different from those of the native protein.

The reaction of $a_5RuH_2O^{2+}$ with sperm whale myoglobin was allowed to proceed for 24 h under anaerobic conditions at pH 7, and the Ru-labeled protein was then oxidized and purified by standard procedures, to give Ru_3Mb.[11] Absences of the imidazole C-2 proton resonances of His-12, His-81, and His-113 in the high-field NMR spectrum of Ru_3Mb pinpoint those residues as the sites of attachment of the a_5Ru^{3+} groups (Figure 1).[12,13]

The three attached a_5Ru^{3+} groups do not appear strongly to perturb the Mb conformation, as judged by comparative measurements of electronic and vibrational spectra. The ability of the heme in Ru_3Mb to bind anions, however, is enhanced greatly over that of the native protein. Cyanide, for example, binds strongly both to the Fe^{III} *and* Fe^{II} forms of Ru_3Mb.[14] The electrostatic influence of the three a_5Ru^{3+} groups is likely responsible for this impressive change in anion affinity, as it is for the very high pI value (~9.2) for Ru_3Mb.

The reduction of O_2 by a variety of organic substrates is catalyzed quite effectively by Ru_3Mb. Good substrates for this " synthetic oxidation–reduction enzyme" include ascorbate and durohydroquinone. Comparisons of reactivity parameters (K_m, k_{cat}) for several substrates with a_5RuIm^{3+}, Ru_3apoMb, and Ru_3Mb suggest that the presence of a dioxygen binding site in Ru_3Mb greatly enhances the base line turnover rate of an a_5RuIm^{3+}-type catalytic system (Table I). In view of the proximity of His-113 to the heme (Figure 2), it is likely that $a_5Ru(His\text{-}113)^{2+}$ transfers an electron rapidly to the heme–dioxygen complex,[15] thereby producing some form of heme-bound peroxide intermediate (whose dissociation may prove to be the rate-limiting step). Clearly, our preliminary work has established that Ru_3Mb is an interesting multisite catalytic system that deserves detailed mechanistic examination.

Acknowledgment. We thank Gary Campbell and Walther Ellis for assistance with certain spectroscopic measurements, and we are indebted to Joan Shelton, Roger Shelton, and Walter Schroeder for performing the tryptic hydrolyses. This research was supported by National Science Foundation Grant CHE80-24863. Fellowship support (R.M.) from Martin Marietta Corp. is acknowledged. NMR experiments were performed at the Southern California Regional NMR Facility supported by National Science Foundation Grant CHE79-16324.

Registry No. Cyanide, 57-12-5; oxygen, 7782-44-7; ascorbic acid, 50-81-7; durohydroquinone, 527-18-4; hydroquinone, 123-31-9; $[Ru(NH_3)_5H_2O][PF_6]_2$, 34843-18-0.

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[11] The reaction between $[Ru(NH_3)_5H_2O](PF_6)_2$ (40-fold excess) and sperm whale myoglobin (Type II, Sigma) at room temperature (pH 7.3; 0.05 M Tris·HCl) was terminated by applying the solution to a Sephadex G-25 column. The Ru_3Mb sample was oxidized by $Co(phen)_3(ClO_4)_3$ and then separated from unreacted Mb by using a CM-52 column (linear gradient of NaCl in 50 mM Tris·HCl, pH 7.3). Ru_3Mb was characterized by isoelectric focusing on LKB ampholine PAG plates (pH range 3.5–9.5; native Mb, pH ~7; Ru_3Mb, pH ~9.2); the Ru:Mb ratio was determined to be 3:1 (±3%) by employing $[^{106}Ru(NH_3)_5Cl]Cl_2$ to prepare $^{106}Ru(NH_3)_5H_2O^{2+}$ and analyzing ^{106}Ru in the protein derivative.

[12] The imidazole C-2 proton resonances in native sperm whale Mb have been assigned (Botelho, L. H.; Friend, S. H.; Matthew, J. B.; Lehman, L. D.; Hanania, G. I. H.; Gurd, F. R. N. *Biochemistry* **1978**, *17*, 5197–5205).

[13] Isolation of the His-81- and His-113-containing tryptic peptides of Ru_3Mb has confirmed those two a_5Ru^{3+} attachment sites, but the His-12-containing peptide has eluded characterization, owing in part to its poor solubility properties (Shelton, J. B.; Shelton, J. R.; Schroeder, W. E., unpublished results). However, the presence of an $a_5Ru(His\text{-}12)^{3+}$ unit may be inferred from our observation that the fluorescence of nearby tryptophans (Trp-7, Trp-14) in apoMb is strongly quenched in Ru_3apoMb.

[14] Very concentrated cyanide solutions ($[CN^-] \sim 1$ M; $[Mb] \sim 40\ \mu M$) are required for >95% formation of the $Mb(Fe^{2+})\cdot(CN^-)$ complex (Keilin, D.; Hartree, E. F. *Biochem. J.* **1955**, *61*, 153–171). In contrast, >95% formation of $Ru_3Mb(Fe^{2+})\cdot(CN^-)$ occurs at $[CN^-] \sim 0.1$ mM for $[Ru_3Mb(Fe^{2+})] \sim 10\ \mu M$.

[15] Dioxygen reduction by ruthenium(II) ammine complexes apparently involves formation of superoxide anion as a reactive intermediate (Stanbury, D. M.; Haas, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518–524). It would be highly surprising if reduced Ru_3Mb with its multiple redox centers did not choose a more felicitous route to peroxide. Indeed, our observation that reduced Ru_3Mb reacts much more rapidly than a_5RuL^{2+} with dioxygen indicates that it does.

Structure and Reactivity of Sterically Hindered Lithium Amides and Their Diethyl Etherates: Crystal and Molecular Structures of $[Li\{N(SiMe_3)_2\}(OEt_2)]_2$ and $[Li(\overline{NCMe_2CH_2CH_2CH_2C}Me_2)]_4$

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Received July 12, 1982

Bulky amides of the alkali metals are extensively employed as reagents in organic chemistry by virtue of the combination of their strong Brønsted basicity and their low nucleophilicity, especially with respect to electrophilic carbon centers;[1] lithium derivatives of secondary amines have a particularly pivotal role. An objective of the present communication is to provide X-ray structural data for two of the key compounds, bis(trimethylsilyl)amido-[2] and (2,2,6,6-tetramethylpiperidinato)lithium in order to place the steric arguments on a firm basis. A further purpose is to note that these compounds are not only bases but also Lewis acids,[3] and hence the choice of donor solvent may be significant.[4] The formation of a lithium amide solvate is expected to affect both the state of molecular aggregation of the amide[6,8] and its hydrocarbon solubility.[10] These properties are of considerable significance in making an appropriate choice of lithium amide reagent as an amido transfer reagent for the synthesis of an amide of another metal. In our own work, we have a strong preference for a *crystalline* lithium amide monoetherate as reagent, because of the following features: (i) confidence with regard to reagent purity and concentration, (ii) availability of a nonpolar solvent as the reaction medium, and (iii) ease of manipulation.[12]

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[1] Cf.: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Horwood-John Wiley: Chichester, 1980; pp 689–691.

[2] The X-ray structure of $\{Li[N(SiMe_3)_2]\}_3$ has been determined: Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 378. Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* **1978**, *157*, 229.

[3] The formation of a 1:1 OEt_2 adduct of $Li[N(SiMe_3)_2]$ has been noted: Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540.

[4] We believe that for metal amides this has not previously been explicitly stated; although for lithium alkyls the role of different solvents such as OEt_2, THF, TMEDA, or PMDETA (pentamethyldiethylenetriamine), upon their structure and reactivity is beginning to be documented.[5]

[5] Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 14.

[6] Variable-temperature ^1H and ^7Li NMR spectra of $Li[N(SiMe_3)_2]$ in several donor solvents were examined and the results interpreted in terms of a monomer ⇄ dimer equilibrium in solution.[7]

[7] Kimura, B. Y.; Brown, T. L. *J. Organomet. Chem.* **1971**, *26*, 57.

[8] We suggest that the lower the state of molecular aggregation, the greater the amide reactivity and selectivity; the extreme case would be for a monomeric solvated lithium amide, and we predict that for example $Li[N(SiMe_3)_2](PMDETA)$ will prove to be a monomer in the crystal and will be outstandingly reactive and selective as a proton abstractor. As circumstantial evidence we cite the monomeric $Li[CH(SiMe_3)\text{-}o\text{-}MeC_6H_4](PMDETA)$.[9]

[9] X-ray data: Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H., unpublished work.

[10] We find that although $\{Li[N(SiMe_3)_2]\}_3$ and $\{Li[\overline{NCMe_2(CH_2)_3C}Me_2]\}_4$ have some *n*-pentane solubility, this is significantly increased for $\{Li[N(SiMe_3)_2](OEt_2)_2\}_2$ or $\{Li[\overline{NCMe_2(CH_2)_3C}Me_2](OEt_2)\}_n$ (the structure of this compound, and hence the value of *n*, is not yet known). We had previously reported[11] that $[Li(OAr)(OEt_2)]_2$ ($Ar = C_6H_5\text{-}4\text{-}Me\text{-}2,6\text{-}t\text{-}Bu_2$) is soluble in $n\text{-}C_6H_{14}$, whereas $[Li(OAr)]_n$ (of unknown structure) is insoluble.

[11] Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.

[12] Our most recent papers on metal amides using $\{Li[N(SiMe_3)_2](OEt_2)\}_2$ concerns $\{ErCl[N(SiMe_3)_2](\mu\text{-}Cl)_2Li(THF)_2\}$,[13] and using $[Li(N\text{-}t\text{-}Bu_2)(OEt_2)]_x$ or $\{Li[\overline{NCMe_2(CH_2)_3C}Me_2](OEt_2)\}_n$ concerns $M(N\text{-}t\text{-}Bu_2)_2$ or $M[\overline{NCMe_2(CH_2)_3C}Me_2]_2$ (M = Ge or Sn).[14]

[13] Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1191.

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Table I. Structural Comparisons of Three Crystalline Lithium Amides[a]

empirical formula	degree of molecular aggregation in crystal	coordination no. of Li	Li–N_{av}, Å	Li–N–Li, deg	N–Li–N_{av}, deg	Si–N–Si, deg	Si–N_{av}, Å
$Li[NCMe_2(CH_2)_3CMe_2]$	tetramer,[b] **2**	2	2.00 (2)	101.5 (3)	168.5 (4)		
$Li[N(SiMe_3)_2]$	trimer,[c] **3**	2	2.00 (2)	92 (2)	147 (3)	118.6 (9)	1.729 (4)
$Li[N(SiMe_3)_2](OEt_2)$	dimer,[d] 1	3	2.06 (1)	74.8 (8)	105.2 (8)	121.9 (4)	1.705 (3)

[a] The $(LiN)_n$ ring conformation in all cases is planar. [b] The four Li atoms and the four N atoms are each coplanar; the N atoms are less than 0.01 Å out of the Li_4 plane. [c] Reference 2; the Li_3N_3 ring is planar to within 0.01 Å. [d] Li–O, 1.95 (2) Å; O–Li–N, 127.4 (4)°; Li–O–C, 121.7 (4)°; C–O–C, 116.6 (8)°, trigonal planar at both O and Li.

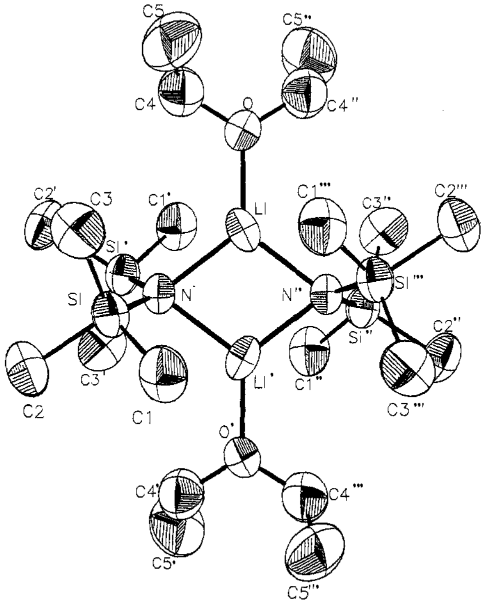

Figure 1. Molecular structure of $\{Li[N(SiMe_3)_2](OEt_2)\}_2$, **1**, with the atoms represented by their 50% probability ellipsoids for thermal motion. The dimer resides about a crystallographic 222 site: one 2-fold axis contains the lithium and oxygen atoms, one the nitrogen atoms, and the third is perpendicular to the Li_2N_2 plane.

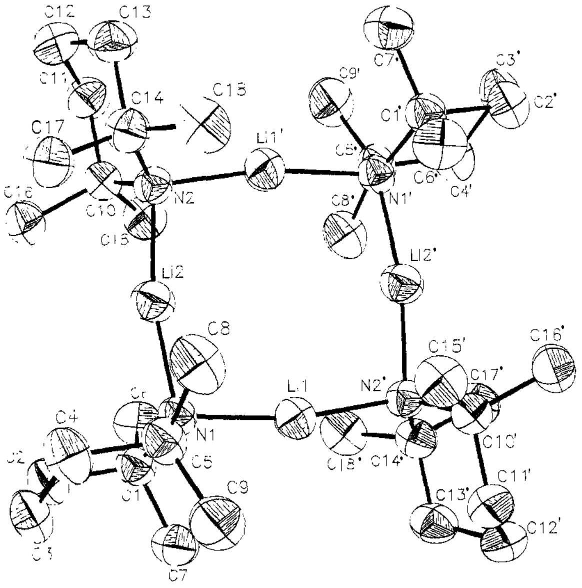

Figure 2. Structure of $[Li(NCMe_2CH_2CH_2CH_2CMe_2]_4$, **2**.

Table II. Some Data for Bulky Lithium Amides[a]

compound	yield,[b] %	mp, °C
$\{Li[N(SiMe_3)_2](OEt_2)\}_2$, 1[c]	72	105–107[d]
$\{Li[N(CMe_2(CH_2)_3CMe_2]\}_4$, 2	68	185–186 dec

[a] Analytically uncharacterized crystalline $[Li(N\text{-}t\text{-}Bu_2)]_n$ (76%) and $[Li(N\text{-}i\text{-}Pr\text{-}t\text{-}Bu)]_m$ (74%) were obtained from the appropriate amine and an equimolar portion of Li-*n*-Bu in *n*-C_6H_{14}. [b] This refers to isolated crystalline material. [c] ^1H NMR (assignments; C_6D_6) δ 9.63 $[Si(CH_3)_3]$, 8.93 (CH_2CH_3), 6.45 (CH_2CH_3); ^{13}C NMR (ppm relative to C_6D_6 at 128.0 ppm, in C_6D_6) 6.05 $[Si(CH_3)_3]$, 14.0 (CH_2CH_3), 63.51 (CH_2CH_3). [d] Cf.[3] mp 95–110 °C dec.

The crystal and molecular structure of $Li[N(SiMe_3)_2](OEt_2)$ (**1**), illustrated in Figure 1,[15] shows the compound to be the bis(μ-bis(trimethylsilyl)amido)dilithium compound with terminal diethyl etherate molecules completing the three-coordinate lithium atom environment. As in $[Li(OC_6H_2\text{-}4\text{-}Me\text{-}2,6\text{-}t\text{-}Bu_2(OEt_2)]_2$,[11] both the lithium and ether oxygen atoms are trigonal planar, and the Li–OEt_2 bond lengths are comparable, 1.961 (11) Å in the aryl oxide. Figure 1 also demonstrates the lipophilic character of compound **1**, a feature also evident for the aryl oxide.

The crystal and molecular structure of $\{Li[NCMe_2(CH_2)_3CMe_2\}_4$ (**2**), illustrated in Figure 2,[16] shows the compound to have a planar eight-membered $(LiN)_4$ ring, with each piperidine ring in chair conformation arranged in staggered relationship to one another so as to provide an inversion center. A two-coordinate lithium environment is not unique, having already been established for $\{Li[N(SiMe_3)_2]\}_3$ (**3**), which, however, has a planar hexagonal $(LiN)_3$ ring.[2] This difference reflects the greater steric demand of the 2,2,6,6-dimethylpiperidinato ligand compared with $\bar{N}(SiMe_3)_2$. A similar effect has been noted, inter alia in cyclic $(XBNY)_n$ chemistry, wherein the six-membered planar borazine ($n = 3$) provides the norm, but sterically demanding ligands X and Y may result in either a square-planar arrangement ($n = 2$) or a crown-shaped tetramer ($n = 4$).[17]

Some significant structural parameters on compounds **1**–**3** are summarized in Table I. Not unexpectedly the Li–N bond length is longer when the $\bar{N}(SiMe_3)_2$ ligand occupies a bridging (**1**) rather than a terminal (**3**) role.

In one preparative experiment, 60 mL of 1.67 M (100 mmol) of *n*-butyllithium solution in *n*-hexane was added dropwise during

---

(14) Lappert, M. F.; Slade, M. J.; Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 621.

(15) Compound **1** crystallizes in the tetragonal space group $P\bar{4}n2$, with lattice constants $a = 9.790$ (3) Å, $c = 17.284$ (5) Å, and $D_c = 0.92$ g cm^{-3} for two dimers in the unit cell. Data were collected on the CAD-4 diffractometer in the usual manner: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. Least-squares refinement based on 604 observed reflections led to a final *R* value of 0.051 (73 varied parameters). Hydrogen atoms were included with fixed contributions, and all non-hydrogen atoms were refined with anisotropic thermal parameters. A series of ψ scans showed that an absorption correction was unnecessary.

(16) Compound **2** crystallizes in the monoclinic space group *C*2/*c*, with lattice constants $a = 16.673$ (6) A, $b = 16.584$ (6) Å, $c = 15.893$ (6) Å, $\beta = 116.76$ (4)°, and $D_c = 1.00$ g cm^{-3} for two tetramers in the unit cell. Data were collected as for **1**. Least-squares refinement based on 1369 observed reflections led to a final *R* value of 0.044 (198 varied parameters). Hydrogen atoms were included with fixed contributions, and all non-hydrogen atoms were refined with anisotropic thermal parameters. As with **1**, no absorption correction was necessary.

(17) Cf. ref 1, p 70.

ca. 2 h to a cooled (0 °C) and stirred solution of hexamethyldisilazane (20 mL, 95 mmol) in 100 mL of diethyl ether. After stirring at 20 °C for ca. 2 h, the white crystals were filtered off, washed with cooled *n*-hexane, dried in vacuo, and recrystallized from cold OEt_2–*n*-C_6H_{14} to afford the analytically pure, air-sensitive compound (**1**).

In another preparation, *n*-butyllithium (37 mL of a 1.6 M solution in *n*-C_6H_{14}, 59.2 mmol) was added dropwise during ca. $^1/_2$ h to a stirred solution of 2,2,6,6-tetramethylpiperidine (10 mL, 59.4 mmol) in *n*-C_5H_{12} (40 mL). The reaction mixture slowly became opalescent, and after stirring overnight, a white precipitate and pale yellow solution was observed. The mixture was filtered, and the white solid was washed with cold (0 °C) *n*-pentane and pumped dry to give the very air-sensitive, slightly pyrophoric, crystals of analytically pure compound (**2**).

Acknowledgment. We are grateful to SERC for the award of a studentship to M.J.S. and a fellowship to A.S. and to the National Science Foundation for partial support (to J.L.A.).

Registry No. 1, 84040-90-4; **2**, 84040-91-5.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes for **1** and **2** (19 pages). Ordering information is given on any current masthead page.

Silane Surface Chemistry of Palladium: Synthesis of Silaethylene, Silacyclobutadiene, and Silabenzene

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Received October 12, 1982

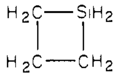
Chemisorption of cycloalkenes on metal surfaces are followed by dehydrogenation processes[1] that often give chemisorbed C_nH_n species, e.g., cyclohexene → benzene[1-3] and cyclooctadiene → cyclooctatetraene.[1] Because these transformations are facile, we have been exploring the reactions of organosilanes with single-crystal metal surfaces[4] as routes to compounds in which there are Si–C bonds of multiple bond order. With platinum and nickel, we observed either no dehydrogenation or gross degradation of the silaalkane.[5] Palladium, however, has furnished dehydrogenation syntheses of silaethylenes, silabenzene, and what appears to be silacyclobutadiene.[6]

Tetramethylsilane on Pd(110) desorbed fully and intact at ~−50 °C analogous to neopentane on Pd(110), which quantitatively desorbed with a T_{max} of ~−60 °C. In sharp contrast, trimethylsilane after adsorption at −135 °C underwent two competing thermal processes: (i) reversible desorption with a maximum desorption rate at −20 °C; (ii) dehydrogenation to form $(CH_3)_2Si{=}CH_2$,[8,9] which desorbed with maximum rates at −40 and +90 °C (the surface was essentially free of Si and C after the desorption experiment). The latter process was accompanied by H_2 desorption, which also exhibited maxima at −40 and +90 °C. Minor dimerization of the silaethylene also occurred: $[-Si(CH_3)_2CH_2-]_2$ desorbed to give a broad peak at ~40 °C. An unexpected feature here was desorption of silaethylene because most alkenes and alkynes ***irreversibly*** chemisorb on clean transition-metal surfaces. Consistent with the organosilane surface chemistry, we have found that acetylene and ethylene chemisorb on Pd(110) in a partially reversible fashion.[10]

Displacement of the silaethylene, $(CH_3)_2Si{=}CH_2$, from the Pd(110) surface was effected with $P(CH_3)_3$. On dosing the crystal face with $P(CH_3)_3$ at +25 °C, there was immediate displacement of the silaethylene, the dimer, $[-Si(CH_3)_2CH_2-]_2$, and trimethylsilane.

The silaethylene $(CH_3)_2Si{=}CH_2$ was also produced in the thermal desorption experiments with $(CH_3)_3SiOSi(CH_3)_3$, $(CH_3)_3SiNHSi(CH_3)_3$, and $(CH_3)_3SiN_3$ on Pd(110). All three also exhibited partially reversible chemisorption. In the azide system, an additional and major product was $[-(CH_3)_2SiN(CH_3)-]_2$.

Silacyclobutane displayed a complex Pd(110) surface chemistry. After adsorption at −135 °C, silanes **1–4** were observed in the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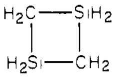
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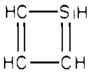
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$H_2Si{=}CH_2$
4

thermal desorption with respective desorption maxima at ~−65, +65, +50, and +70 °C, respectively. Ethylene and hydrogen were observed with similar T_{max} of 60–80 °C. All these species were observed in a chemical displacement reaction with $P(CH_3)_3$. Silacyclobutadiene is a new compound, and its characterization must be considered tentative in that it is based solely on mass spectrometric data. The parent ion was less intense than the parent-minus-one ion, as expected for a species with one Si–H bond. Ostensibly, silaethylene[9c] was the precursor to the dimer **2**. Consistent with this presumption, the ratio of **4** to **2** increased when the heating rate was increased from 25 to 75 °C s^{-1}.

Silacyclohexane, initially adsorbed on Pd(110) at −135 °C, also underwent two competing surface reactions: reversible desorption (T_{max} = −25 °C) and dehydrogenation to give silabenzene,[12] SiC_5H_6 (two T_{max} of 90 and 190 °C), and H_2 (two T_{max} of 15 and 190 °C). This chemistry parallels that of cyclohexene, which gave benzene with a T_{max} (C_6H_6) of 220 °C and also of piperidine, which gave pyridine with T_{max} (NC_5H_5) of 115 and 155 °C.[10] Silabenzene was not displaced by $P(CH_3)_3$ from the surface generated from silacyclohexane at temperatures of 25–70 °C.

There are a number of remarkable features to this Pd(110) chemistry. One is the extensive degree of reversible chemisorption of unsaturated hydrocarbons like acetylene, ethylene, and of course, silaethylene and silabenzene. Secondly, these results suggest a practical synthesis of silaethylenes, silacyclobutadienes, and silabenzenes by palladium-catalyzed dehydrogenation of organosilanes, an aspect now under study in our laboratories.[13,14] Also,

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[1] Tsai, M.-C.; Stein, J.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 3533–3534.

[2] Gates, B. C.; Katzer, J. R.; Schuitt, G. C. A. "Chemistry of Catalytic Processes"; McGraw Hill: New York, 1979; pp 222–247.

[3] (a) Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2539–2543. (b) Tsai, M.-C.; Muetterties, E. L. *J. Phys. Chem.* **1982**, *86*, 5067.

[4] See references in ref 3 for the equipment, techniques, and procedures for these ultrahigh vacuum experiments. Adsorption was generally effected at −135 °C, and desorption studies were usually done with 25 °C s^{-1} heating rates.

[5] Tsai, M.-C.; Friend, C. M.; Johnson, A. L.; Muetterties, E. L., unpublished data.

[6] The contrasting behavior of palladium with respect to platinum might be traced to a uniquely low Pd–Si bond energy.[7]

[7] Auwiera-Matieu, A. V.; Peeters, R.; McIntyre, N. S.; Drowart, J. *Trans. Faraday Soc.* **1970**, *66*, 809–816.

[8] This compound was characterized only by its mass spectrum. The essential absence of a parent-minus-one ion clearly indicated that this species contained no Si–H bond. This silaethylene molecule has been prepared by thermolysis of tetramethylsilane and trimethylsilane.[9] The alternative formulation of such species as silylenes is critically reviewed by Schaefer.[9c]

[9] (a) Fritz, G.; Grobe, J.; Kummer, D. *Adv. Inorg. Radiochem.* **1965**, *7*, 364. (b) Davidson, I. M. T.; Lamberty, C. A. *J. Chem. Soc. A* **1977**, 882. (c) Schaefer, H. F., III *Acc. Chem. Res.* **1982**, *15*, 283–290.

[10] Gentle, T. M.; Muetterties, E. L., to be published.

[11] References to the generation by thermal processes, mass spectrum, and trapping of silabenzene are given in ref 12.

[12] (a) Solouk, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51. (b) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246.

[13] Since compounds with Si–C multiple bonds readily dimerize or polymerize, the ultrahigh vacuum reaction conditions are ideal for observation of such compounds. However, this technique is impractical for the generation of sufficient quantities for chemical trapping experiments. We plan to examine Pd-catalyzed organosilane dehydrogenation reactions under flow conditions by using very short contact times and matrix or chemical trapping conditions.

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