6. The ^{119}Sn NMR spectrum[12] of a slightly larger scale reaction[13] exhibited singlet resonances for **6** (δ 118.42), $Me_3SnOSnMe_3$ (δ 114.03), and Me_3SnH (δ −102.33), and there was a single resonance at δ −101.55 in the ^{29}Si NMR spectrum. Except for **6**, all compounds in the reaction mixture are volatile and can be conveniently removed in vacuo (70 °C, 10^{-3} mTorr, 14 h) to afford a spectroscopically pure product. Fine colorless needles of **6** were obtained by recrystallization from hexane at −40 °C.

The reactions[14] of **6** with $Me_4SbOSiMe_3$ and $Me_4SbOCMe_3$ (C_6D_6, 25 °C) afford quantitative yields of **7** and the corresponding stannyl ethers (i.e., $Me_3SnOSiMe_3$ and $Me_3SnOCMe_3$). ^{13}C and ^{29}Si NMR spectra of the crude products obtained after evaporation of the volatiles (70 °C, 10^{-3} mTorr, 8 h) both consist of single resonances (^{13}C δ 11.44; ^{29}Si δ −104.33) and are clearly indicative of a spherosilicate with five-coordinate Me_4Sb groups.[4] A typical crude product is spectroscopically pure, but microcrystalline **7** can be obtained by recrystallization from hexane at −40 °C.

The facility with which heterosiloxane bonds can be heterolytically cleaved at the heteroatom (i.e., Si–O–M → [SiO^-] + [M^+])[15] provides a wealth of interesting chemical possibilities, ranging from our initial goal to synthesize supermolecular aluminosilsesquioxanes to the preparation of entirely new framework silicates under aprotic conditions. We have only begun to explore the chemistry of these new spherosilicates, but the observation that **7** reacts with Me_3SiCl and Me_3SnCl to afford **5** and **6**, respectively, is clearly consistent with our expectation that **7** would function as a labile, aprotic source of $[Si_8O_{20}]^{8-}$. Our efforts to use these spherosilicates to synthesize larger silsesquioxane and aluminosilsesquioxane frameworks will be presented in due course.

Acknowledgment. These studies were supported by the National Science Foundation (Grants CHE-8703016 and CHE-9011593) and an NSF-Presidential Young Investigator Award (Grant CHE-8657262). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. F.J.F. gratefully acknowledges financial support from an Alfred P. Sloan Foundation Research Fellowship. We also thank Professor Walter G. Klemperer (University of Illinois) for helpful comments.

Department of Chemistry
University of California
Irvine, California 92717

Frank J. Feher*
Keith J. Weller

Received October 31, 1990

---

(12) For an excellent review of ^{119}Sn NMR spectroscopy, including a large compilation of ^{119}Sn chemical shifts and coupling constants, see: Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73–186.

(13) In a typical reaction, $Me_3SnOSnMe_3$ (1.508 g, 4.39 mmol) was added to a suspension of **4** (230 mg, 0.542 mmol) in benzene. The mixture was stirred for 1 h at 25 °C; then the volatiles were removed in vacuo (70 °C, 10^{-3} mTorr, 14 h) to afford a quantitative yield of spectroscopically (^{1}H and ^{13}C NMR) pure **6**. Recrystallization from hexane (+25 to −40 °C) afforded fine white needles (54%). For **6**: ^{1}H NMR (500.13 MHz, C_6D_6, 23 °C) δ 0.362 (J_{Sn-H} = 58.2.1, 59.2 Hz); $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 23 °C) δ −2.91; $^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 23 °C) δ −101.55; $^{119}Sn\{^1H\}$ NMR (37.3 MHz, C_6D_6, 23 °C) δ 118.42; mass spectrum (EI, 70 eV, 200 °C) *m/e* (relative intensity) 1840 (100%, $M^+ - CH_3$), 1662 (30%, $M^+ - CH_3 - Me_3Sn$), 165 (50%, Me_3Sn^+); mp 184–186 °C. Anal. Calcd (found) for $C_{24}H_{72}O_{20}Si_8Sn$: C, 15.54 (15.93); H, 3.91 (3.79).

(14) In a typical reaction, a benzene solution of **6** (400 mg, 0.216 mmol) and $Me_3COSbMe_4$ or $Me_3SiOSbMe_4$ (1.94 mmol) were stirred overnight at 25 °C. Evaporation of the solvent and volatiles (70 °C, 10^{-3} mTorr, 8 h) afforded a quantitative yield of spectroscopically (^{1}H and ^{13}C NMR) pure **7**. Fine microcrystals of **7** were obtained in 60% yield by recrystallization from hexane (+25 to −40 °C). For **7**: ^{1}H NMR (500.13 MHz, C_6D_6, 23 °C) δ 1.083 ($w_{1/2}$ = 23 Hz); $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 23 °C) δ 11.44; $^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 23 °C) δ −104.33; mass spectrum (EI, 70 eV, 200 °C) *m/e* (relative intensity) 180 (50%, Me_4Sb^+), 165 (80%, Me_3Sb^+), 151 (100%, Me_2Sb^+); mp >400 °C. Anal. Calcd (found) for $C_{32}H_{96}O_{20}Si_8Sb$: C, 21.05 (17.63); H, 5.40 (5.05). The combustion analysis of **7** consistently gives carbon and hydrogen contents that are lower than expected. This is presumably because the oxidation of these highly siliceous compounds is often incomplete. (To facilitate combustion, our samples are usually mixed with WO_3 in tin capsules and allowed an extended combustion time (Desert Analytics)). Considering the source of **7** and its reactions with (TMS)Cl and Me_3SnCl, which give quantitative yields of **5** and **6**, we are confident of our structural assignment.

(15) (a) Voronkov, M. G.; Maletina, E. A.; Roman, V. K. *Heterosiloxanes. Derivatives of Non-Biogenic Elements*; Harwood Academic Publishers: London, 1988; see also references cited therein. (b) Schindler, F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 683–94. (c) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 201–11.

Electron Transfer in Inorganic Nitrogen Fixation[1]

The biological reduction of dinitrogen involves a series of concomitant electron- and proton-transfer steps. Within this context, dinitrogen complexes of molybdenum(0) and tungsten(0) react with strong acids to produce ammonia, or hydrazine and ammonia.[2-6] The initial phase of the reaction, which encompasses protonation and intramolecular electron reorganization, leads to the rapid formation of a hydrazido(2−) complex;[1,5,7-10] e.g. eq 1,

$$\textit{trans-}[Mo(N_2)_2(dpepp)(PPh_3)] + 2HBr \rightarrow [MoBr(NNH_2)(dpepp)(PPh_3)]Br + N_2 \quad (1)$$

$$2\{Mo^{IV}(NNH_2)\} \xrightarrow{4H^+} 2\{Mo^{III}\} + 2NH_4^+ + N_2 \quad (2)$$

where dpepp = $PhP(CH_2CH_2PPh_2)_2$. The final phase, in THF solution, involves disproportionation[11] (intermolecular electron transfer) of the hydrazido(2−) complex to yield about 1 mol of ammonia/mol of Mo and 0.5 mol of N_2/mol of Mo (eq 2).[5] In CH_2Cl_2 solution, hydrazine is formed in addition to ammonia and N_2. In order to achieve the goal of developing a catalytic cycle for dinitrogen reduction, coupling of a reducing agent and a proton source is required. We wish to report the discovery of simple two-electron-reducing agents that fulfill the role of reducing the hydrazido(2−) ligand to ammonia, thus circumventing disproportionation (see Table I).

Reaction of *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$ (**1**), where dppe = $Ph_2PCH_2CH_2PPh_2$, with HBr (20 mol) in CH_2Cl_2 (48 h) produced ammonia, hydrazine, and N_2 in yields of 0.39, 0.44, and 1.39 mol/mol of **1**, respectively, for a 100% nitrogen atom balance.[11] Addition of $SnCl_2$ (4 mol) to a similar reaction mixture caused significant changes in the yields of reduction products: 1.18, 0.25, and 1.19 mol/mol of **1**, respectively, for a 100% nitrogen atom balance and ca. 300% increase in the yield of ammonia.[12,13]

---

(1) Reactions of Coordinated Dinitrogen. 28. Part 26: George, T. A.; Kaul, B. B. *Inorg. Chem.* **1990**, *29*, 4969–4974.

(2) (a) George, T. A.; Tisdale, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 5157–5159. (b) George, T. A.; Tisdale, R. C. *Inorg. Chem.* **1988**, *27*, 2909–2912.

(3) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852–1860.

(4) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461–7467.

(5) Baumann, J. A.; Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K.; Noddings, C. M. *Inorg. Chem.* **1985**, *24*, 3568–3578.

(6) Lazarowych, N. J.; Morris, R. H.; Ressner, J. M. *Inorg. Chem.* **1986**, *25*, 3926–3932.

(7) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766–1776. (b) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973–1980.

(8) George, T. A.; Tisdale, R. C. *Polyhedron* **1989**, *8*, 1756–1757.

(9) (a) George, T. A.; Koczon, L. M.; Tisdale, R. C.; Gebreyes, K.; Ma, L.; Shaikh, S.; Zubieta, J. *Polyhedron* **1990**, *9*, 545–551. (b) Gebreyes, K.; George, T. A.; Koczon, L. M.; Tisdale, R. C.; Zubieta, J. *Inorg. Chem.* **1986**, *25*, 405–407.

(10) Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 917–925.

(11) Kaul, B. B.; Hayes, R. K.; George, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 2002–2003.

0020-1669/91/1330-0882$02.50/0

Table I. Yields[a] of Nitrogen-Containing Products from Reactions of Dinitrogen Complexes with HBr[b] in CH_2Cl_2 at 23 °C for 46–48 h with Substrate

compd[c]	substrate (mol)	mol of product[a]			% N balance[d]
		NH_3	N_2H_4	N_2	
1		0.39	0.44	1.39	100
1	$SnCl_2$ (2)	0.71	0.54	1.20	100
1	$SnCl_2$ (4)	1.18	0.25	1.19	100
1	$SnBr_2$ (4)	1.00	0.38	1.13	100
1	GeI_2 (4)	1.24	0.13	1.22	99
1	$[Et_4N][SnCl_3]$ (4)	0.70	0.50	1.17	100
1	$Sn(acac)_2$ (4)	0.29	0.02	1.18	68
1	$ZnCl_2$ (4)	0.56	0.33	1.40	100
2		0	0.24	1.30	77
2	$SnCl_2$ (4)	0.72	0.20	1.19	86
2	GeI_2 (4)	0.87	0.14	1.36	97
2	$[Et_4N][SnCl_3]$ (4)	0.46	0.18	1.20	81
2	$ZnCl_2$ (4)	0.01	0.21	1.27	75

[a] mol/mol of Mo. [b] 20 mol/mol of Mo. [c] **1** = *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$, **2** = *trans*-$[Mo(N_2)_2(PS\text{-}diphos)(PPh_2Me)_2]$. [d] [(mol of N/mol of Mo)/2] × 100.

This is the first example of the successful use of a chemical reducing agent to effect the conversion of a hydrazido complex into ammonia.[14]

More dramatic evidence for the redox involvement of $SnCl_2$ comes from the reactions of the polymer-anchored N_2 complex *trans*-$[Mo(N_2)_2(PS\text{-}diphos)(PPh_2Me)_2]$ (**2**), where PS-diphos = $-P(Ph)CH_2CH_2PPh_2$ attached to polystyrene (2% divinylbenzene). **2** reacted with HBr in CH_2Cl_2 to give 0.24 mol of hydrazine/mol of **2** and *no ammonia*.[11] Addition of HBr and $SnCl_2$ to CH_2Cl_2-swollen **2** resulted in yields of ammonia of 0.70 mol/mol of **2**; hydrazine yields were unchanged.

If tin(II) is behaving as a reducing agent, then germanium(II) compounds should be better. Indeed, use of GeI_2 in place of $SnCl_2$ resulted in increased yields of ammonia (see Table I). Tin(II) halides readily pick up halide ion to form SnX_3^-, which is likely to be present in these reactions. Addition of $[Et_4N][SnCl_3]$ in place of $SnCl_2$ afforded similar increases in the yields of ammonia. When **2** was treated with a Lewis acid such as $ZnCl_2$ together with HBr, no ammonia was formed.

A possible mode of interaction of tin(II) with the hydrazido complex is through a Mo–Sn bond formed by coordination of SnX_3^- to $[MoBr(NNH_2)(dppe)(PPh_2Me)_2]^+$ after loss of phosphine (a prerequisite for ammonia/hydrazine formation[5]). There are many examples of SnX_3^- covalently bonded to transition metals.[15] Interestingly, addition of monomeric tin(II) acetylacetonate, $Sn(acac)_2$,[16] caused a decrease in the amount of ammonia, hydrazine particularly, and N_2 formed.

With tin(II) acting as a reducing agent, a tin(IV) product will be formed. If SnX_3^- is the ligand, then two-electron oxidation coupled with coordination of halide ion to tin(IV) would result in displacement of SnX_4. No such simple scenario can be proposed for the formation of a stable tin(IV) complex (such as $Sn(acac)_2Br_2$) derived from $Sn(acac)_2$ in a noncoordinating solvent. In other words, $SnCl_2$ (in the form of SnX_3^-) and $Sn(acac)_2$ are both able to coordinate to Mo to form a precursor complex, but only the former can accomplish two-electron transfer because of the relative stability of the successor complex and immediate products.

The success of two-electron-reducing agents to "turn on" the hydrazido complex derived from **2** to afford ammonia closely parallels electrochemical studies carried out on Mo and W complexes. For example, following the two-electron reduction of $[W(Tos)(NNH_2)(dppe)_2]^+$ (Tos = tosylate), a complex that does not produce ammonia with acid alone, ammonia was formed.[17] Similarly, two-electron reduction of the dialkylhydrazido complex, $[MoBr(N\overline{NCH_2(CH_2)_3C}H_2)(dppe)_2]^+$, produced $[Mo(\overline{NCH_2(CH_2)_3C}H_2)(dppe)_2]$, which when treated with HBr yielded piperidine and the molybdenum imido complex $[MoBr(NH)(dppe)_2]^+$.[18]

The effect of adding $SnCl_2$ and HBr to **2** is very similar to that of adding $[Mo(N_2)_2(PPh_2Me)_4]$ and HBr to **2**.[11] It is difficult to see much resemblance between the two. The apparent requirement for loss of a phosphine before ammonia or hydrazine is formed suggests an inner- rather than outer-sphere mechanism. One common denominator is the presence of halide ion. Perhaps electron transfer involves halide ion bridging between metal centers. Further work is underway to isolate intermediates and discover other suitable reducing agents.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM-38613) for support of this work.

---

(12) Evidence of $SnCl_2$ acting as a reducing agent in reactions of intermediates in N_2 reduction has been reported: Jackson, M. A. Ph.D. Dissertation, University of Nebraska, 1988. An unsuccessful attempt to employ $SnCl_2$ to reduce hydrazido(2−) complexes has been noted: Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074–2082.

(13) When $N_2H_4\cdot 2HCl$ was treated with $HBr/SnCl_2$ in CH_2Cl_2 (46 h), no ammonia was formed. A small amount of N_2 was evolved.

(14) In acid reactions in which preformed hydrazido(2−) complexes were reacted with $SnCl_2$, the results were the same as those obtained from reactions with **1** and $SnCl_2$. Protonation of the bis(dinitrogen) complexes is very fast; see ref 10.

(15) Holt, M. S.; Wilson, W. I.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11–49.

(16) For many examples of $Sn(acac)_2$ behaving as a ligand, see ref 15.

(17) (a) Pickett, C. J.; Talarmin, J. *Nature (London)* **1985**, *317*, 652–653. (b) Pickett, C. J.; Ryder, K. S.; Talarmin, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1453–1457.

(18) (a) Hussain, W.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1982**, 747–748. (b) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1989**, 425–430.

Department of Chemistry
University of Nebraska—Lincoln
Lincoln, Nebraska 68588-0304

T. Adrian George*
Bharat B. Kaul

Received December 17, 1990