) Independent studies of complex formation between dimethylsilylene and CO have been carried out simultaneously with ours. See: Arrington, C. A.; Petty. J. T.; Payne, S. E.; Haskins, W. C. K. *J. Am. Chem. Soc.* **1988**, *110*, 6240.

(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.

(7) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Si, Ge, Sn & Pb Compds.* **1986**, *9*, 1, 75.

0002-7863/88/1510-7228$01.50/0