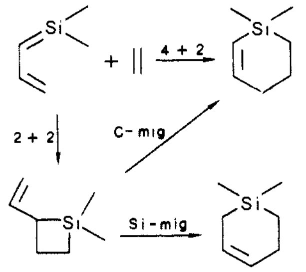
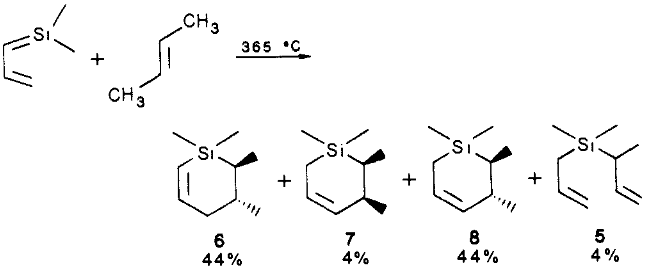
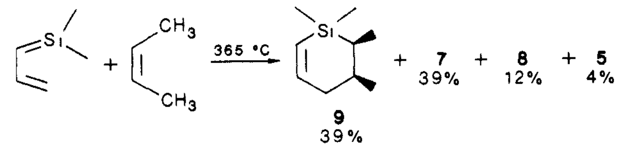


the acyclic 3,4,4-trimethyl-4-silahepta-1,6-diene (**5**) (4%), *trans*-1,1,5,6-tetramethyl-1-silacyclohex-2-ene (**6**) (44%), and *cis*- and *trans*-1,1,5,6-tetramethyl-1-silacyclohex-3-enes (**7**) and (**8**) (4% and 44%), respectively. Reaction of **1** with *cis*-2-butene also provides four adducts: **5** (4%) and *cis*-1,1,5,6-tetramethyl-1-silacyclohex-2-ene (**9**) (39%) along with **7** and **8** (39% and 12%), respectively.





Stereospecific formation of the cyclic 2-enes **6** and **9** (>99%) requires that **1**, despite the highly polarized and unsymmetrical distribution of four $\pi$ electrons,[9] produces the six-membered ring without rotation of the central C–C bond of the two-electron component. This is the first example in which a *siladiene* reacts stereospecifically with an olefin in an orbital symmetry allowed 4 + 2 cycloaddition.[10]

The mechanisms by which the cyclic 3-enes **7** and **8** are obtained require a process in which olefin stereochemistry is partially lost. From (*E*)-2-butene, retention of the trans relation between adjacent methyls in the cyclic 3-ene is 92% but only 76% from (*Z*)-2-butene. A likely rationale is that the silene end of **1** reacts with slight nonstereospecificity with the alkene to yield the substituted 2-vinyl-1-silacyclobutane **10**. Although the stereochemistry of the 2 + 2 cycloaddition of silenes to alkenes is not known, it has been reported that (*E*)- and (*Z*)-1,1,2,3-tetramethyl-1-silacyclobutane each fragment with ≥20% loss of starting stereochemistry in the 2-butene product.[11] Microscopic reversibility then dictates that the silene/alkene 2 + 2 cycloaddition also proceeds with some loss of stereochemistry in formation of the four-membered ring.

Expansion of the diastereomeric intermediates **10** by migration of the Si–C bond to the terminal methylene of the vinyl substituent can account for the formation of the *E* and *Z* isomers **7** and **8**. Such a rearrangement may be considered an example of the 1,3-sila-sigmatropic shift previously reported to occur with inversion of configuration at the migrating silicon center.[12] Since **6** and **9** are produced stereospecifically, it appears that they do not derive from any C–C ring expansion of diastereomeric **10**. Curious but also consistent with this interpretation is that facile ring expansion via silicon migration precludes the 1,5-sigmatropic hydrogen shift previously observed for pyrolysis of substituted 3-vinylsilacyclobutanes.[13] Further, **10** does not appear to fragment to silenes and substituted 1,3-dienes.

Relative amounts of the symmetry allowed 4 + 2 cyclic 2-enes and the forbidden 2 + 2 cyclic 3-enes are of theoretical interest. The major cycloaddition path of **1** and ethylene is the 2 + 2 mechanism (51%) and similarly, in reaction with (*E*)- and (*Z*)-2-butene, products from the "biradical" path predominate. Surprisingly, $\Delta G^{\ddagger}$ of the allowed and stereospecific Diels–Alder path must be slightly higher than that of the forbidden and partially stereospecific 2 + 2 mechanism.[14] Although the rules of orbital symmetry correctly depict the stereochemistry of 4 + 2 and 2 + 2 cycloadditions of 1-silabutadiene, they do not account for the faster rate of the forbidden reaction. Possibly the polarization of **1**, known to have greater negative charge density on C(2) than C(4),[8] may emphasize the importance of coulombic forces in such cycloadditions.[15]

**Acknowledgment.** We gratefully acknowledge the Robert A. Welch Foundation, the Dow Corning Corporation, and the N. T.S.U. Faculty Research Fund for financial support of this work. We thank the Mass Spectrometry Facilities at M.I.T. and Rice University for obtaining high resolution mass spectra.

**Supplementary Material Available:** Spectroscopic data ($^{13}$C, $^{1}$H NMR, and mass spectra) and experimental methods are available for all new compounds (3 pages). Ordering information is given on any current masthead page.

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[9] Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1981**, *103*, 6313.

[10] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: 1970.

[11] Conlin, R. T.; Namavari, M.; Chickos, J. S.; Walsh, R. *Organometallics*, submitted for publication.

[12] Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

[13] Conlin, R. T.; Bobbitt, K. L. *Organometallics* **1987**, *6*, 1406.

[14] See ref 3. Halogenated olefins and dienes also are known to yield four- and six-membered rings. Bartlett, P. D. *Quart. Rev.* **1970**, *24*, 473.

[15] Other influences on the mechanism of the Diels–Alder reaction have been critically reviewed: Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *9*, 779.

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# A Cu$_2$–O$_2$ Complex. Crystal Structure and Characterization of a Reversible Dioxygen Binding System

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*Received February 24, 1988*

In this paper, we describe the first X-ray crystallographic characterization of a copper–dioxygen complex, formed by the addition of O$_2$ to a copper(I) compound. The detailed structural characterization of a Cu$_n$–O$_2$ species has been a longtime goal of researchers investigating copper/dioxygen reactivity, because of (i) interest in copper-containing proteins such as hemocyanin (Hc)[1] (anthropod and mollusc O$_2$ carrier), the monooxygenases tyrosinase and dopamine $\beta$-hydroxylase,[1a,2] oxidases such as laccase[3] and the iron–copper-containing cytochrome *c* oxidase[4] and (ii) the synthetic utility of copper compounds in oxidation reactions.[5]

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[1] (a) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1–57. Solomon, E. I. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 44–108. (b) Lontie, R.; Witters, R. *Met. Ions Biol. Syst.* **1981**, *13*, 229–258.

[2] (a) Lerch, K. *Met. Ions Biol. Syst.* **1981**, *13*, 143–186. (b) Villafranca, J. J. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 263–290.

[3] Spira-Solomon, D. J.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 6421–6432.

[4] (a) Naqui, A.; Chance, B.; Cadenas, E. *Annu. Rev. Biochem.* **1986**, *55*, 137–166. (b) Witt, S. N.; Chan, S. I. *J. Biol. Chem.* **1987**, *262*, 1446–1448.

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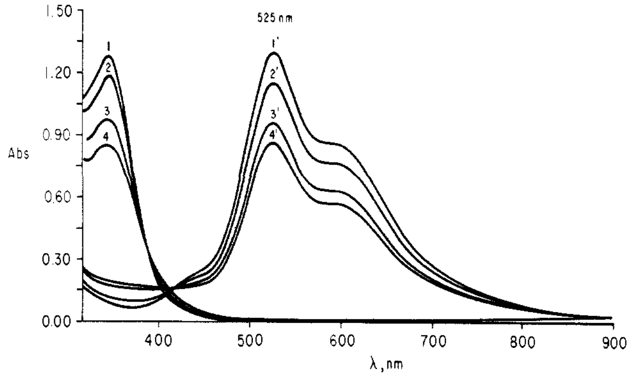
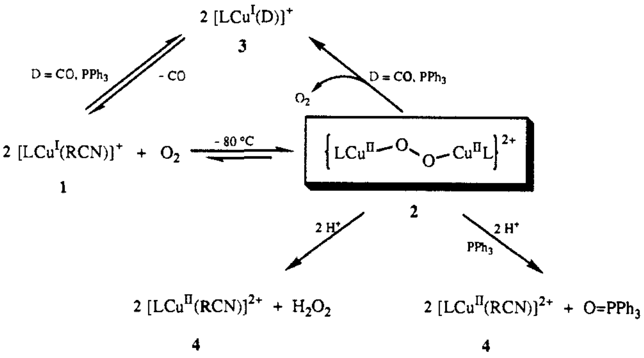


**Figure 1.** UV-vis spectra demonstrating the reversible $O_2$ and CO binding behavior of $[LCu(RCN)]^+$ (**1**) in EtCN (carbonyl cycling). Reaction of **1** ($\lambda_{max}$ = 340 nm, spectrum 1) with $O_2$ (−80 °C) generates the dioxygen adduct $[\{LCu\}_2(O_2)]^{2+}$ (**2**; $\lambda_{max}$ = 525 nm, spectrum 1′). Saturating with CO while warming effects the displacement of $O_2$ and formation of $[LCu(CO)]^+$ (**2**) (featureless spectrum, not shown). Removal of the CO ligand with vacuum/Ar-purge cycles regenerates **1** (spectrum 2), and the process can be repeated, as shown.

**Scheme I**



The tripodal tetradentate ligand tris[(2-pyridyl)methyl]amine (L)[6] can be used to form the new cationic copper(I) complexes $[LCu(D)]^+$ (**1**, D = RCN; **3a**, D = Co; **3b**, D = $PPh_3$) (Scheme I).[7a] In either $CH_3CH_2CN$ (EtCN) or $CH_2Cl_2$,[7b] reaction of the orange compound **1** with dioxygen at −80 °C ($O_2$:Cu = 0.50 ± 0.05, manometry[8] in EtCN) produces an intensely purple-colored complex, $[\{LCu\}_2(O_2)]^{2+}$ (**2**), which is EPR silent (77 K, 2-Me-THF/EtCN, 2:1) and is characterized by UV-vis absorptions at 525 ($\epsilon$ = 11 500 $M^{-1}$ $cm^{-1}$), 590 (sh, $\epsilon$ = 7600) (Figure 1, spectrum 1′), and 1035 nm ($\epsilon$ = 160).

Crystals of $[\{LCu\}_2(O_2)](PF_6)_2 \cdot 5Et_2O$ (**2**-$(PF_6)_2$) were grown from a solution of **1**-$(PF_6)$ reacted with $O_2$ at −85 °C in EtCN, which was then layered with cold diethyl ether. X-ray data were obtained at −90 °C for the thermally and hydrolytically unstable material.[9-11] The complex is best described as a peroxo dicopper(II) species (vide infra), and, as shown in Figure 2, it contains a trans $\mu$-1,2-$O_2^{2-}$ group (derived from $O_2$) bridging the two Cu(II) ions. There is one dinuclear copper(II) complex per unit cell with a crystallographic inversion center between the two atoms O1 and O1′. As found in other Cu(II) complexes with L,[6] the Cu atom is pentacoordinate with a distorted trigonal bipyramidal geometry. The equatorial ligands are the pyridyl N2, N3, and N4 donors, with aliphatic amine (N1) and peroxo oxygen (O1) atoms occupying axial sites. The Cu–Cu′ separation is 4.359 (1) Å, and the O1–O1′ bond length is 1.432 (6) Å. These structural parameters are similar to those for peroxo-bridged dicobalt(III) complexes.[12]

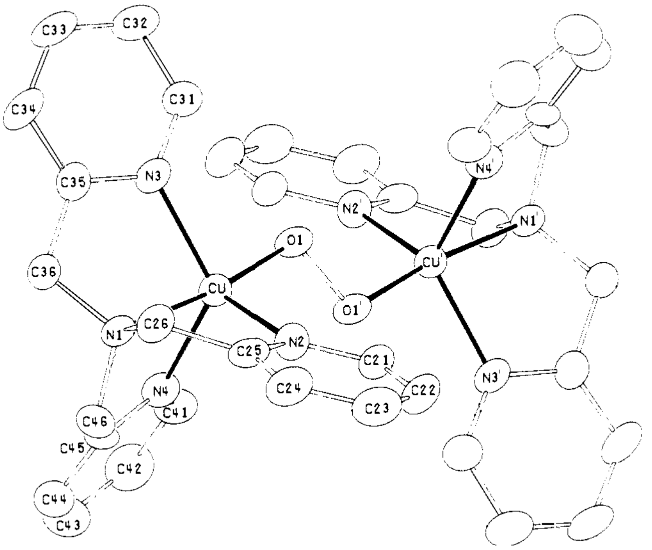


**Figure 2.** ORTEP diagram of the dioxygen complex $[\{LCu\}_2(O_2)]^{2+}$ (**2**) showing the atom labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Cu⋯Cu′, 4.359 (1); O1–O1′, 1.432 (6); Cu1–O1, 1.852 (5); Cu1–N1, 2.104 (6); Cu1–N2, 2.102 (6); Cu1–N3, 2.024 (7); Cu1–N4, 2.082 (7); O1–Cu1–N1, 173.7 (3); O1–Cu1–N2, 104.8 (2); O1–Cu1–N3, 92.4 (3); O1–Cu1–N4, 102.6 (3); N1–Cu1–N2, 79.6 (2); N1–Cu1–N3, 81.4 (3); N1–Cu1–N4, 79.9 (3); N2–Cu1–N3, 120.6 (3); N2–Cu1–N4, 109.1 (3); N3–Cu1–N4, 121.9 (3); Cu1–O1–O1′, 107.7 (2).

The binding of $O_2$ (and CO) to **1** is reversible, as evidenced by the reactions interconverting complexes **1**–**3** (Scheme I). (i) When a vacuum is applied to $[\{LCu\}_2(O_2)]^{2+}$ (**2**) in EtCN while heating briefly, the purple solution decolorizes, and $[LCu(EtCN)]^+$ (**1**) is produced. Rechilling (<−80 °C) followed by introduction of $O_2$ regenerates **2**. (ii) Via the formation of **1**, dioxygen can be displaced from **2** by reaction with either $PPh_3$ or CO (in EtCN) to give the adducts $[LCu(D)]^+$ (**3a** or **3b**; >90% **3b** isolated, trace of O=$PPh_3$ produced). In both cases, $O_2$ is detected qualitatively

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[5] (a) Gampp, H.; Zuberbühler, A. D. In *Met. Ions Biol. Syst.* **1981**, *12*, 133–190. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

[6] (a) Karlin, K. D.; Hayes, J. C.; Shi, J.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106–4108. (b) Zubieta, J.; Karlin, K. D.; Hayes, J. C. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D.; Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1983; pp 97–108.

[7] (a) Based on an X-ray structure of $[LCu(PPh_3)](PF_6)$ (**3b**) and NMR data (Karlin, K. D., et al., unpublished results); complexes $[LCu(D)]^+$ (**1** and **3**) contain D-coordinated Cu(I) with one dangling uncoordinated pyridine group from L. $[LCu(CH_3CN)](PF_6)$ (**1**): Anal. Calcd for $C_{20}H_{21}CuF_6N_5P$: C, 44.49; H, 3.92; N, 12.97. Found: C, 44.67; H, 3.96; N, 12.74. $[LCu(CO)](ClO_4)$ (**3a**): IR (Nujol) $\nu$ (CO), 2075 $cm^{-1}$. Anal. Calcd for $C_{19}H_{18}ClCuN_4O_5$: C, 47.41; H, 3.77; N, 11.64. Found: C, 47.73; H, 3.87; N, 11.70. $[LCu(PPh_3)](PF_6)$ (**3b**): Anal. Calcd for $C_{36}H_{33}CuF_6N_4P_2$: C, 56.81; H, 4.37; N, 7.36. Found: C, 57.29; H, 4.29; N, 7.46. (b) Complex **1** reacts irreversibly with dichloromethane to give $[LCu(Cl)]^+$, but **2** can be prepared and handled in $CH_2Cl_2$ if solid **1** is added to $O_2$-saturated $CH_2Cl_2$ (−80 °C).

[8] (a) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668–2679.

[9] (a) Cold samples of **2** (powder or crystals) can be redissolved to give the same UV-vis spectrum seen from material prepared in situ. A solid-state spectrum (Nujol mull) of fresh solid also shows the characteristic absorptions in the 500–600-nm region. (b) A $^1H$ NMR spectrum of chemically reduced crystalline **2**-$(PF_6)_2$ (reaction with KCN in $CD_3NO_2$) at room temperature shows the presence of diethyl ether.

[10] $[\{LCu\}_2(O_2)](PF_6)_2 \cdot 5Et_2O$ (**2**-$(PF_6)_2$) crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 11.062 (3) Å, $b$ = 12.758 (4) Å, $c$ = 13.280 (5) Å, $\alpha$ = 96.72 (3)°, $\beta$ = 110.57 (3)°, $\gamma$ = 103.73 (3)°, $V$ = 1663 (1) $Å^3$, and $Z$ = 1. A Nicolet R3m/V diffractometer was used in the 2$\theta$-scan mode to collect 4215 unique reflections of which 2512 reflections with $F_o \geq 6\sigma|F_o|$ were used in the solution and refinement. The positional parameters of the copper atom were determined by the Patterson method. The remaining nonhydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were calculated and fixed at 0.96 Å from carbon. All non-hydrogen atoms in the cation, anion, and nondisordered diethyl ether ($Et_2O$) molecules were refined anisotropically; five molecules of lattice $Et_2O$ per dinuclear unit were identified and located in the final stages of refinement (one $Et_2O$ disordered about a center of symmetry). The structure was refined to the current residual values of $R$ = 0.0581 and $R_w$ = 0.0580 (Mo K$\alpha$, $\lambda$ = 0.71073 Å).

[11] Supplementary Material.

[12] (a) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1. (b) Jones, R. D.; Sommerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *2*, 139. (c) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, 137–203.

by passing the gas produced through a test solution of alkaline pyrogallol,[8] and for $PPh_3$, near quantitative (95%) evolution of $O_2$ is observed by manometry. (iii) CO can be used to effect repetitive "carbonyl cycling" where in EtCN, $O_2$ is displaced from $[\{LCu\}_2(O_2)]^{2+}$ (**2**) giving $[LCu(CO)]^+$ (**3a**), CO is removed from **3a** via vacuum/Ar-purge cycles (room temperature) providing $[LCu^I(RCN)]^+$ (**1**), and rechilling of **1** followed by oxygenation regenerates **2** (Figure 1).

If the reaction of $PPh_3$ with $[\{LCu\}_2(O_2)](PF_6)_2$ (**2**-$(PF_6)_2$) is carried out in the presence of acid ($2HPF_6 \cdot Et_2O$), $O{=}PPh_3$ (97%) is produced instead, along with the dicationic complex, $[LCu^{II}(MeCN)](PF_6)_2$ (**4**-$(PF_6)_2$; 61% isolated[13]). This undoubtedly occurs via $PPh_3$ oxidation by $H_2O_2$ since direct protonation of **2**-$(PF_6)_2$ ($2HPF_6 \cdot Et_2O$, −80 °C) provides **4**-$(PF_6)_2$ (77% isolated) and $H_2O_2$ (81%, iodometric titration) (Scheme I).

$[\{LCu\}_2(O_2)]^{2+}$ (**2**) possesses certain features which are similar to those observed for oxy-Hc, including the reversible binding of $O_2$ to the Cu(I) precursor and the protonation reaction to give $H_2O_2$ and a met form (e.g., Cu(II)).[1] The peroxo dicopper(II) description for $[\{LCu\}_2(O_2)]^{2+}$ (**2**) also derives from the presence of the low-energy band at 1035 nm, which is a d–d absorption diagnostic of copper in the 2+ oxidation state.[14] The strong bands in the 500–600-nm range are tentatively assigned as $O_2^{2-} \rightarrow Cu(II)$ LMCT transitions. The fact that **2** is EPR silent and exhibits reasonably sharp ligand resonances in its $^1H$ NMR spectrum (−80 °C, $CD_2Cl_2$), in the absence of a bridging ligand other than peroxide, shows that an $O_2^{2-}$ ligand by itself is capable of mediating moderate to strong antiferromagnetic coupling between Cu(II) ions.[15-17] Complex **2** is not a precise model for oxy-Hc, since it possesses a trigonal (and not tetragonal[1a]) Cu(II) environment and a substantially different UV–vis pattern,[1a] and the *trans*-$\mu$-1,2-$O_2^{2-}$ bridging mode is inconsistent with the observed 3.6 Å Cu···Cu distance (by EXAFS[18]) in the protein.[17b]

The present results, along with others,[8,16a-c,19,20] show that a variety of structurally and spectroscopically distinct copper dioxygen species exist and that previous difficulties encountered in characterizing discrete $Cu_n$–$O_2$ species (e.g., Cu(I) disproportionation, kinetic lability of Cu(I) and Cu(II), moisture sensitivity, copper-catalyzed peroxide decomposition) can be overcome. The chemistry seen in this system shows that it is possible to bind dioxygen reversibly with *mono*nuclear copper(I) complexes and *without* an additional bridging ligand (i.e., besides $O_2^{2-}$), analogous to reactions observed between cobalt(II) complexes and dioxygen.[12] The ligation and structural features observed in $[\{LCu\}_2(O_2)]^{2+}$ (**2**) provide us with a system where the magnetic and spectroscopic contributions of an $O_2^{2-}$ ligand can be assessed and serve as a useful framework for the design of new systems for our ongoing investigations of $Cu(I)_n/O_2$ reactivity.

**Acknowledgment.** We thank the National Institutes of Health through Grants GM 28962 and GM 34909 for support of this research.

**Supplementary Material Available:** Listings of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors (4 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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[13] $[LCu^{II}(MeCN)](PF_6)_2$ isolated this way was identified by comparison to authentic $[LCu^{II}(MeCN)](ClO_4)_2$: IR (Nujol) $\nu$ (CN), 2315, 2290 cm$^{-1}$. Anal. Calcd for $C_{20}H_{21}Cl_2CuN_5O_8$: C, 40.45; H, 3.56; N, 11.79. Found: C, 40.55; H, 3.53; N, 11.80.

[14] No d–d bands are expected for complexes of a closed shell $d^{10}$ Cu(I) ion.

[15] Magnetically coupled dinuclear Cu(II) complexes can exhibit isotropically shifted ligand $^1H$ NMR absorptions where the shift (and broadening) decrease with increasing $|2J|$: (a) Kitagawa, S.; Munakata, M.; Yonezawa, M. *J. Fac. Sci. Technol. Kinki Univ.* **1984**, *19*, 63–68. (b) Dei, A.; Gatteschi, D.; Piergentili, E. *Inorg. Chem.* **1979**, *18*, 89–93. (c) Byers, W.; Williams, R. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 555–560.

[16] Other instances of magnetically coupled $Cu^{II}_n$–$O_2$ ($n$ = 1 or 2) species exhibiting sharp ligand $^1H$ NMR spectra are as follows: (a) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057–4059. (b) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196–1207. (c) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 151–152.

[17] (a) In addition to the example in this report, we[16b] and others[16c] have described magnetically coupled $Cu_2$–$O_2$ complexes having (i) no apparent bridging ligand other than $O_2^{2-}$ and (ii) spectroscopic properties qualitatively resembling those of oxy-Hc. (b) An additional "endogeneous" bridging ligand for the copper ions in oxy-Hc (most likely $OH^-$ or $H_2O$) has been suggested as the primary mediator of the strong magnetic coupling (e.g., diamagnetic) observed. See ref 1a and 16b,c for recent discussions and the following: Wilcox, D. E.; Long, J. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 2186–2194. Lorösch, J.; Haase, W. *Biochemistry* **1986**, *25*, 5850–5857.

[18] (a) Co, M. S.; Hodgson, K. O.; Eccles, T. K.; Lontie, R. *J. Am. Chem. Soc.* **1981**, *103*, 984–986. (b) Brown, J. M.; Powers, L.; Kincaid, B.; Larrabee, J. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 4210–4216.

[19] (c) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 8308–8309.

[20] (a) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219–327. (b) *Biological & Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1986; Vol. 2. (c) Also, see Bulkowski and Summers (Bulkowski, J. E.; Summers, W. E., III In ref 6b, pp 445–456) for an X-ray structure reported to contain $Cu_2(O_2)$ moieties, although severe disorder precludes an unambiguous conclusion.

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## Palladium-Catalyzed Regular Insertion of Isonitriles into Silicon–Silicon Linkage of Polysilane

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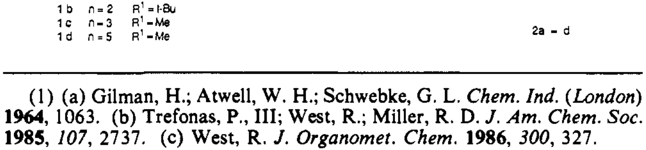
*Received February 25, 1988*

Recently, much attention has been directed toward silicon-containing polymers due to their chemical and physical properties.[1] Consequently, syntheses and synthetic methods for the preparation of silicon-containing polymers are desirable. In a previous paper,[2] we described a new insertion reaction of isocyanide into the silicon–silicon linkage of disilanes, which is catalyzed by palladium(0) tetrakis(triphenylphosphine) complex. Now, we have found that poly-insertion of isocyanide into polysilanes is catalyzed by a palladium catalyst to give poly[sila(N-substituted)imines]. Noteworthy is the observation that an isocyanide molecule is regularly inserted into each silicon–silicon linkage of polysilanes.

Octamethyltrisilane (**1a**) was heated at reflux in toluene for 3 h with 2,6-xylyl isocyanide in the presence of a catalytic amount of palladium(II) acetate to give 1,1,1,3,3,5,5,5-octamethyl-2,4-bis(2,6-xylylimino)-1,3,5-trisilapentane (**2a**),[3] which was isolated as a yellow crystalline solid (isolated yield 56%) from ethanol or hexane. **2a** (mp 105–106 °C): IR (KBr disk) 1546 cm$^{-1}$; UV (cyclohexane solution $\lambda_{max}$ 406 nm ($\epsilon$ 420). The $^1H$ NMR spectrum of **2a** is noteworthy in that the very broad signal, assigned to the $(CH_3)_3Si$ and $(CH_3)_2Si$ groups, appeared between $\delta$ −0.25



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[3] Spectral and analytical data for poly[sila(N-substituted)imines] (**2**) are as follows. $^1H$ NMR spectra were measured in $CDCl_3$ with cyclohexane as an internal standard. **2a**: IR (KBr) 1594, 1546 cm$^{-1}$; $^1H$ NMR $\delta$ −0.25–0.70 (br, 24 H), 1.97 (s, 12 H), 6.70–7.12 (m, 6 H); $^{13}C$ NMR (benzene-$d_6$, 80 °C) $\delta$ −0.19 (br), 18.64, 123.19, 123.54, 128.14, 155.72, 217.3 (br); mass spectrum, $m/z$ 466 (M$^+$). Anal. Calcd for $C_{26}H_{42}N_2Si_3$: C, 66.89; H, 9.07; N, 6.00. Found: C, 66.81; H, 9.07; N, 6.05. **2b**: IR (KBr) 1592, 1546 cm$^{-1}$; $^1H$ NMR $\delta$ −0.15 (s, 9 H), 0.05 (s, 6 H), 0.31 (s, 6 H), 1.31 (s, 9 H), 1.93 (s, 6 H), 2.03 (s, 6 H), 6.72–7.05 (m, 6 H); mass spectrum, $m/z$ 508 (M$^+$). **2c**: IR (KBr) 1592, 1544 cm$^{-1}$; $^1H$ NMR $\delta$ −0.41–0.82 (br, 30 H), 1.95 (s, 12 H), 2.01 (s, 6 H), 6.62–7.04 (m, 9 H); mass spectrum, $m/z$ 655 (M$^+$).

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