tetramer. Thus, the two C_2O_2 planes within each butterfly unit are at a 113.4° angle whereas the two CuC_2 planes form a 97.1° angle.

The short C≡C distances and large C≡C—R bend back angles for **3** both indicate that the alkyne is less perturbed than alkynes in other dinuclear metal complexes.[7] The C≡C—R angles range from 148 (2)° to 156 (2)°. These are much larger than those usually observed for dinuclear complexes and are even larger than those observed in most mononuclear complexes.[8] For comparison with copper structures, these angles are 139.0 (7)° and 138.2 (4)° for **1** and range from 156.6 (14)° to 159.5 (14)° for the two independent molecules in **2**. Both of these structural features imply that back-bonding to the alkyne in **3** is significantly less important than in other dinuclear complexes.

All three complexes show moderately short Cu–Cu distances (considering those within the butterfly units for **3**). Although a normal two-electron bond is not expected between two d^{10} metal centers, calculations have shown that a weak attractive interaction does exist.[9] This may explain the displacement of the copper atoms toward each other out of the O_2C_2 planes for **3**. In both **1** and **2** the geometry about the copper atom is planar.

In view of the known tendency of copper(I) to form high nuclearity aggregates with bridging ligands,[10] it seems likely that a variety of new polynuclear copper complexes containing bridging alkyne ligands may be accessible.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this project (D.L.R.) and the National Science Foundation under Grant No. CHE 86-12862 (R.D.A.).

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (12 pages); a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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[7] Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* 1985, *4*, 1612.

[8] Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* 1988, *7*, 189.

[9] (a) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* 1978, *17*, 2187. For recent discussions of d^{10}–d^{10} interactions see: (b) Merz, K. M., Jr.; Hoffmann, R. *Inorg. Chem.* 1988, *27*, 2120. (c) Cotton, F. A.; Feng, X.; Matusz, M.; Poli, R. *J. Am. Chem. Soc.* 1988, *110*, 7077.

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1-Sila-3-azacyclobutanes: The Insertion of Isocyanides into Silaaziridines

A. G. Brook,* A. K. Saxena, and J. F. Sawyer

Lash Miller Chemical Laboratories
University of Toronto
Toronto, M5S 1A1 Canada

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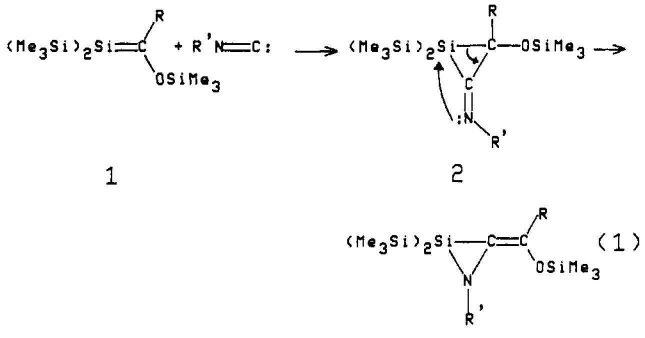
Summary: Stable silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (R = Ad (Ad = 1-adamantyl), Mes (Mes = 2,4,6-trimethylphenyl)) reacted with 2,6-dimethylphenyl isocyanide giving rise to stable compounds shown by X-ray crystallography to be 1-sila-3-azacyclobutanes. Similar four-membered ring compounds were also formed when a silene of this type bearing a mesityl group on the sp^2-hybridized carbon atom reacted with *tert*-butyl isocyanide. The insertion of isocyanide into the Si–N bond of an initially formed silaaziridine is proposed to account for these products.

We have recently reported[1] that the silenes **1** of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (R = *t*-Bu, Ad; Ad = 1-adamantyl) react with alkyl isocyanides $R'N{=}C{:}$ (R′ = *t*-Bu, $CMe_2CH_2CMe_3$ (isooctyl)) to yield solid, relatively stable silaaziridines **3**. Evidence indicated that the initially formed silacyclopropanimines **2** undergo clean rapid thermal rearrangements even at −40 °C to the isomeric silaaziridines (eq 1).[1]



3

We have now found that if either the isocyanide bears an aryl group and/or the silene bears an aryl group on the sp^2-hybridized carbon, the first observed isolable products are the result of the reaction of two molecules of isocyanide with each molecule of silene. This family of compounds, whose members **4a–d** have very similar NMR resonances (see Table I), was shown through the X-ray crystal structure of one member (see below) to be 1-sila-3-azacyclobutanes, the first reported examples of this ring system.

Thus, when the silenes **1** (R = Ad or Mes) were generated (by photolysis of the related acylsilane $(Me_3Si)_3SiCOR$ in C_6D_6 using 360-nm radiation at 0 °C) in the presence of the aryl isocyanide $R''N{=}C{:}$ (R″ = 2,6-dimethylphenyl), the compounds obtained were the 1-sila-3-azacyclobutanes **4a** and **4d**, respectively. Similarly the four-membered 1-sila-3-azacyclobutane **4c** was obtained when $(Me_3Si)_2Si{=}C(OSiMe_3)Mes$ was generated in the presence of *t*-BuN=C:.

Under nonphotochemical conditions, preformed silene **1** (R = Ad), when treated in the dark at −70 °C with 1 equiv of aryl isocyanide, gave a mixture of silaaziridine **3** (R′ = Ar) and 1-sila-3-azacyclobutane **4a** (R′ = Ar), the latter being the major product. This is in contrast to the exclusive formation of silaaziridine **3** (R′ = alkyl) when preformed silene **1** (R = Ad) was treated with an alkyl isocyanide. When silaaziridine **3** (R = Ad, R′ = *t*-Bu) was treated with an equivalent of aryl isocyanide in the dark, no reaction occurred, but reaction occurred slowly when the mixture was photolyzed to give the mixed species **4b** as two geometric isomers in about 3:2 proportions. Only one isomer was observed for each of **4c** and **4d**.

It is evident from the above results that the formation of the silaazacyclobutanes is usually a nonphotochemical process that requires the presence of an aryl group either on the isocyanide or on the sp^2-hybridized carbon of the silene. Delocalization of electron density on the ring ni-

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[1] Brook, A. G.; Kong, Y. K.; Saxena, A. K.; Sawyer, J. F. *Organometallics* 1988, *7*, 2245.

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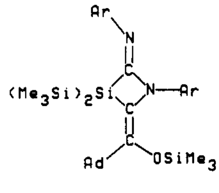
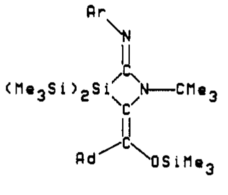
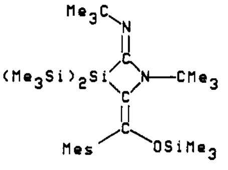
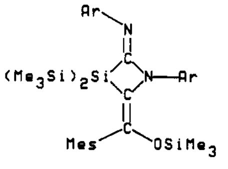
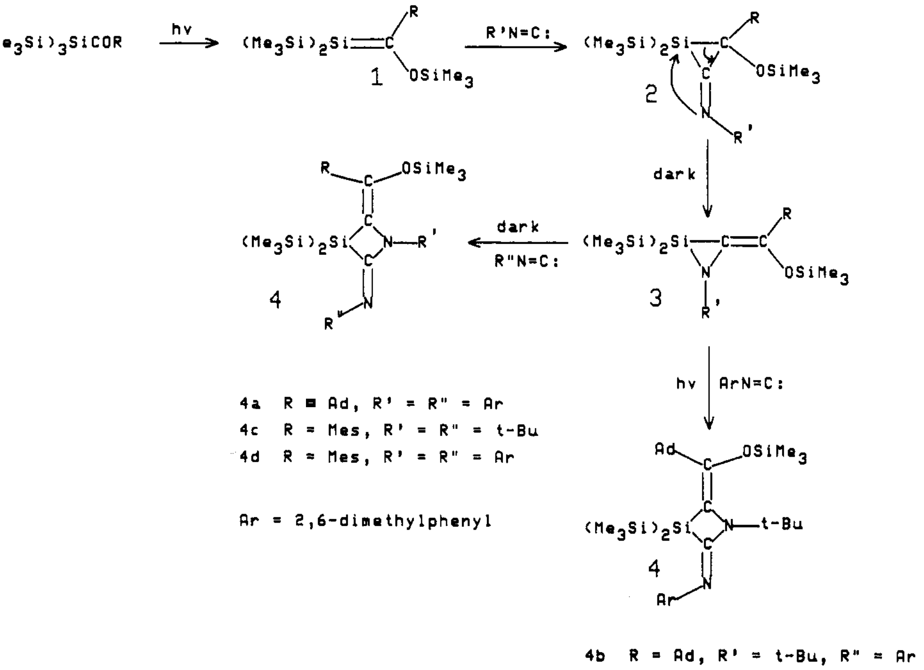
Table I. Selected NMR Data (in Ppm) for 1-Sila-3-azacyclobutanes (in C_6D_6)[a]

						
	4a		4b			
	major	minor	major	minor	4c	4d
			^{1}H			
Me_3Si	0.31	0.33	0.39	0.42	0.08	0.36
Me_3SiO	0.01	0.20	−0.11	−0.09	−0.08	−0.07
			^{13}C			
Me_3Si	0.36	0.69	1.59	0.35	0.70	0.21
Me_3SiO	1.63	2.96	1.76	1.46	1.42	0.30
ring *C*=N	167.39	164.38	167.38	*c*	159.84	166.33
ring *C*=C	119.93	*c*	121.84	119.54	125.16	122.41
			^{29}Si			
Me_3Si	-14.10	-13.92	-14.49	-14.10	-15.40	-14.62
Me_3SiO	13.50	14.83	12.53	13.50	11.85	13.76
ring Si	-18.02	-12.74	-18.02	-11.79	-18.59	-20.93

[a] Ar = 2,6-dimethylphenyl; Mes = 2,4,6-trimethylphenyl. [b] In C_7D_8. [c] Could not be assigned.

Scheme I



trogen atom into the aromatic rings presumably weakens the Si–N bond of the silaaziridines, permitting insertion of a molecule of isocyanide into the ring, probably initiated by the nucleophilic attack of the isocyanide on the ring silicon atom of the silaaziridine. The sequence of reactions believed to be involved is shown in Scheme I.

These novel silaheterocycles 4 have been fully characterized spectroscopically. The characteristic and similar NMR chemical shifts for these air and moisture sensitive compounds are given in Table I. One of the compounds, **4a**[2] (R = Ad, R′ = R″ = 2,6-dimethylphenyl) gave colorless crystals of a single geometric isomer from benzene[3] whose crystal structure revealed the 1-sila-3-azacyclobutane ring having two opposing exocyclic, C1–C3 and C2–N2, double bonds (Figure 1).

The SiC_2N ring in 4 is completely planar with substituent atoms N2, C3, O1, C11, C21, and C31 deviating from this plane by distances of −0.033 (3), 0.150 (3), 0.309 (2), −0.361 (4), −0.088 (4), and 0.025 (4) Å, respectively. The ring nitrogen atom is somewhat flattened with N1 only 0.138 (3) Å $\{\Delta_N\}$ above the C1–C2–C11 plane.

The Si–C ring distances in **4a** [1.902 (4) and 1.944 (4) Å] are distinctly different due to the different exocyclic environments, but their mean value [1.923 Å] is very comparable to the Si–C(sp^2) ring distances reported for 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene.[6] In **4a** the $SiMe_3$ substituents at Si1 are twisted by ca. 10° away from an

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[2] When **4a** was formed by cophotolysis of the acylsilane and aryl isocyanide, two isomers were formed in about a 95:5 ratio, and the major isomer was easily obtained pure by crystallization from benzene. However, when the aryl isocyanide was added to preformed silene in the dark at about −20 °C, the isomers were formed in about 1:1 proportions.

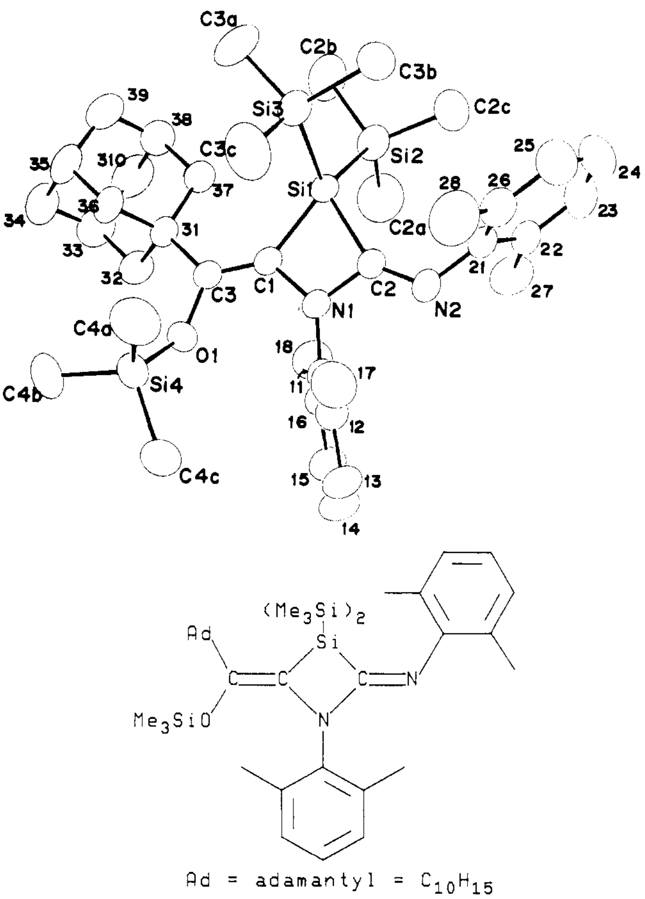

Figure 1. ORTEP view of the 1-sila-3-azacyclobutane **4a** showing the crystallographic numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): C1–C3 = 1.327 (6), C1–N1 = 1.454 (5), N1–C2 = 1.407 (5), C2–N2 = 1.265 (5), C3–O1 = 1.404 (4), Si4–O1 = 1.653 (3), N1–C11 = 1.434 (5); C3–C31 = 1.523 (5); C1–Si1–Si2 = 123.8 (1), C1–Si1–Si3 = 114.5 (1), C2–Si1–Si2 = 115.2 (1), C2–Si1–Si3 = 112.6 (1), C1–N1–C11 = 129.4 (3), C2–N1–C11 = 122.5 (3), Si1–C1–C3 = 140.5 (3), N1–C1–C3 = 127.5 (3), Si1–C2–N2 = 146.1 (3), N1–C2–N2 = 122.8 (3), C1–C3–O1 = 119.8 (3), C1–C3–C31 = 125.6 (3), O1–C3–C31 = 114.3 (3); C1–Si1–C2 = 72.4 (2), C1–N1–C2 = 105.2 (3), Si1–C1–N1 = 91.3 (2), and Si1–C2–N1 = 91.0 (2).

eclipsed arrangement, with Si–Si–C and C–Si–C angles in the range 106.9–112.7 (3)°.

We are continuing these studies by investigating the scope, generality, and the mechanisms involved in these unusual reactions.

Acknowledgment. We are grateful to the Natural Science and Engineering Research Council of Canada for financial support of this research and to Dr. Y. K. Kong for preliminary experiments.

Supplementary Material Available: Final crystallographic details for the structure refinement of 1-sila-3-azacyclobutane **4a** consisting of final positional and thermal parameters, complete bond lengths and bond angles, and least-squares mean planes (9 pages); a listing of final structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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(3) Properties of **4a**: air-sensitive, light brown solid; mp 208 °C. MS Calcd for $C_{38}H_{60}N_2OSi_4$: 672.3782. Found: 672.3762. Large well-formed block-shaped crystals of **4a** as a benzene solvate slowly reacted in air and hence were cut to size and rapidly transferred to Lindemann capillaries in a glovebag under dry argon. Crystal data: $C_{38}H_{60}N_2OSi_4 \cdot C_6H_6$; fw = 750.4; monoclinic; space group $P2_1/n$; $a = 9.917$ (3) Å, $b = 23.811$ (4) Å, $c = 19.431$ (7) Å; $\beta = 97.94$ (2)°; $U = 4544$ Å^3; $D_{calcd} = 1.10$ g cm^{-3} for $Z = 4$; $T = 298$K. Unit cell dimensions based on 25 reflections ($8.8 < \theta < 13.9°$) centered on an Enraf-Nonius CAD4 diffractometer (graphite-monochromatized Mo K$\bar{\alpha}$ radiation) and a fairly large crystal of overall dimensions 0.35 × 0.40 × 0.47 mm. Intensity data collection [ω–2θ scans over $(0.60 + 0.35 \tan \theta)°$, maximum scan time 55 s] gave 8905 data (including standards) in the octants $h,k,\pm l$ with $2\theta \leqslant 50°$. A further 2500 symmetry-related data with $2\theta \leqslant 32°$ and an incomplete shell of data with $50 < 2\theta < 55°$ completed the data collection. The crystal was recentered several times during data collection. Lorentz, polarization, and slight (+5%) corrections for intensity fluctuations of standard reflections were applied. Rejection of 1698 systematically absent or zero F_o data and the averaging of 1884 symmetry equivalent reflections ($R_{merge}(F) = 0.026$) gave a final data set of 7563 reflections. Structure solution used direct methods followed by standard refinements. All H atoms except those in the benzene solvent were included in calculated positions. Blocked least-squares refinements minimizing $\sum_w \Delta F^2$ (all non-H atoms except solvent anisotropic) converged (maximum $\Delta/\sigma = 0.09$) to $R = 0.0586$ ($wR = 0.0640$) for 4610 reflections with $F > 6\sigma(F)$ $\{w = [\sigma^2(F) + 0.001\,414F^2]^{-1}$ and maximum $\Delta P = 0.40$ e Å$^{-3}\}$. Scattering factors stored in programs were from ref 4. Programs: Enraf-Nonius SDP package on PDP 11/23 and SHELX on Gould 9705 computers.[5]

(4) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England (Present distributor D. Reidel, Dordrecht), 1974; Vol. IV.

(5) Frenz, B. A. *Enraf-Nonius Structure Determination Package*; Texas A&M University: College Station, TX, 1981. Sheldrick, G. M. *SHELX-76*, Cambridge University: Cambridge, England.

(6) Ishikawa, M.; Matsuzawa, S.; Hirotsu, K.; Kamitori, S.; Higuchi, T. *Organometallics* **1984**, *3*, 1930.

Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 7. A Novel Bonding Mode That Stabilizes Metal Triangles[1]

Evan P. Kyba,*,† **Michael C. Kerby,**‡ **Ram P. Kashyap, John A. Mountzouris, and Raymond E. Davis***

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

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Summary: Two heterotetrametalla tetrahedral clusters, containing the Mo_2Co_2 (**3**) and $MoCo_3$ (**4**) cores, have been synthesized. A key part of the supporting ligand framework in each of these clusters is an *o*-phenylenebis(μ-*tert*-butylphosphido) moiety, which exhibits a novel bonding mode in stabilizing a metal triangle. Cluster **3** undergoes a thermal rearrangement to an isomer at temperatures >75 °C, in which, inter alia, the bis(μ-*tert*-butylphosphido) ligand migrates on the metal triangle. The activation parameters for this process are reported, as are the crystal structures of **3** and **7**.

We have been concerned for some time in the stabilization of metal–metal bonds by utilizing what we have termed linked bis(μ-phosphido and -sulfido) supporting ligands.[2] In particular, we have used the *o*-phenylene link between μ-phosphido groups (as in **1**) because it rigidly enforces a cisoid relationship between the ligating sites. There is now a relatively convenient synthetic route to *o*-phenylenebis(*sec*-phosphines), which are immediate precursors of **1** (Scheme I).[3] This type of ligand has stabilized unusual iron clusters,[4] an interesting triply

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† Current address: Conner Research Center, Alcon Laboratories, Inc., 6201 South Freeway, Fort Worth, TX 76134.

‡ Current address: Exxon Corporate Research, Rte 22 East, Annandale, NJ 08801.

(1) For the preceding paper in this series, see: Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Hassett, K. L.; Davis, R. E. *J. Organomet. Chem.* **1988**, *346*, C19.

0276-7333/89/2308-0852$01.50/0