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 ^{1}H 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*-μ-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) ν (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 ^{1}H 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 ^{1}H 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. Lorōsch, 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.

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

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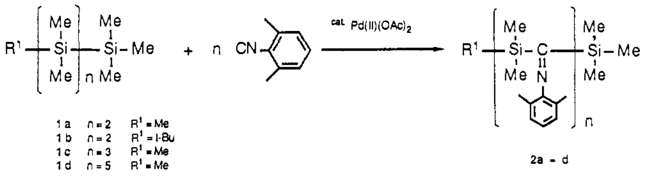
Recently, much attention has been directed toward silicon-containing polymers due to their chemical and physical properties.[1] Consequently, syntheses and synthetic methods for the preparation of silicon-containing polymers are desirable. In a previous paper,[2] we described a new insertion reaction 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 λ_{max} 406 nm (ϵ 420). The ^{1}H 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 δ −0.25



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[1] (a) Gilman, H.; Atwell, W. H.; Schwebke, G. L. *Chem. Ind.* (*London*) **1964**, 1063. (b) Trefonas, P., III; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737. (c) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

[2] Ito, Y.; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293.

[3] Spectral and analytical data for poly[sila(N-substituted)imines] (**2**) are as follows. ^{1}H NMR spectra were measured in $CDCl_3$ with cyclohexane as an internal standard. **2a**: IR (KBr) 1594, 1546 cm^{-1}; ^{1}H NMR δ −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) δ −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}; ^{1}H NMR δ −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}; ^{1}H NMR δ −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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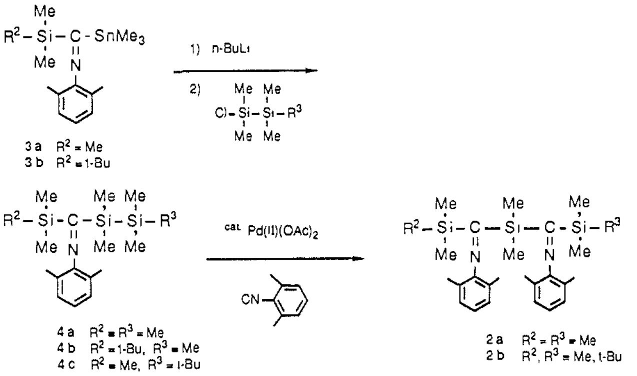
and 0.70 at room temperature, which split into two slightly broad singlets at δ −0.03 and 0.32 with a relative intensity of 3:1 at 90 °C. The temperature dependence of the ^{1}H NMR spectra shows that the syn–anti interconversion of *N*-2,6-xylylimines is rapid enough to sharpen the $(CH_3)_3Si$ and $(CH_3)_2Si$ signals at 90 °C.

2,4-Bis(2,6-xylylimino)-1,3,5-trisilapentane (**2a**) (yield 60%)[3] was also obtained by a palladium-catalyzed reaction of 2,6-xylyl isocyanide with 1-[(trimethylsilyl)(2,6-xylylimino)methyl]-1,1,2,2,2-pentamethyldisilane (**4a**),[4] which was prepared from [(trimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**3a**) and chloropentamethyldisilane according to the reported procedure.[5]



Similarly, 1-*tert*-butyl-1,1,2,2,3,3,3-heptamethyltrisilane (**1b**) reacted with 2,6-xylyl isocyanide in the presence of palladium(II) acetate to afford 1-*tert*-butyl-1,1,3,3,5,5,5-heptamethyl-2,4-bis(2,6-xylylimino)-1,3,5-trisilapentane (**2b**) (yield 82%),[3] which was recrystallized from ethanol. **2b** (mp 79–81 °C): IR (KBr) 1546 cm^{-1}; UV (cyclohexane solution) λ_{max} 410 nm (ε 620).

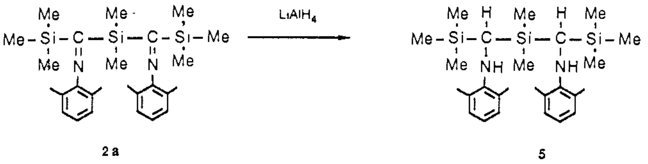
The same 2,4-bis(2,6-xylylimino)-1,3,5-trisilapentane (**2b**) was prepared by palladium-catalyzed insertion of 2,6-xylyl isocyanide into either 1-[(*tert*-butyldimethylsilyl)(2,6-xylylimino)methyl]-1,1,2,2,2-pentamethyldisilane (**4b**)[4] or 1-[(trimethylsilyl)(2,6-xylylimino)methyl]-2-*tert*-butyl-1,1,2,2-tetramethyldisilane (**4c**).[4] These findings excluded the possibility of successive insertion of two 2,6-xylyl isocyanides into the silicon–silicon linkage of polysilane.

The palladium-catalyzed regular insertion of isocyanides into polysilane was successfully applied to tetrasilane; e.g., the reaction of decamethyltetrasilane (**1c**) with 2,6-xylyl isocyanide produced the expected 1,1,1,3,3,5,5,7,7,7-decamethyl-2,4,6-tris(2,6-xylylimino)-1,3,5,7-tetrasilaheptane (**2c**)[3] in 34% isolated yield as a yellow crystalline solid. **2c** (mp 110–112 °C): IR 1544 cm^{-1}; UV (cyclohexane solution) λ_{max} 407 nm (ε 540).

Further extension of the poly-insertion of 2,6-xylyl isocyanide into permethylhexasilane (**1d**) afforded a mixture that included the expected poly[sila(*N*-2,6-xylyl)imine] (**2d**), whose mass spectrum gave the corresponding molecular ion peak.

An experimental procedure for the palladium-catalyzed regular insertion of 2,6-xylyl isocyanide into polysilane is exemplified with octamethyltrisilane. A mixture of 2,6-xylyl isocyanide (0.89 g, 6.8 mmol), octamethyltrisilane (0.46 g, 2.2 mmol), and palladium(II) acetate (0.05 g, 0.2 mmol) in toluene (8 mL) was heated at reflux for 3 h under a nitrogen atmosphere. In order to remove the remaining 2,6-xylyl isocyanide, the reaction mixture was stirred with copper(I) chloride (2.1 g, 21 mmol) for 5 h at room temperature and then subjected to flash chromatography (hexane–toluene solvent) on Florisil, which was pretreated with triethylamine. The solvent was evaporated and the remaining yellow solid was crystallized from ethanol to give **1a** (0.58 g, 56%).

Reduction of the imino groups of **2a** was readily performed by treatment with $LiAlH_4$ in Et_2O at room temperature to afford 1,1,1,3,3,5,5,5-octamethyl-2,4-bis(*N*-2,6-xylylamino)-1,3,5-trisilapentane (**5**)[6] in 85% yield.



The poly-insertion of isocyanides into polysilanes of high molecular weight is being undertaken in this laboratory.

Acknowledgment. The work was supported in part by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, No. 62115003).

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[4] **4a**: IR (KBr) 1594, 1544 cm^{-1}; ^{1}H NMR δ −0.30–0.50 (br, 24 H), 1.95 (s, 6 H), 6.67–7.02 (m, 3 H); mass spectrum, *m/z* 335 (M$^+$). Anal. Calcd for $C_{17}H_{33}NSi_3$: C, 60.82; H, 9.91; N, 4.17. Found: C, 60.63; H, 10.04; N, 4.13. **4b**: IR (KBr) 1594, 1540 cm^{-1}; ^{1}H NMR δ −0.15 (s, 6 H), 0.02 (s, 9 H), 0.24 (s, 6 H), 1.02 (s, 9 H), 1.98 (s, 6 H), 6.60–7.00 (m, 3 H); mass spectrum, *m/z* 377 (M$^+$). **4c**: IR (KBr) 1594, 1542 cm^{-1}; ^{1}H NMR δ −0.12 (br s, 9 H), 0.10 (s, 6 H), 0.40 (br s, 6 H), 0.93 (s, 9 H), 1.97 (s, 6 H), 6.63–7.02 (m, 3 H); mass spectrum, *m/z* 377 (M$^+$).

[5] Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1987**, *109*, 7888.

[6] **5** (mp 86–87 °C): IR (KBr) 3428, 1594 cm^{-1}; ^{1}H NMR δ −0.05 (br s, 24 H), 2.23 (br s, 12 H), 2.97–3.23 (m, 4 H), 6.50–6.90 (m, 6 H); mass spectrum, *m/z* 470 (M$^+$).

Cycloaddition Reactions of Silyloxyacetylenes with Ketenes: Synthesis of Cyclobutenones, Resorcinols, and Δ-6-Tetrahydrocannabinol

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The utility of alkyoxyacetylenes (R—C≡C—OR′) in synthesis[2] has been limited by lack of simple, general methods for their preparation with widely varied R groups.[3] Recently we reported a single-pot preparation of triisopropylsilyloxyacetylenes **4** from esters **1**.[4] Herein we report that such silyloxyacetylenes are useful substitutes for alkoxyacetylenes in 2 + 2 cycloaddition reactions with both ketenes and cyclobutenone-derived vinylketenes, affording cyclobutenone **2** and resorcinol **6** products, respectively.

In parallel with precedents for alkoxyacetylenes,[5] it was found that on bubbling ketene[6] through solutions of silyloxyacetylenes **4** at 0 °C, 3-silyloxycyclobutenones **2** were formed. Yields were high whether the R group in **4** and **2** had a primary, secondary, or tertiary center as its point of attachment (Chart I, entries 1–3);[7]

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[1] Smith Kline & French Postdoctoral Research Scientist, 1985–1987.

[2] Brandsma, L.; Bos, H. J. T.; Arens, J. F. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; pp 751–860. See also ref 12 below as well as footnote 2 of ref 3e.

[3] While a number of alkoxyacetylene preparations have been published, most lack generality in the nature of possible attachments to the acetylenic carbon, and/or require multiple steps, and/or utilize explosive intermediates. See: (a) Jones, E. R. H.; Eglington, G.; Whiting, M. C.; Shaw, B. L. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. 4, p 404. (b) Newman, M. S.; Geib, J. R.; Stalick, W. M. *Org. Prep. Proc. Int.* **1972**, *4*, 89. (c) Moyano, A.; Charbonnier, F.; Greene, A. *J. Org. Chem.* **1987**, *52*, 2919. (d) Raucher, S.; Bray, B. L. *J. Org. Chem.* **1987**, *52*, 2332. (e) Pericas, M. A.; Serratosa, F.; Valenti, E. *Tetrahedron* **1987**, *43*, 2311 and numerous citations provided in ref 3c–e.

[4] Kowalski, C. J.; Lal, G. S.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 7127.

[5] See ref 2, pp 805–807.

[6] Ketene was generated via pyrolysis of acetone, see: Hanford, W. E.; Sauer, J. C. *Org. React.* **1946**, *3*, 109.

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