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Metal Hydrides as Electron Donors. The Mechanism of Oxidative Cleavage with Tris(phenanthroline) Complexes of Iron(III)

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The group 4 metal hydrides HMR_3 (M = silicon, germanium, tin; R = alkyl, phenyl) react spontaneously with 2 equiv of tris(phenanthroline)iron(III) perchlorate, $FeL_3(ClO_4)_3$, in acetonitrile solutions. Although the second-order kinetics (first order in each reactant) indicate that the selective cleavage of only the hydrido–metal bond proceeds from a rate-limiting bimolecular process, there is no significant deuterium kinetic isotope effect. The free-energy dependence of the second-order rate constant k_H for the silicon and germanium hydrides follows the Marcus relationship with slope α close to the theoretical value of 8.5 for an outer-sphere electron-transfer process. The paramagnetic cation HMR_3^+, similar to that formed by electron impact or photoionization of HMR_3, is postulated to be a metastable intermediate which undergoes spontaneous scission of the hydrogen–metal bond, followed by a further rapid oxidation of the fragment by a second equivalent of FeL_3^{3+}. The rate-limiting, outer-sphere mechanism for HMR_3 accords with that previously established for electron transfer between the related series of peralkylmetals MR_4 and the same FeL_3^{3+} complexes. The electron-transfer rate constants k_H and k_R for HMR_3 and MR_4, respectively, are compared for their sensitivity to changes in the standard reduction potentials $E°$ of FeL_3^{3+} and the gas-phase ionization potentials I_D of HMR_3 and MR_4. Polarization and solvation effects appear to be especially important in electron transfer from metal hydrides, especially those of tin.

Introduction

The addition of group 4 metal hydrides to olefins is catalyzed by various transition-metal complexes.[1,2] Oxidative adducts have been proposed as intermediates[3-5] which have been demonstrated to be formed reversibly in some cases, e.g.[6]
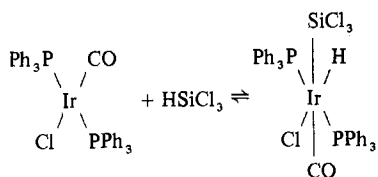
Group 4 metal hydrides, particularly those of tin, can also function directly as reductants (i.e., hydride donors).[7,8] However, there is surprisingly little quantitative information available as to how the hydrogen–metal bond is broken and the hydrogen atom transferred from metal hydrides in such processes.

In order to probe the nature of the activated complex for the oxidative cleavage of metal hydrides, we examined the direct reaction with a series of substitution-inert iron(III) complexes of polypyridine-type ligands in which the reduction potentials $E°$ can be systematically varied.[9] The group 4 metal hydrides consisted of the trialkylmetal derivatives HMR_3 where M = silicon, germanium, and tin in which the use of

Table I. Stoichiometric Consumption of Tris(phenanthroline)iron(III) by Organometallic Hydrides–Effect of Oxygen[a]

HMR$_3$	Fe(phen)$_3^{3+}$ consumed[b]	
	anerobic	O$_2$ satd
Me$_3$SnH	1.8 ± 0.3	1.6 ± 0.3
n-Bu$_3$SnH	2.0 ± 0.2	1.9 ± 0.2
n-Bu$_3$SnD	2.0 ± 0.2	1.9 ± 0.2
Ph$_3$SnH	1.9 ± 0.2	1.8 ± 0.2
Et$_3$GeH	2.0 ± 0.2	2.0 ± 0.2
n-Bu$_3$GeH	1.9 ± 0.3	1.9 ± 0.3

[a] In acetonitrile solutions at 25 °C containing $(1.5-5.1) \times 10^{-4}$ M HMR$_3$ and $(2.7-12.4) \times 10^{-3}$ M Fe(phen)$_3$(ClO$_4$)$_3$. [b] Equiv/mol of HMR$_3$.

Table II. Acid Released during Cleavage of Organometallic Hydrides by Tris(phenanthroline)iron(III) Perchlorate[a]

HMR$_3$	[HMR$_3$], M × 10^{-2}	[H$^+$ produced], M × 10^{-2}	H$^+$/HMR$_3$
n-Bu$_3$SnH	1.4	1.3	0.93
	1.5	1.4[b]	1.00
	1.8	1.8[b]	0.93
Ph$_3$SnH	1.1	1.3[b]	1.00
	1.4	1.4	1.00
n-Bu$_3$GeH	1.3	1.1[b]	0.85
	1.5	1.6	1.00
	1.5	1.3	0.87

[a] In anerobic acetonitrile at 25 °C. [b] In O$_2$-saturated solutions.

different alkyl groups (R) allowed variations of the steric properties and the ionization potentials of these reductants.

Results

The cleavage of these metal hydrides was examined in acetonitrile solutions with tris(polypyridine) complexes of iron(III) FeL_3^{3+}, where L = 2,2′-bipyridine and various substituted 1,10-phenanthrolines. The progress of the reaction is visually apparent by the change in color from the characteristic blue of these iron(III) complexes to the red reduced iron(II) products.

Products and Stoichiometry. The amount of iron(III) consumed for each equivalent of organometallic hydride was measured by allowing a known concentration of HMR_3 to react with a three- to fourfold excess of $FeL_3(ClO_4)_3$. The stoichiometric relationship between iron(III) consumed and iron(II) produced was then readily determined quantitatively

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Table III. Rate Constants for Oxidative Cleavage of Trialkylmetal Hydrides by Iron(III) Complexes[a]

HMR$_3$	Fe(4,7-Ph$_2$-phen)$_3^{3+}$	Fe(bpy)$_3^{3+}$	Fe(phen)$_3^{3+}$	Fe(5-Cl-phen)$_3^{3+}$	Fe(5-NO$_2$-phen)$_3^{3+}$
Me$_3$SnH	$(1.3 \pm 0.2) \times 10^{-1}$	$(2.6 \pm 0.3) \times 10^{-1}$	$(5.0 \pm 0.6) \times 10^{-1}$	$(8.9 \pm 0.7) \times 10^{-1}$	1.6 ± 0.3
Et$_3$SnH	$(1.5 \pm 0.3) \times 10^{-1}$	$(2.5 \pm 0.3) \times 10^{-1}$	$(3.7 \pm 0.2) \times 10^{-1}$	1.4 ± 0.2	2.9 ± 0.3
n-Bu$_3$SnH	6.4 ± 0.3	5.6 ± 0.4 $(5.4 \pm 0.5)^b$	$(1.2 \pm 0.2) \times 10$ $((1.3 \pm 0.3) \times 10)^b$	$(4.1 \pm 0.2) \times 10$	$(9.3 \pm 0.6) \times 10$
Ph$_3$SnH	$(2.8 \pm 0.3) \times 10^{-2}$	$(3.0 \pm 0.2) \times 10^{-2}$ $((3.1 \pm 0.4) \times 10^{-2})^b$	$(4.0 \pm 0.3) \times 10^{-2}$ $((3.8 \pm 0.4) \times 10^{-2})^b$	$(1.4 \pm 0.2) \times 10^{-1}$	$(4.5 \pm 0.2) \times 10^{-1}$
Et$_3$GeH	$(7.3 \pm 0.5) \times 10^{-3}$	$(7.6 \pm 0.1) \times 10^{-3}$	$(1.7 \pm 0.3) \times 10^{-2}$ $((1.5 \pm 0.3) \times 10^{-2})^b$	$1.2 \pm 0.2 \times 10^{-1}$ $((1.1 \pm 0.3) \times 10^{-1})^b$	$(6.4 \pm 0.5) \times 10^{-1}$
n-Bu$_3$GeH	$(4.5 \pm 0.6) \times 10^{-3}$	$(4.1 \pm 1.0) \times 10^{-2}$	$(9.7 \pm 1.1) \times 10^{-2}$	$(5.7 \pm 1.2) \times 10^{-1}$	5.4 ± 0.4
Et$_3$SiH	$(1.9 \pm 0.4) \times 10^{-4}$	$(3.1 \pm 0.6) \times 10^{-4}$	$(6.2 \pm 1.0) \times 10^{-4}$	$(5.4 \pm 0.6) \times 10^{-3}$	$(5.9 \pm 0.6) \times 10^{-2}$
i-Pr$_3$SiH	$(5.0 \pm 0.5) \times 10^{-4}$	6.0 ± 10^{-4} ^{c}	1.2 ± 10^{-3} ^{c}	$(1.1 \pm 0.2) \times 10^{-2}$	$(4.0 \pm 0.4) \times 10^{-2}$

^{a} In deoxygenated acetonitrile solutions at 25 °C. Numbers refer to second-order rate constants in M^{-1} s^{-1}. ^{b} Rate constants in O$_2$-saturated acetonitrile solutions. ^{c} Only one determination.

Table IV. Deuterium Kinetic Isotope Effects for Oxidative Cleavage of Butylstannane and Ethylsilane by Iron(III) Complexes[a]

FeL$_3$(ClO$_4$)$_3$	k_H(R$_3$MH)	k_D(R$_3$MD)	k_H/k_D
		R$_3$M = n-Bu$_3$Sn	
Fe(phen)$_3$(ClO$_4$)$_3$	12 ± 2	10 ± 1	1.2 ± 0.4
Fe(5-Cl-phen)$_3$(ClO$_4$)$_3$	41 ± 2	29 ± 3	1.4 ± 0.3
Fe(5-NO$_2$-phen)$_3$(ClO$_4$)$_3$	93 ± 6	66 ± 6	1.4 ± 0.3
		R$_3$M = Et$_3$Si	
Fe(bpy)$_3$(ClO$_4$)$_3$	$(3.1 \pm 0.6) \times 10^{-4}$	$(2.6 \pm 0.4) \times 10^{-4}$	1.2 ± 0.5
Fe(phen)$_3$(ClO$_4$)$_3$	$(6.2 \pm 1.0) \times 10^{-4}$	$(4.6 \pm 0.1) \times 10^{-4}$	1.3 ± 0.3 $(1.2 \pm 0.1)^b$
Fe(5-Cl-phen)$_3$(ClO$_4$)$_3$	$(5.4 \pm 0.6) \times 10^{-3}$	$(3.7 \pm 0.4) \times 10^{-3}$	1.5 ± 0.3
Fe(5-NO$_2$-phen)$_3$(ClO$_4$)$_3$	$(5.9 \pm 0.6) \times 10^{-2}$	$(4.2 \pm 0.4) \times 10^{-2}$	1.4 ± 0.3

^{a} Numbers refer to second-order rate constants in M^{-1} s^{-1}. ^{b} Determined by the relative rate method.

from their molar absorptivities [e.g., λ_{max} 592 (ϵ 5.79 $\times$ 10^2) for Fe(phen)$_3^{3+}$ and λ_{max} 502 nm (ϵ 1.31 $\times$ 10^4) for Fe-(phen)$_3^{2+}$].[10] The results in Table I indicate that 2 equiv of iron(III) is consumed for each HMR$_3$, independent of whether the reaction is carried out under anerobic conditions or in the presence of a large excess of oxygen.

The organometallic hydride is rapidly and selectively cleaved at the single hydrido–metal bond. For example, Me$_3$SnH shows the hydride resonance at δ 4.58 (multiplet) in the ^{1}H NMR spectrum in CD$_3$CN and a doublet resonance for the methyl protons (δ 0.15 (J = 3 Hz)) in the expected 9:1 intensity ratio. Reaction with 2 equiv of Fe(phen)$_3$(ClO$_4$)$_3$ is essentially complete on mixing and produces 1 equiv of tri-methyltin perchlorate [Me$_3$SnClO$_4$, δ 0.67)], which was quantitatively identified by comparison with an authentic sample. Analysis of the IR spectrum of the product (solution) revealed no residual Sn–H absorptions between 1800 and 1900 cm^{-1}. The hydrogen released during the reaction is indicated by the change in pH of the solution and the amount measured quantitatively as described in the Experimental Section. One equivalent of acid is liberated for each mole of metal hydride in Table II according to the overall stoichiometry

$$2FeL_3^{3+} + HMR_3 \rightarrow 2FeL_3^{2+} + MR_3^+ + H^+ \quad (1)$$

Kinetics of Metal–Hydride Cleavage. The rates of oxidative cleavage of metal hydrides were followed spectrophotometrically at 25 °C in acetonitrile solutions by the appearance of the iron(II) bands, by using either a conventional (Cary) or a stopped-flow (Durrum-Gibson) spectrophotometer. The degassed solutions were maintained at constant ionic strength with either lithium or tetraethylammonium perchlorate. The reactions obeyed second-order kinetics, being first order in each reactant.

$$-d[FeL_3^{3+}]/dt = 2k[HMR_3][FeL_3^{3+}] \quad (2)$$

The kinetic experiments were usually carried out with the iron(III) complex in excess to approximate pseudo-first-order conditions for at least 2.5 half-lives. (This procedure was necessitated by the lability of some of these trialkylmetal hydrides, particularly the tin derivatives which are prone to produce some distannane.[11]) The rates were unaffected by the presence of oxygen, by changes in ionic strength from 0.01 to 0.1 and by the addition of the reduced iron(II) complex in an equimolar amount. The second-order rate constants listed in Table III were carried out in at least duplicate.

The Deuterium Kinetic Isotope Effect. To ensure reliability, we obtained two independent measures of the kinetic isotope effect. First, the absolute second-order rate constants for M–H and M–D cleavages were measured separately for tri-n-butylstannane or triethylsilane and their deuterated derivatives, respectively, with a series of four iron(III) complexes in Table IV. For triethylsilane, the kinetic isotope effect obtained in this manner was also compared with that measured directly by a competition method in which an excess of an equimolar mixture of HSiEt$_3$ and DSiEt$_3$ was treated with a limited amount of iron(III) complex, and the change in concentrations of the respective silanes was measured by IR spectroscopy at ν_{Si-H} 2090 and ν_{Si-D} 1520 cm^{-1}. On the basis of both the competitive as well as the absolute measurements of rates, we conclude that metal–hydride cleavage by iron(III) proceeds with no significant deuterium kinetic isotope effect.

Electrochemical Measurements of Iron(III) Complexes. The reduction potentials of low-spin tris(2,2'-bipyridine) and -(1,10-phenanthroline) complexes of iron(III) perchlorate were measured in acetonitrile solutions by cyclic voltammetry.[10] All

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Table V. Cyclic Voltammetry of $FeL_3(ClO_4)_3$ Complexes in Acetonitrile Solution

L	$E°$, V vs. SHE	$\Delta,^a$ mV	$i_c/i_a{}^b$
5-nitro-1,10-phenanthroline	$1.41_7 \pm 0.006$	72	1.02
5-chloro-1,10-phenanthroline	$1.31_7 \pm 0.001$	67	1.01
1,10-phenanthroline	$1.22_0 \pm 0.001$	68	1.00
2,2'-bipyridine	$1.21_2 \pm 0.003$	70	1.02
4,7-diphenyl-1,10-phenanthroline	$1.15_5 \pm 0.001$	65	1.01

^{a} Separation of anodic and cathodic peaks at 50 mV s^{-1} scan rate. ^{b} Ratio of charging currents for the cathodic (i_c) and anodic (i_a) waves; from ref 10.

**Table VI.** Ionization Potentials of Trialkylmetal Hydrides^a

HMR$_3$	$I_D(I)$, eV	$I_D(II)$, eV
Et$_3$SiH	9.9	10.7
i-Pr$_3$SiH	9.5	10.4
Et$_3$GeH	9.6	10.5
n-Bu$_3$GeH^b	9.37	10.2
Me$_3$SnH	9.9	10.6
Et$_3$SnH	9.1	10.0
n-Bu$_3$SnH	8.8	9.8
i-Pr$_3$SnH	8.6	9.7
Ph$_3$SnH^b	9.04	9.6 (sh)

^{a} From ref 14 unless indicated otherwise. ^{b} From ref 15.

the iron(III, II) redox couples were completely reversible in this medium as indicated by the separation of about 68 mV between the cathodic and anodic peaks and the same magnitudes of their charging currents as listed in Table V. The values are calibrated relative to ferrocene which has been shown to be electrochemically well-behaved in this medium.[13]

Ionization Potentials of Trialkylmetal Hydrides. The ionization potentials I_D of the various metal hydrides in the gas phase, i.e.

$$HMR_3 \rightarrow HMR_3{}^+ + e^- \qquad (3)$$
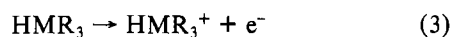
were obtained from their photoelectron spectra, which all show two principal low-energy bands resulting from the ionization from the e and a$_1$ bands, as expected for molecules with local C_{3v} symmetry. The ionization potentials $I_D(I)$ and $I_D(II)$ in Table VI are associated with the M–C and M–H ionizations, respectively.[14]

Attempts to measure the reversible oxidation potentials $E°$ by cyclic voltammetry were unsuccessful since the voltammograms were irreversible even at scan rates as high as 10 V s^{-1} and temperatures as low as -35 °C in acetonitrile solutions. However, a linear relationship may be expected between the ionization potential and the oxidation potential for a series of *homologous* metal hydrides, i.e.[10]

$$I_D + \Delta E_{solv} = \beta E° + \text{constant} \qquad (4)$$

provided the changes in solvation ΔE_{solv} are invariant.

Discussion

The facility with which the coordinatively saturated iron(III) complexes selectively cleave organometallic hydrides raises several important mechanistic questions. First, is the hydrogen transferred from the metal center as a hydride or as a hydrogen atom or a proton? Second, what is the nature of the activation process, and how is it related to the driving force for the cleavage? In the following, we will first focus on the mechanistic pathway for metal–hydride cleavage and then discuss
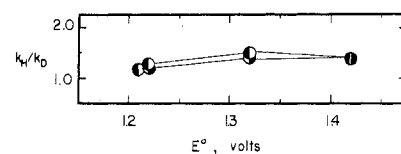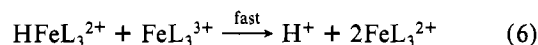

Figure 1. Relationship of the deuterium kinetic isotope effect and the driving force ($E°$) in the oxidative cleavage of (○) n-Bu$_3$SnH and (●) Et$_3$SiH by (phenanthroline)iron(III) complexes in acetonitrile.

the rate-limiting activation process itself.

I. Mechanism of the Oxidative Cleavage of Metal Hydrides. The ease of oxidative cleavage of group 4A trialkylmetal hydrides by iron(III) complexes according to the stoichiometry in eq 1 is dependent on the metal center as well as the alkyl ligands. Thus the metal reactivity decreases in the order Sn > Ge > Si (generally as $10^4:10^2:10$), and the ligand reactivity decreases in the order n-butyl > methyl > phenyl (roughly as $10^2:10:1$ for stannanes). Both trends are in accord with electron release into the M–H σ bond as an important factor[10,16] in enhancing metal hydride reactivity. Indeed the direct transfer of a hydrido ligand to iron(III), as included in Scheme I, would provide a most straightforward explanation for these results. The mechanism in Scheme I also accords with the observed second-order kinetics in eq 2, which necessitates the hydridoiron(III) intermediate to be oxidized in a fast subsequent step (eq 6) by the second equivalent of iron(III) required by the stoichiometry.

Scheme I

$$HMR_3 + FeL_3{}^{3+} \rightarrow MR_3{}^+ + HFeL_3{}^{2+} \qquad (5)$$

$$HFeL_3{}^{2+} + FeL_3{}^{3+} \xrightarrow{\text{fast}} H^+ + 2FeL_3{}^{2+} \qquad (6)$$

The mechanism in Scheme I is inconsistent with the absence of a deuterium kinetic isotope effect, indicating that the M–H bond itself is not actually ruptured in the rate-limiting activation process. We must be forewarned, however, that the use of kinetic isotope effects is not without some ambiguities, since it is known that the magnitude of k_H/k_D is sensitive to the driving force (ΔH) as well as steric, polar, and element effects.[17] The isotope effect is generally maximum when ΔH is close to 0 and hydrogen transfer is nearly symmetrical in the transition state. Furthermore, the falloff in k_H/k_D as a result of the symmetry effect can be important with elements beyond the first row such as silicon, germanium, and tin.[18,19] Thus it is possible for the small isotope effects in Table IV to represent a hydride transfer which proceeds via a very early (or late) transition state.

Figure 1 shows, however, that k_H/k_D for HSnBu$_3$ and HSiEt$_3$ remains singularly *invariant* with various FeL$_3{}^{3+}$ complexes of differing oxidation potentials which are sufficient to span a 20- to 200-fold range in rates of cleavage with substrates differing by more than a factor of 10^4 in reactivity. The invariance of k_H/k_D despite changes in the reduction potential $E°$ of the iron(III) complex is only consistent with a transition state for hydride transfer whose location along the reaction coordinate does not vary with the driving force. A common intermediate would fulfill this requirement, and such

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a two-step process is included in Scheme II, in which electron transfer in eq 7 is rate limiting.[20]

Scheme II

$$FeL_3{}^{3+} + HMR_3 \xrightarrow{k_H} FeL_3{}^{2+} + HMR_3{}^{+} \quad (7)$$

$$HMR_3{}^{+} + FeL_3{}^{3+} \xrightarrow{fast} MR_3{}^{+} + H^+ + FeL_3{}^{2+} \quad (8)$$

According to the mechanism in Scheme II, the paramagnetic metal hydride cation, $HMR_3{}^{+}$, is an actual intermediate. Such species have already been identified in the gas phase as the parent molecular ion in the mass spectra of various trialkylmetal hydrides.[12] However, they are too transient in solution to detect by either cyclic voltammetry or ac polarography, suggesting their lifetimes to be less than 1 ms. Under these circumstances, it is possible (and reasonable to expect) that they undergo prior unimolecular fragmentation in preference to direct oxidation by $FeL_3{}^{3+}$ (which is a bimolecular process as described in eq 8). Two modes of spontaneous decomposition are available for these radical cations, viz.

$$HMR_3{}^{+} \rightarrow \cdot MR_3 + H^+ \quad (9)$$

$$HMR_3{}^{+} \rightarrow MR_3{}^{+} + H\cdot \quad (10)$$
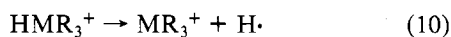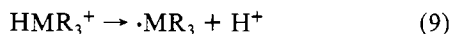
Either pathway would eventually lead to the same overall stoichiometry as that in eq 1. Thus, if a trialkylmetal radical $\cdot MR_3$ were produced as in eq 9, its oxidation by $FeL_3{}^{3+}$ would be rapid

$$\cdot MR_3 + FeL_3{}^{3+} \rightarrow MR_3{}^{+} + FeL_3{}^{2+} \quad (11)$$
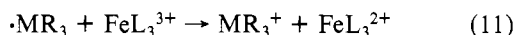
as would the oxidation of hydrogen atom produced in eq 10

$$H\cdot + FeL_3{}^{3+} \rightarrow H^+ + FeL_3{}^{2+} \quad (12)$$
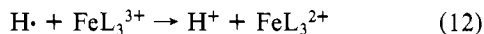
The singular absence of any observable effect of added oxygen, on either the rates or products of cleavage, strongly favors the second pathway. Thus trialkylmetal radicals such as tributyltin are known to react with oxygen at close to diffusion-controlled rates.[21]

$$R_3Sn\cdot + O_2 \rightarrow R_3SnOO\cdot \quad (13)$$
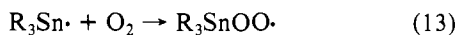
The ESR spectrum of the stannylperoxy radical generated in butyronitrile solution consists of a singlet at $g = 2.025$, and its persistence is unaffected by the presence of either 10^{-2} M $Fe(phen)_3{}^{3+}$ or $Fe(phen)_3{}^{2+}$, as detailed further in the Experimental Section. Nonetheless, no such paramagnetic species can be observed when the reaction of n-Bu_3SnH and $Fe(phen)_3{}^{3+}$, which is rapid even at -76 °C, is carried out under 1 atm of oxygen in a 1:10 v/v solution of acetonitrile and butyronitrile. On the other hand, in the alternative pathway for cleavage (i.e., eq 10), it is noteworthy that the trapping of hydrogen atom by dioxygen would have no overall effect on either the rate or the product of cleavage since (1) it occurs subsequently to the rate-limiting step and (2) the hydroperoxy product itself is also oxidized by $FeL_3{}^{3+}$, i.e.[22]

$$HOO\cdot + FeL_3{}^{3+} \rightarrow H^+ + O_2 + FeL_3{}^{2+} \quad (14)$$
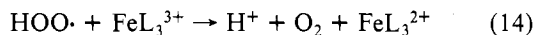
Under these conditions, oxygen is continually recycled as an innocuous participant and exerts no cumulative effect.
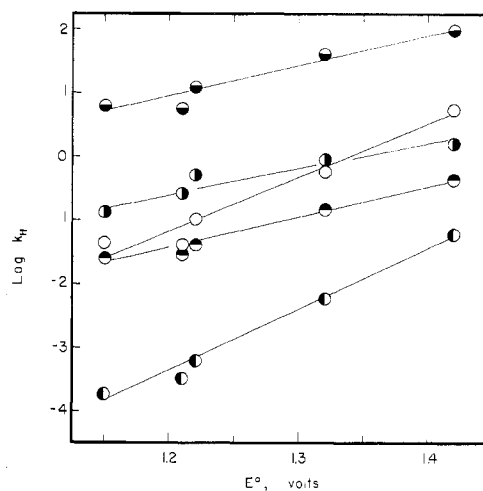
Figure 2. Correlation of the electron-transfer rate constants ($\log k_H$) with the reduction potentials of iron(III) complex for some representative metal hydrides: ◓, n-Bu_3SnH; ◑, Me_3SnH; ○, n-Bu_3GeH; ◐, Ph_3SnH; ◒, Et_3SiH.

II. Metal Hydrides as Donors in Electron Transfer with Iron(III) Complexes. Our attention is now directed to the rate-limiting activation process itself, which proceeds in Scheme II by electron transfer between the metal hydride acting as an electron donor and the iron(III) complex as an oxidant. Indeed, tris(phenanthroline) complexes of iron(III) are well-known to react by outer-sphere electron-transfer mechanisms with a variety of inorganic reductants such as iron(II), cerium(III), manganese(II), and cobalt(II).[23] More directly relevant to the issue here, the participation of the same tris(phenanthroline)iron(III) complexes has also been recently observed in outer-sphere processes with organometals. Thus tetralkylmetals, MR_4, of the group 4A elements are the peralkyl analogues of the trialkylmetal hydrides examined in this study. As such, it should be instructive to compare the structure factors involved in the rate constant k_R for electron transfer from MR_4, i.e.[10]

$$MR_4 + FeL_3{}^{3+} \xrightarrow{k_R} MR_4{}^{+} + FeL_3{}^{2+} \quad (15)$$

with the rate constant k_H for HMR_3 in eq 7. We are particularly concerned in the following discussion as to whether electron transfer occurs from metal hydrides by an outer-sphere process.

According to Marcus,[24] the rate constant k_{et} for outer-sphere electron transfer is related to the free energy change ΔG. The theoretical dependence is simply given by

$$\Delta G^{\ddagger} = {}^{1}/_{4}\lambda(1 + \Delta G/\lambda)^2 \quad (16)$$

where $\Delta G^{\ddagger}$ is the free energy of activation for electron transfer and λ is a parameter related to the reorganization of the inner and outer coordination spheres of the reactants. If the reorganization term 2λ is $\gg \Delta G$, the quadratic term drops out and eq 16 simplifies to[25]

$$\Delta G^{\ddagger} = \lambda/4 + \Delta G/2 \quad (17)$$

(20) The small deuterium kinetic isotope effects (Table IV) in electron transfer may be a secondary isotope effect due to small differences in the HOMO energies of the protio and deuterio metal hydrides [compare: Pryor, W. A.; Hendrickson, W. H., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 1582; Pryor, W. A. *ACS Symp. Ser.* **1978**, *No. 69*, 33] and differences in the reorganization energies which are functions of the vibrational force constants (vide infra).
(21) Howard, J. A.; Tait, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 8349.

(22) Compare: McClune, G. J.; Fee, J. A.; McCluskey, G. A.; Groves, J. T. *J. Am. Chem. Soc.* **1977**, *99*, 5220. See also Experimental Section.
(23) (a) Sutin, N. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 2, p 611. (b) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.
(24) (a) Marcus, R. J.; Zwolinski, B. J.; Eyring, H. *J. Phys. Chem.* **1954**, *58*, 432. (b) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (c) Marcus, R. A. *Ibid.* **1957**, *26*, 867. (d) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21. (e) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

Table VII. Correlation of the Rates (log k_{H}) of Electron Transfer from Trialkylmetal Hydrides with the Reduction Potentials of the Iron(III) Complexes

	log k_{H}		
HMR$_3$	L = phen	L = O$_2$N-phen	α
Et$_3$SiH	−3.19	−1.23	9.0
i-Pr$_3$SiH	−2.92	−1.40	7.7
Et$_3$GeH	−1.77	−0.19	7.8
n-Bu$_3$GeH	−1.01	0.73	8.2
Me$_3$SnH	−0.30	0.20	3.9
Et$_3$SnH	−0.43	0.46	4.9
n-Bu$_3$SnH	1.08	1.97	4.8
Ph$_3$SnH	−1.40	−0.35	4.8

For a series of (phenanthroline)iron(III) complexes reacting with a common organometal, a linear correlation would exist between the rate constants (log k_{et}) and the reduction potential ($E°$), i.e.[26]

$$\log k_{et} = 8.5E° + \text{constant} \qquad (18)$$

The slope of 8.5 in this correlation is equivalent to 0.5 in the free energy relationship in eq 17.

The second-order rate constants (log k_{H}) for the reactions of various group 4A metal hydrides are plotted in Figure 2 against the reversible reduction potentials of the tris(phenanthroline)iron(III) complexes listed in Table V. In every case, a linear correlation is obtained, in accord with the electron-transfer mechanism in Scheme II. Since electron transfer could occur via the π orbitals of the 1,10-phenanthroline ligands, the negative deviations consistently observed with the analogous tris(2,2′-bipyridine)iron(III) complex would derive from the less extensive π conjugation in this ligand. It is noteworthy that the points for the iron(III) complex with the most sterically hindered ligand, L = 4,7-diphenyl-1,10-phenanthroline, are included in the correlation and fall close to the line, suggesting a transition state in which the trialkylmetal hydride is located along the periphery of the iron(III) complex.

The slopes α of the family of lines in Figure 2 are tabulated in Table VII, together with the absolute rate constants for the reaction of each metal hydride with the tris(phenanthroline)- and tris(nitrophenanthroline)iron(III) complexes. It is striking that the slopes for the silicon and germanium hydrides are all rather close to the theoretical value of $\alpha = 8.5$ for an outer-sphere process. However, the slopes for the tin hydrides are consistently smaller than this value, and they are all grouped around a value of $\alpha = 4$–5.
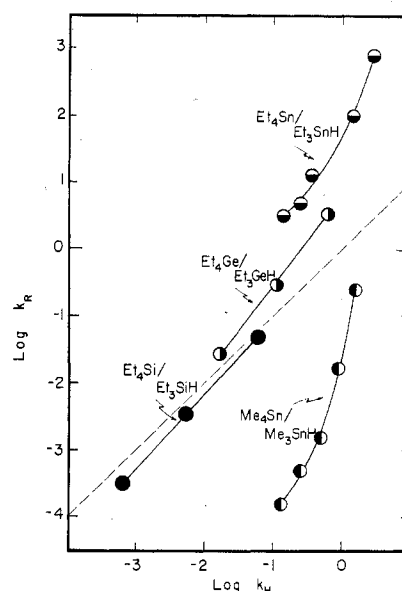
The failure of the series of tin hydrides to attain an outer-sphere slope may be qualitatively attributed to neglect of the reorganization terms. For example, if λ in eq 17 is actually proportional to $\Delta G°$, a linear correlation of log k_{et} vs. $E°$ would still obtain but with altered slope. Such a situation could arise from a strong ion–dipole interaction between the metal hydride and iron(III) in the precursor complex

$$R_3MH + FeL_3^{3+} \rightleftharpoons [R_3\overset{\delta+}{M}\text{–}\overset{\delta-}{H}FeL_3^{3+}] \qquad (19)$$

Highly polarizable metal hydrides are particularly prone to this type of perturbation, the magnitude of which should be

Figure 3. Relative kinetic sensitivity of tetraalkylmetals (log k_R) and trialkylmetal hydrides (log k_{H}) to changes in the driving force during electron transfer: ⊖, Et$_4$Sn/Et$_3$SnH; ◑, Et$_4$Ge/Et$_3$GeH; ●, Et$_4$Si/Et$_3$SiH; ◐, Me$_4$Sn/Me$_3$SnH. Data are taken from Table III and ref 10. The dashed line, drawn with a slope of 1, represents the equikinetic relationship.

proportional to $\Delta G°$.[27] The expression for the inner-sphere reorganization energy λ_i can be written as[28]

$$\lambda_i = [f_i^R f_i^P / (f_i^R + f_i^P)](\Delta r_i)^2 \qquad (20)$$

where f^R and f^P represent the vibrational force constants and Δr is the change in length of the M–H bond in the precursor complex and the product, respectively. The extent to which the metal hydride is already polarized in the precursor complex would lead to diminished values of f^R and Δr and hence of λ. Among group 4A metals, the labile tin hydrides are expected to be more highly polarizable than their silicon and germanium analogues,[29] and the effects of ion–dipole interactions are felt to the strongest degree in these compounds. Furthermore, tin hydrides are rather unique in this regard, since the tin alkyls behave normally, and a wide variety of tetraalkyltin compounds and (phenanthroline)iron(III) complexes correlate k_R (in eq 15) and $E°$ with a Marcus slope of precisely $\alpha = 8.5$.[10] Thus any alternative explanation for the unique value of α for trialkyltin hydrides must focus on the inherent difference between the tin–hydride and tin–alkyl bond.[30] The difference

(25) (a) Wong, C. L.; Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.*, in press. (b) In eq 16 and 17, $\Delta G = \Delta G° + w_p - w_r$, where $\Delta G°$ is the standard free energy change accompanying electron transfer, λ corresponds to $4(\Delta G^* - w_r)$ at $\Delta G = 0$, and the work terms w_r and w_p represent the energies required to bring the reactants and products, respectively, to their mean separation r^* in the activated complex. For the neutral HMR$_3$, $w_r = 0$.

(26) Ng, F. T. T.; Henry, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 3606. See also ref 10.

(27) (a) Especially if the charge-transfer component is included [compare: Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961. (b) The strong polarization of the metal–hydride bond in electron-transfer reactions also accounts for the scission of the metal–hydride bond in preference to the metal–alkyl bond, despite the fact that the HOMO is centered on the latter (see Table VI). (c) We wish to distinguish this effect from that of an inner-sphere mechanism in which the increase in rate derives from both the lowering of the reorganization energies and also an increase in the adiabaticity due to increase in orbital overlap between iron(III) and the metal hydride. It is not clear how steric effects, which are useful probes for inner-sphere mechanisms,[10] would differentiate these pathways since they are also a factor in ion–dipole interactions. (d) Alternatively, the diminished values of α for the tin hydrides in Table VIII may be attributed to variations in w_p in proportion to I_D. See ref 25a for a discussion of this point.

(28) Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press: New York, 1966; p 125.

(29) Deduced from the Lorenz–Lorentz equation by using the refractive indexes of Et$_3$SiH (1.4120) and Et$_3$SnH (1.4725).

(30) Chemically, the difference is shown by the high susceptibility of tin hydrides to electrophiles. Thus the difference in reactivity of hydrides: SnH >> GeH > SiH is magnified relative to that of the alkyls: SnCH$_3$ > GeCH$_3$ > SiCH$_3$ [compare: (a) Sawyer, A. K.; Brown, J. E.; Hanson, E. L. *J. Organomet. Chem.* **1965**, *3*, 464; (b) Sawyer, A. K.; Kuivila, H. G. *Chem. Ind. (London)* **1961**, 260; (c) Sawyer, A. K.; Kuivila, H. G. *J. Org. Chem.* **1962**, *27*, 837].
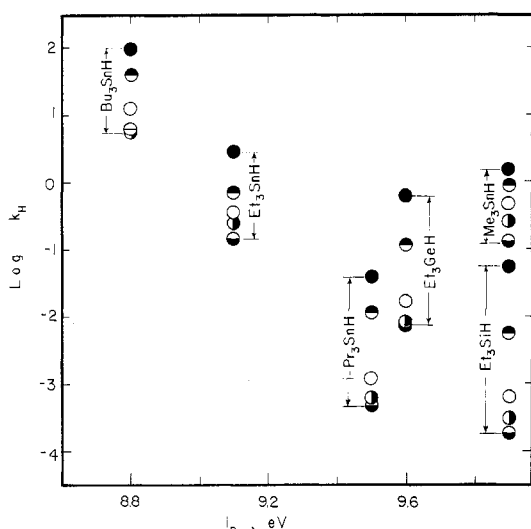
Figure 4. Relationship between the rates of electron transfer (log k_H) and the ionization potentials $I_D(I)$ of trialkylmetal hydrides for five series of FeL_3^{3+} where L is (◒) 4,7-Ph$_2$-phen, (◑) bpy, (O) phen, (◓) 5-Cl-phen, and (●) 5-O$_2$N-phen.

is also illustrated in an alternative way. In Figure 3, the slope of the plot of the electron-transfer rate constant k_H for the trialkylmetal hydride vs. k_R for the corresponding tetraalkylmetal represents a measure of the relative sensitivity of R_4M and R_3MH to the driving force (i.e., $E°$) for electron transfer. The dashed line in Figure 3, drawn with a slope of 1, represents a hypothetical pair in which the transition states for electron transfer from R_4M and R_3MH are similarly polarized. Two trends are noteworthy. First, this correlation for the silicon pair (Et_4Si/Et_3SiH) and the germanium pair (Et_4Ge/Et_3GeH) is linear, indeed with slopes close to 1. On the other hand, both tin pairs (viz., Me_4Sn/Me_3SnH and Et_4Sn/Et_3SnH) have slopes which are about twice those for the ethylsilicon and the ethylgermanium pairs. In other words, a given trialkyltin hydride is about half as sensitive to electron transfer as the corresponding tetraalkyltin, especially in comparison with the silicon and germanium pairs. (This difference is equivalent to the difference in $\alpha(H)$ in Table VII, since tetraalkylmetals have $\alpha(R) = 8.5$ with M = lead, tin, germanium, and silicon.[10]) Such a decrease in sensitivity for the series of R_3SnH would arise if the tin–hydride bond were already highly polarized (as in the precursor complex in eq 19) prior to electron transfer. Second, the constancy in the ratios of the rate constants k_R/k_H with changes in the reduction potential of iron(III) is violated only with the tin pairs, the plots of Et_4Sn/Et_3SnH and Me_4Sn/Me_3SnH in Figure 3 showing a distinct upward curvature. The effect cannot be attributed solely to the tin center since a similar plot for the tetraalkylmetal pairs (e.g., Et_4Pb/Et_4Sn, Et_4Sn/Et_4Ge, etc.) is linear, with slopes consistently rather close to one.[10] Part of the ambiguity undoubtedly arises from our inability to obtain a measure of λ for trialkylmetal hydrides from the standard oxidation potentials (i.e., $R_3MH \rightarrow R_3MH^+ + e^-$) due to the electrochemical irreversibility of these couples. The absence of these data severely hampers an evaluation of solvation effects which are expected to be highly variable in this series of rather polar metal hydrides. Differences in solvation are doubtlessly an important factor in the scatter of points in Figure 4 of the otherwise linear correlation of the rates of electron transfer (log k_H) with the ionization potentials of trialkylmetal hydrides measured in the gas phase. It is noteworthy that the same type of correlation with log k_R for a wide variety of tetraalkylmetals including silicon, germanium, tin, and lead derivatives follows a single linear correlation over

a span of eight decades in rates.[10]

Summary and Conclusions

The cleavage of metal–hydride bonds in a series of trialkylmetal hydrides HMR$_3$ of silicon, germanium, and tin with tris(polypyridine)iron(III) complexes FeL_3^{3+} occurs by a rate-limiting electron-transfer process, i.e.

$$HMR_3 + FeL_3^{3+} \xrightarrow{k_H} HMR_3^+ + FeL_3^{2+}$$
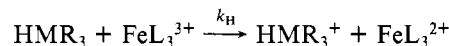
The free energy dependence of the electron-transfer rate constants k_H for the silicon and germanium hydrides follows the Marcus relationship with slope α close to the theoretical value of 8.5. The diminished values of $\alpha \approx 5$ for the series of tin hydrides can be ascribed to a highly polarized precursor complex in which dominant ion–dipole interactions arise from the polarizability of the Sn–H bond. The importance of solvation in the reactions of metal hydrides is indicated by the scatter of the data when log k_H is plotted against the gas-phase ionization potential I_D of the metal hydrides. In contrast, electron transfer from the corresponding series of the quasispherical, homoleptic tetraalkylmetals, MR$_4$, i.e.

$$MR_4 + FeL_3^{3+} \xrightarrow{k_R} MR_4^+ + FeL_3^{2+}$$
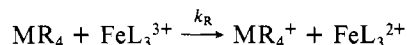
is well-behaved.[10] The rate constants k_R for tin as well as germanium and silicon all follow the Marcus relationship with $\alpha = 8.5$. Moreover, the correlation of log k_R with I_D is precisely linear over a 10^8 range in rates.

Experimental Section

Materials. The trialkyltin hydrides and deuterides were prepared from the corresponding trialkyltin chlorides by reduction with lithium aluminum hydride and deuteride, respectively. The trialkyltin chlorides were obtained by disproportionation of the tetraalkyltin with $^1/_3$ equiv of stannic chloride, followed by heating to reflux and recrystallization or vacuum distillation.[31] The tetraalkyltin compounds were prepared from stannic chloride and the appropriate Grignard reagent by using a standard procedure. The physical properties and IR and NMR characteristics of the trialkyltin hydrides obtained in the present study agreed with those reported previously.[12] The silicon and germanium analogues were also prepared by a similar procedure:[32,33] Et$_3$GeH, bp 125 °C (752 mm), δ_{Ge-H} 3.68 (multiplet), ν_{Ge-H} 1960 cm^{-1}; n-Bu$_3$GeH, bp 124 °C (20 mm), δ_{Ge-H} 3.70 (multiplet), ν_{Ge-H} 1980 cm^{-1}; Et$_3$SiH, bp 110 °C (752 mm), δ_{Si-H} 3.58 (multiplet), ν_{Si-H} 2090 cm^{-1}; Et$_3$SiD, bp 110 °C (752 mm), ν_{Si-D} 1520 cm^{-1}; i-Pr$_3$SiH, δ_{Si-H} 3.50 (multiplet), ν_{Si-H} 2065 cm^{-1}.

Reagent grade acetonitrile was refluxed over calcium hydride, treated with potassium permanganate, and redistilled from phosphorus pentoxide through a 19-plate bubble plate column.

Pyridinium perchlorate was prepared by adding a stoichiometric amount of 70% perchloric acid to a prechilled 1:4 pyridine/water mixture. The resulting white crystals were filtered off and washed with 1:6 ethanol/diethyl ether mixture and finally with diethyl ether. The deuterated pyridinium perchlorate was prepared by recrystallizing the above sample from D$_2$O. All solution or solid IR spectra were taken by a Perkin-Elmer 467 grating infrared spectrophotometer.

Handling and Storage of Metal Hydrides. Metal hydrides, particularly trialkyltin hydrides, are susceptible to decomposition by heat, silicone grease, and metallic surfaces.[34] Reproducible results are difficult to obtain unless extreme caution is exercised in their handling and storage. Glassware cleaned with chromic acid cleaning solution must be avoided, but those washed with a solution of potassium hydroxide in ethanol, followed by numerous and thorough rinsings with water, gave reproducible results. The stannanes were transferred with an all-glass hypodermic syringe and stored at −20 °C under an argon atmosphere in Schlenk flasks equipped with Teflon stopcocks. All hydrides were redistilled in vacuo immediately prior to use.

(31) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459.
(32) (a) Johnson, O. H. *Chem. Rev.* **1951**, *48*, 259. (b) Quane, D.; Bottei, R. S. *Ibid.* **1963**, *63*, 403. (c) Eaborn, C. "Organosilicon Compounds"; Academic Press: New York, 1960.
(33) George, P. D.; Ladd, J. R. *J. Org. Chem.* **1962**, *27*, 340.
(34) Birham, E. R.; Ladd, J. R. *Inorg. Synth.* **1970**, *12*, 53.

Kinetic Studies. Metal hydrides, especially the tin hydrides, are sensitive to moisture and oxygen, which necessitated all the glassware, syringes, and solvents to be thoroughly dried and purged with argon. Most of the kinetic studies were carried out in a Pyrex cuvette containing a known concentration of iron(III) complex in predegassed acetonitrile and sealed with a serum cap. The change in absorbance of the iron(III) phenanthroline-type and bipyridine complexes was monitored at 510 and 520 nm, respectively, at 25 °C with a Cary 14 spectrophotometer. The $Fe(bpy)_3^{3+}$, $Fe(phen)_3^{3+}$, and $Fe(5-Cl-phen)_3^{3+}$ showed negligible decomposition over a period of 3 to 4 h, but $Fe(4,7-Ph_2-1,10-phen)_3^{3+}$ and $Fe(5-NO_2-1,10-phen)_3^{3+}$ slowly decomposed to the corresponding iron(II) complexes on standing. Apparently the rates of autodecomposition are dependent on the concentrations of the iron(III) complexes. For example, 3.0×10^{-3} M solutions of $Fe(4,7-Ph_2-1,10-phen)_3^{3+}$ and $Fe(5-NO_2-1,10-phen)_3^{3+}$ in acetonitrile ($\mu = 0.1$ (NaClO_4)) at 25 °C showed an increase in absorbance of 0.03 and 0.04, respectively, over a period of 2 h. These changes were corrected for in the kinetic studies involving the rather slow reactions of the silicon and germanium hydrides.

Thermal decomposition also posed an additional problem in the handling of tin hydrides. Whenever the kinetics were studied using tin hydrides in excess, an initial rapid reaction was observed due to the reaction between the iron(III) complex and the products of thermal decomposition (probably hexaalkylditin). Reproducible kinetics with the tin hydrides could only be obtained when the reactions were carried out with the iron(III) complex in excess of the tin hydride. For most reactions using the tin and germanium hydrides, the concentrations of the iron(III) complex and metal hydride employed were in the ranges of 1.6–6.8 and 0.16–0.49 mM, respectively. For reactions with the silicon hydrides, the concentrations of the iron(III) complex and the silicon hydride were 5.0–19.0 and 0.34–1.5 mM, respectively. The reactions with the silicon and germanium hydrides were also studied by using the metal hydrides in excess relative to the iron(III) complex; the concentrations of the metal hydrides employed were in the range of 0.03–0.25 M. All the reactions, with the exception of some with tri-*n*-butylstannane, were followed by monitoring the rate of formation of the iron(II) complexes with a Cary 14 spectrophotometer. The reactions of tri-*n*-butylstannane with $Fe(5-Cl-phen)_3^{3+}$ and $Fe(5-NO_2-phen)_3^{3+}$ were followed on a Durrum-Gibson stopped-flow spectrophotometer. In the latter experiments, separate solutions of the metal hydrides and the iron(III) complexes were made up in predegassed acetonitrile and transferred by means of all-glass hypodermic syringes. For the reactions in which iron(III) complexes were employed in excess, the second-order rate constants were obtained from the initial rate of formation of the iron(II) complex, the initial concentrations of the corresponding iron(III) complexes and the metal hydrides, and the molar absorptivity of the iron(II) complexes [$Fe(phen)_3^{2+}$, ϵ_{510} 1.30×10^4; $Fe(4,7-Ph_2-1,10-phen)_3^{2+}$, ϵ_{510} 1.26×10^4; $Fe(5-Cl-1,10-phen)_3^{2+}$, ϵ_{510} 9.33×10^3; $Fe(5-NO_2-1,10-phen)_3^{2+}$, ϵ_{510} 1.1×10^4; $Fe(bpy)_3^{2+}$, ϵ_{520} 8.24×10^3].[10] Alternatively, when triethylsilane, triethylgermane, and tri-*n*-butylgermane were employed in excess, the rate constants were also obtained from the slopes of the plots of $\ln (D_\infty - D_t)$ vs. time, where D_∞ and D_t represent the final absorbance and absorbances at certain time intervals, respectively. The rate constants obtained in this manner agreed with those obtained by the initial rate method to within 6–22%. All first-order plots were linear for 1.5–2.5 half-lives in the reactions with silicon and germanium hydrides.

Analysis of Proton Release. The acid released during reaction was measured by the change in pH by using a glass electrode (Sargent S-30072-15) equipped with a Beckman expanded-scale pH meter as follows. A solution containing a known concentration of $Fe(phen)_3(ClO_4)_3$ in acetonitrile was purged with argon in a two-necked flask equipped with the glass electrode. After the initial pH reading was taken, the glass electrode was quickly withdrawn while flushing with argon and the flask sealed with a serum cap. A stoichiometric amount of metal hydride was introduced with the aid of a microsyringe, and the solution was allowed to stir under an argon atmosphere until completion. The pH of the solution was recorded with a glass electrode calibrated with standard buffer solutions (Fisher Scientific Co.). For the subsequent use in an acetonitrile medium, the electrode was allowed 15–20 min for equilibration. Since the pH was recorded in an acetonitrile medium containing $Fe(phen)_3^{2+}$ and $MR_3(ClO_4)$, it was difficult to correct for the change in activity of the H^+. In order to analyze quantitatively the amount of released H^+, it was more convenient to use the method of standard addition in the following way.
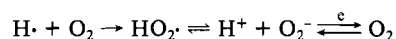
After taking the final pH reading, we added a known amount [equivalent to 5×10^{-3} M] of 70% perchloric acid by means of a microsyringe, and after allowing 15–20 min for equilibration, we recorded the pH reading again. The same procedure was repeated two to three times. (It is reasonable to assume that the very small amount of water introduced did not affect the activity of H^+ and that, within a small concentration range of $[H^+]$, its activity would remain constant.) The same procedure was also used in those experiments in which oxygen-saturated acetonitrile was employed. A typical result for a reaction commencing with $[n-Bu_3SnH] = 1.4 \times 10^{-2}$ M was initial pH 7.50 and final pH 2.10. Let X be the $[H^+]$ after reaction, then the $[H^+]$ present, the pH, and the apparent $[H^+]$ are serially as follows: X M, 2.10, 7.94×10^{-3} M; $(X + 5) \times 10^{-3}$ M, 1.90, 1.26×10^{-2} M; $(X + 1.0) \times 10^{-2}$ M, 1.80, 1.58×10^{-2} M; $(X + 2.0) \times 10^{-2}$ M, 1.65, 2.24×10^{-2} M; $(X + 3.0) \times 10^{-2}$ M, 1.55, 2.82×10^{-2} M. On the basis of these results, an increment corresponding to 5×10^{-3} M $[H^+]$ represents an apparent $[H^+]$ of $(3.1 \pm 0.2) \times 10^{-3}$ M, and a factor of 1.6 was needed to convert the apparent $[H^+]$ to actual $[H^+]$. The result yields $X = 1.30 \times 10^{-2}$ M.

Analysis of H+ Release as the Pyridinium Perchlorate. The amount of H^+ released can also be quantitatively analyzed as the pyridinium perchlorate as follows. A known amount of alkylmetal hydride was allowed to react with 2 equiv of iron(III) phenanthroline complex. After complete reaction, a solution containing 4 equiv of sodium tetraphenylborate was added, followed by an approximately 20-equiv excess of pyridine. The acetonitrile and pyridine were then removed in vacuo. The remaining solid was extracted with a known amount of hot water for 20 min and the NMR spectrum of the solution recorded. This method makes use of the complete insolubility of the tetraphenylborate salt of iron(II) phenanthroline in water.

Alternatively, the pyridinium perchlorate can be qualitatively analyzed by IR spectroscopy. In this case, sodium tetraphenylborate was not added after reaction, and the IR spectrum of remaining solid was taken immediately after evaporating the acetonitrile and pyridine. Due to the explosive nature of perchlorates, no attempts were made to dry the remaining solid thoroughly. The pyridinium perchlorates could be identified by their characteristic absorption ν_{N-H} ~3200 cm^{-1}, which was partly obscured by the broad ν_{O-H} band. In order to trace the origin of the proton, we used *n*-butyltin deuteride in place of *n*-Bu_3SnH. In this case, the previous method of isolating the pyridinium perchlorate could not be employed due to exchange of the pyridinium proton with the solvent. Tri-*n*-butyltin deuteride afforded the deuterated pyridinium perchlorate which could be identified by its IR absorption ν_{N-D} at 2380 cm^{-1}. The absorption due to ν_{N-H} was also present. The ratio ν_{N-D}/ν_{N-H} was approximately 4:1. The small amount of ν_{N-H} absorption may have arisen from exchange with adventitious water.

Trapping of Paramagnetic Intermediates. The stannylperoxy radical *n*-$Bu_3SnOO\cdot$ was generated from tri-*n*-butyltin hydride by irradiating a solution containing it and di-*tert*-butyl peroxide in butyronitrile at −76 °C. The ESR spectrum of *n*-$Bu_3SnOO\cdot$ consisted of an unresolved singlet ($g = 2.025$)[21] which persisted with a half-life of about 3 min at −76 °C. The rate of decay of *n*-$Bu_3SnOO\cdot$ was not affected by the presence of either $Fe(phen)_3^{3+}$ or $Fe(phen)_3^{2+}$ in approximately 10^{-2} M concentrations. The oxidative cleavage of *n*-Bu_3SnH by $Fe(phen)_3^{3+}$ was rapid even at −76 °C in a mixed solvent consisting of 1:10 v/v acetonitrile and butyronitrile. When this reaction was carried out under 1 atm of oxygen directly in the cavity of the ESR spectrometer, no paramagnetic species could be detected. The possibility that *n*-$Bu_3Sn\cdot$ is an intermediate but rapidly quenched by FeL_3^{3+} in preference to oxygen must be considered. If so (on the basis of estimates of the decay rate of *n*-$Bu_3SnOO\cdot$ of 50 M^{-1} s^{-1}, a detection limit of 10^{-6} M *n*-$Bu_3SnOO\cdot$, and a rate constant of 10^9 M^{-1} s^{-1} between *n*-$Bu_3Sn\cdot$ and dioxygen), we guess that this rate constant must be in excess of 10^{10} M^{-1} s^{-1} to preclude oxygen scavenging.

The alternative pathway involving hydrogen atom generation in eq 10 is not dependent on the rate of oxygen scavenging since HOO$\cdot$ is also oxidized by iron(III) to H^+ and O_2^-.[22] Furthermore, HOO$\cdot$ is a moderately strong acid with $pK_A = 4.9$ and is probably ionized in acetonitrile solution.[35] The oxidation of the superoxide ion by iron(III) is expected to be fast, leading to an overall process

$$H\cdot + O_2 \rightarrow HO_2\cdot \rightleftharpoons H^+ + O_2^- \overset{e}{\rightleftharpoons} O_2$$

(35) Hayon, E.; Simic, M. *Acc. Chem. Res.* **1974**, *7*, 114.

etc.

Electrochemistry and Photoelectron Spectra. The apparatus for the electrochemical measurements were described previously.[12] The photoelectron spectra were taken from ref 14 and 15.

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Structural Characterization of the Iron-Bridged "Double-Cubane" Cluster Complexes [Mo$_2$Fe$_7$S$_8$(SC$_2$H$_5$)$_{12}$]$^{3-}$ and [M$_2$Fe$_7$S$_8$(SCH$_2$C$_6$H$_5$)$_{12}$]$^{4-}$ (M = Mo, W) Containing MFe$_3$S$_4$ Cores

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The reaction system (R'$_4$N)$_2$MS$_4$ (M = Mo, W)/FeCl$_3$/RSH/NaOMe in methanol or ethanol at ambient temperature has afforded four principal products, [M$_2$Fe$_6$S$_9$(SR)$_8$]$^{3-}$ (**1**), [M$_2$Fe$_6$S$_8$(SR)$_9$]$^{3-}$ (**2**), [M$_2$Fe$_7$S$_8$(SR)$_{12}$]$^{3-}$ (**3**), and M$_2$Fe$_7$S$_8$(SR)$_{12}$]$^{4-}$ (**4**), which have been isolated as crystalline R'$_4$N$^+$ salts. The structures of **1** and **2** (M = Mo; R = Et) have been previously reported and consist of two MoFe$_3$S$_4$(SR)$_3$ cubane-type clusters linked through the Mo atoms by (μ-S)(μ-SEt)$_2$ and (μ-SEt)$_3$ bridges, respectively. The structures of **3** (M = Mo, R = Et) and **4** (M = Mo, W; R = CH$_2$Ph) have been determined by single-crystal X-ray diffraction. (Me$_3$NCH$_2$Ph)$_3$[Mo$_2$Fe$_7$S$_8$(SEt)$_{12}$] crystallizes in the orthorhombic space group *Pbcn* with *a* = 32.868 (6) Å, *b* = 12.922 (2) Å, *c* = 19.844 (5) Å, and *Z* = 4. (*n*-Bu$_4$N)$_4$[M$_2$Fe$_7$S$_8$(SCH$_2$Ph)$_{12}$] crystallizes in the monoclinic space group *P2$_1$/c* with *Z* = 2 and *a* = 15.883 (4) Å, *b* = 35.035 (7) Å, *c* = 15.836 (4) Å, and β = 109.20 (2)° (M = Mo) and *a* = 15.871 (10) Å, *b* = 34.991 (14) Å, *c* = 15.814 (8) Å, and β = 109.88 (4)° (M = W). The three anions have an imposed center of symmetry and are of the "double-cubane" type. Each anion contains two MFe$_3$S$_4$(SR)$_3$ clusters with trigonally distorted MFe$_3$S$_4$ cores which are connected through their M atoms by M-(SR)$_3$Fe(SR)$_3$M bridging units. The dimensions of the cores do not exhibit any chemically significant differences; those of the Mo and W complexes **4** are essentially indistinguishable and provide a further example of isometric replacement of the two atoms in analogous compounds. The primary dimensional differences reside in the Fe(SR)$_6$ bridge subunits which possess distorted trigonal-antiprismatic coordination. These differences are satisfactorily interpreted in terms of Fe(III) (probably low spin) in **3** and high-spin Fe(II) in **4**, thereby showing that in the couples [M$_2$Fe$_7$S$_8$(SR)$_{12}$]$^{3-,4-}$ the central Fe atom and not a cluster is the redox site. Whereas the triply bridged units M[X$_3$]M are common in molybdenum and tungsten chemistry, the "extended" triple bridges in **3** and **4** are the first of this kind to be structurally demonstrated. Other structural features of these anions are also discussed.

Introduction

In the course of our synthetic approach to the molybdenum-containing site in the FeMo proteins of nitrogenase,[1] we are examining reaction system 1 (M = Mo, W) comprised of

$$(R'_4N)_2MS_4 + 3FeCl_3 + 10RSH + 10NaOMe \xrightarrow[\text{EtOH}]{\substack{\sim 25\,°C \\ \text{MeOH}}}$$

$$\begin{array}{r} (R'_4N)_3[M_2Fe_6S_9(SR)_8]\ (\mathbf{1})\ + \\ (R'_4N)_3[M_2Fe_6S_8(SR)_9]\ (\mathbf{2})\ + \\ (R'_4N)_3[M_2Fe_7S_8(SR)_{12}]\ (\mathbf{3})\ + \\ (R'_4N)_4[M_2Fe_7S_8(SR)_{12}]\ (\mathbf{4})\ \ (1) \end{array}$$
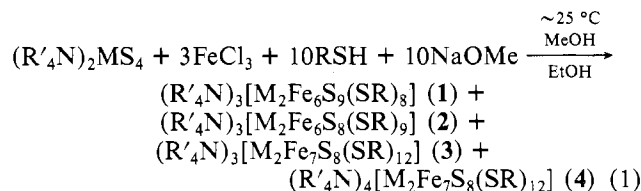
elementary reagents. The first products isolated were salts of anions **1**[2,3] and **2**[3] (M = Mo; R = Et). Crystallographic studies have established the indicated "double-cubane" structures in which two clusters containing MoFe$_3$S$_4$ cores are linked via (μ-S)(μ-SEt)$_2$ (**1**) or (μ-SEt)$_3$ (**2**) bridges between the two Mo atoms. Christou et al.[4,5] have independently
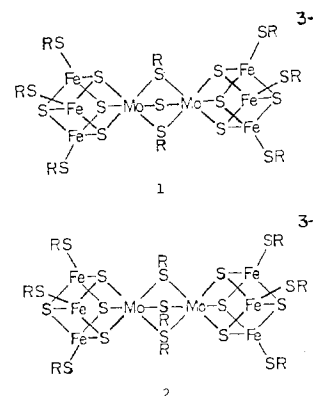
prepared other examples of **2** (M = Mo; R = Ph, CH$_2$CH$_2$OH), whose structures are essentially isodimensional with that of [Mo$_2$Fe$_6$S$_8$(SEt)$_9$]$^{3-}$.[3] Structures **1** and **2** are of relevance to the problem of modeling the Mo site in nitrogenase. The extended X-ray absorption fine structure (EXAFS) of the Mo spectra of several FeMo proteins[6] and of the FeMo

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(2) T. E. Wolff, J. M. Berg, C. Warrick, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **100**, 4630 (1978).
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(5) G. Christou, C. D. Garner, F. E. Mabbs, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 91 (1979).