to the positive salt effect of $Ce(NO_3)_3$.

Clearly, no breaking of the methyl C–H bond takes place in the rate-determining step of the oxidation of **1**. This unequivocally shows that the electron and the proton are lost in subsequent steps, in agreement with the mechanism reported in Scheme I. The formation of the radical cation occurs in the slow step of the reaction as also shown by the observation that the addition of Ce(III) does not retard the rate nor significantly change the k_H/k_D value. Further support for this mechanism comes from the observation that whereas the rate is unaffected by isotopic substitution, the product composition is different for **1** and **1d**, a smaller amount of side-chain substitution at the 2-position being observed with the latter substrate. Accordingly, product composition is determined in the second step which *must* exhibit a kinetic deuterium isotope effect.

The formation of a radical cation from **2** and **3** is easier than from **1**, owing to the lower ionization potential of the former substrates. It also follows that the reactions of **2** and **3** should occur by the radical cation mechanism, the presence of a deuterium kinetic isotope effect and a rate-retarding effect of Ce(III) being determined by a contribution of the rate of the proton abstraction step (eq 2) to the reaction rate.[9] That is, we suggest that, as we go from **1** to **3**, we pass from a situation where $k_2 \gg k_{-1}[\mathrm{Ce(III)}]$ to a situation where $k_2 \lesssim k_{-1}[\mathrm{Ce(III)}]$. With **1**, the condition $k_2 \gg k_{-1}[\mathrm{Ce(III)}]$ clearly holds in all the investigated range of added Ce(III) concentrations. With both **2** and **3**, we are instead in a situation where $k_{-1}[\mathrm{Ce(III)}]$ and k_2 are of comparable magnitude, and consequently by increasing [Ce(III)], an increase in k_H/k_D is observed, especially with **2**. Very likely the changeover of the rate-determining step takes place on going from **2** to **2d**. With the former only a little contribution of the proton-transfer step to the rate is indicated by the small retarding effect of Ce(III); with **2d** such a contribution instead becomes significant (in this case k_2 is smaller than with **2** since hydrogen has been replaced by deuterium) and the rate is strongly slowed down by Ce(III).

On the basis of the above considerations (also supported by the values of k_H/k_D in the absence of added Ce(III)), it would seem that the k_2/k_{-1} ratio decreases in the order **1** > **2** > **3**. Probably, this is mainly due to a decrease, in the same order, of the rate of proton-transfer process. Accordingly, a k_2 value smaller for **2**$^{+\cdot}$ than for **1**$^{+\cdot}$ is in agreement with the finding that the rate of proton transfer from a polymethylbenzene radical cation decreases with the increase in the number of methyl groups.[2c,12] It is also likely that k_2 decreases on going from **2**$^{+\cdot}$ to **3**$^{+\cdot}$, since the difference in the capacity of stabilizing a radical cation and a benzylic free radical should be much greater for a methoxy than for a methyl group. Thus, the conversion into the free radical should be energetically more costly for **3**$^{+\cdot}$ than for **2**$^{+\cdot}$.

Finally, it appears that in these reactions there can be such a delicate balance between $k_{-1}[\mathrm{Ce(III)}]$ and k_2 that even subtle changes of the substrate structure can change the slow step of the reaction. Thus, in the study of these oxidations, the determination of the deuterium kinetic isotope effect for a *single* substrate can be of limited significance for drawing general conclusions.

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[9] The possibility of a secondary deuterium kinetic isotope effect should be considered. Actually, the reversible oxidation potential of **2d** has been found about 5 mV lower than that of **2**, and this difference allows us to calculate a secondary deuterium kinetic isotope effect of about 1.2 for the formation of **2**$^{+\cdot}$ from **2**. On this basis even lower, and, therefore, negligible values of secondary k_H/k_D should be predicted for the reactions involving **1** and **3**, since in these cases only a CH_3 group has been replaced by a CD_3 group. Significantly larger secondary k_H/k_D (up to ~2) should be, in contrast, possible on the basis of a recent study of charge-transfer complexes of alkyl aromatic compounds.[10] However this prediction seems somewhat in contrast with the finding that K_D/K_H is ~1.1 (an inverse isotope effect!) for the association of *p*-xylene and toluene with fluoranil.[11]

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Polyoxoanion Supported Metal Carbonyls: Syntheses of the $[(OC)_3M(Nb_2W_4O_{19})]^{3-}$ Anions (M = Rhenium and Manganese)

Sir:

The reaction between d^6 metal carbonyl complexes and metal oxide surfaces yields surface-bound species whose chemical and physical properties have been examined extensively.[1] The variety of behaviors displayed by these species has led us to undertake a systematic study of metal carbonyl units bound to the oxide surfaces of polyoxoanion clusters. In this communication, we report the synthesis and characterization of the first adducts of this type, the $[(OC)_3Re(Nb_2W_4O_{19})]^{3-}$ anion and its manganese analogue, containing metal tricarbonyl units bonded to a triangle of oxygen atoms on the surface of the $Nb_2W_4O_{19}^{4-}$ anion.

Refluxing a solution of $[(n\text{-}C_4H_9)_4N]_4(Nb_2W_4O_{19})$ (**1**),[2] prepared from aqueous $Na_2[(CH_3)_4N]_2(Nb_2W_4O_{19})$[4] by using a cation-exchange resin, and an equimolar amount of $[(OC)_3Re(NCCH_3)_3](PF_6)$[5] for 2 h in CH_3CN under N_2 followed by cooling to −30 °C yields a pale yellow crystalline product formulated as $[(n\text{-}C_4H_9)_4N]_3[(OC)_3Re(Nb_2W_4O_{19})]$ (**2**)[6a] after recrystallization from $CH_3CN/CH_3C_6H_5$ by slow evaporation. The IR spectrum of **2**[6b] contains (1) two bands in the carbonyl stretching region characteristic of a C_{3v} metal tricarbonyl unit,[7] (2) the same pattern of absorptions in the 850–1000-cm^{-1} terminal oxygen stretching region observed for **1**[2b] displaced to higher energy by 25–40 cm^{-1}, and (3) absorptions in the 700–850-cm^{-1} bridging oxygen region which differ in number, frequency, and shape from those observed for **1** in the same region. If the 18-electron rule is applied to Re, these data favor an anion structure for **2** in which a $(OC)_3Re^+$ unit is bonded to a triangle of three contiguous bridging oxygen atoms of the $Nb_2W_4O_{19}^{4-}$ anion.[8] They fail, however, to indicate the locations of the Nb and W centers within the $Nb_2W_4O_{19}^{4-}$ unit relative to the Re atom. Since X-ray diffraction studies have thus far been plagued by disorder problems,[9] an ^{17}O NMR

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[2] (a) Anal. Calcd for $C_{64}H_{144}N_4Nb_2W_4O_{19}$: C, 35.02; H, 6.61; N, 2.55; Nb, 8.46; W, 33.50. Found: C, 34.95; H, 6.67; N, 2.47; Nb, 8.36; W, 33.62. (b) IR (Nujol, 650–1000 cm^{-1}) 733 (sh, br), 783 (s, br), 880 (s), 892 (s), 927 (s), 950 (m) cm^{-1}. Cf. ref 3.

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[6] (a) Anal. Calcd for $C_{51}H_{108}N_3ReNb_2W_4O_{22}$: C, 27,56; H, 4.90; N, 1.89; Re, 8.38; Nb, 8.36; W, 33.08. Found: C, 27.60; H, 4.97; N, 1.85; Re, 8.21; Nb, 8.60; W, 32.85. (b) IR (Nujol, 700–1000 cm^{-1}) 740 (s), 759 (sh), 810 (s), 826 (sh) [bridging oxygens], 884 (m) [cation], 918 (s), 928 (s), 960 (s), 978 (m) [terminal oxygens] cm^{-1}. IR (CH_3CN, 1850–2050 cm^{-1}) 1897 (s, br), 2020 (s) cm^{-1}.

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[8] This mode of bonding bridging oxygen bonding has been observed in $Mn(Nb_6O_{19})_2^{12-}$ and proposed for $(H_2NCH_2CH_2NH_2)(H_2O)M(III)(Nb_6O_{19})^{5-}$, M = Cr, Co: Flynn, C. M.; Stucky, G. D. *Inorg. Chem.* **1969**, *8*, 178, 335.

[9] Day, V. W.; Thompson, M. R., unpublished results.

[10] Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1978**, *100*, 4891.

Table I. 13.5 MHz ^{17}O NMR Spectral Data[a]

compd, temp, °C	chemical shifts,[b] line widths,[c] assignments[d]							
	ONb	OW	ONb_2	ONbW	OW_2	ONbWRe	OW_2Re	ONb_2W_4
1, 27	753 (231) [I]	691 (247) [G, H]	491 (110) [F]	433 (99) [D, E]	374 (269) [B, C]			*h* [A]
1, 79	757 (332) [I]	692 (114) [G, H]	495 (174) [F]	437 (98) [D, E]	376 (109) [B, C]			−46 (44) [A]
2, 27	812 (508) [S, T]	753, 737 (190, 190) [N, P, Q, R]	520 (348) [M]	471,[e] 459[f] (267)[g] [I, J, K, L]	413, 407 400, 396 (294)[g] [E, F, G, H]	162 (226) [C, D]	113 (140) [B]	*h* [A]
2, 79	810 (516) [S, T]	754, 737 (108, 108) [N, P, Q, R]	523 (434) [M]	461[f] (299)[g] [I, J, K, L]	415, 409 402, 398 (271)[g] [E, F, G, H]	164 (217) [C, D]	115 (108) [B]	*h* [A]

[a] See Figure 1 for representative spectra. [b] Positive chemical shifts in ppm downfield from pure H_2O at 25 °C; ±3 ppm if line width (lw) <200 Hz, ±5 ppm if lw = 200–400 Hz, ±7 ppm if lw > 400 Hz. [c] In parentheses; ±20 Hz if lw <100 Hz, ±40 Hz if lw = 100–400 Hz, ±60 Hz if lw >400 Hz. [d] In brackets; see Figure 2 for labeling scheme. [e] Shoulder. [f] Chemical shift of band peak, not center of band (see spectrum in Figure 1). [g] Combined line width of all resonances in this region, measured at half-height of most intense peak in region. [h] Resonance not observed due to insufficient enrichment.

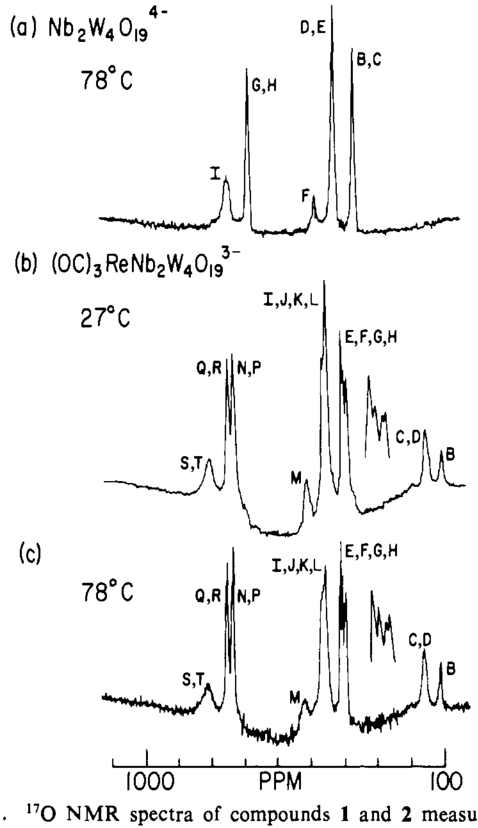

Figure 1. ^{17}O NMR spectra of compounds **1** and **2** measured from CH_3CN solutions. Assignments utilize the lettering schemes given in Figure 2. See Table I for numerical data. The insets in (b) and (c) are expansions of the 400-ppm region.

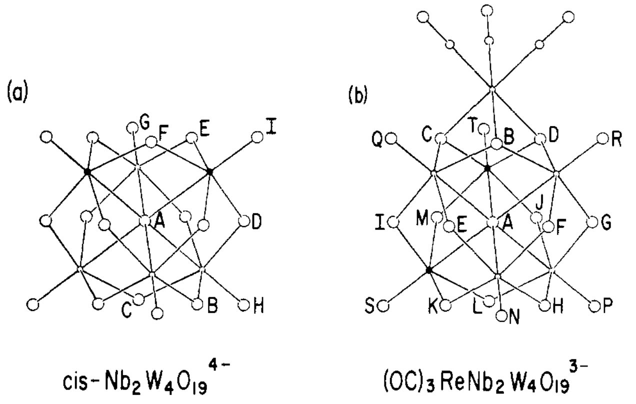

Figure 2. The C_{2v} structure of the $Nb_2W_4O_{19}^{4-}$ anion in **1** is shown in (a). Small filled circles represent niobium atoms, small open circles represent tungsten atoms, and large open circles represent oxygen atoms. One member of each set of symmetry-equivalent oxygens is labeled. The C_2 axis passes through O_F, O_A, and O_C; O_I, O_D, O_H, and the C_2 axis lie in one mirror plane; and the second mirror plane contains the C_2 axis and the O_G atoms. The C_1 structure proposed for the $[(OC)_3Re(Nb_2W_4O_{19})]^{4-}$ anion in **2** is shown in (b). The $Re(CO)_3$ unit appears at the top of the picture, and the remaining atoms in the structure are represented as in (a). Letters label the oxygen atoms.

spectroscopic study was undertaken in order to resolve this structural ambiguity.

The ^{17}O NMR study proceeded in two steps. First, compound **1** was enriched by exchange with hot, ^{17}O-enriched water. The chemical shift data and temperature-dependent line width behavior observed for enriched **1** (see Table I and Figure 1a) were then utilized to confirm the proposed[3] cis-metal configuration in **1** (see Figure 2a), employing precisely the same procedures followed in ref 10 for the *cis*-$V_2W_2O_{19}^{4-}$ anion. Second, spectral data for **2** (see Table I and Figure 1b,c), prepared from ^{17}O-enriched **1** and unenriched $[(OC)_3Re(NCCH_3)_3](PF_6)$ as described above, were obtained. The key feature of these data is the presence of four resonances in the OW_2 region (see insets, Figure 1b,c). If one assumes that the metal tricarbonyl unit in $[(OC)_3Re(Nb_2W_4O_{19})]^{3-}$ is bonded to a triangle of three bridging oxygens in the C_{2v} *cis*-$Nb_2W_4O_{19}^{4-}$ anion (see above), then only three diastereomers are possible. With the labeling scheme of Figure 2a, one diastereomer employs an O_F–O_E–O_E triangle as the $(OC)_3Re^+$ binding site, the second employs an O_C–O_B–O_B triangle, and the third employs an O_E–O_D–O_B triangle. The first diastereomer contains three symmetry-nonequivalent types of OW_2 oxygens, the second contains only one type of OW_2 oxygen, and the third contains four symmetry-nonequivalent OW_2 oxygens. The observation of four resonances for **2** in the OW_2 region therefore rules out the first two isomers and is consistent with the third possible isomer shown in Figure 2b.

The manganese analogue of **2**, $[(n\text{-}C_4H_9)_4N]_3[(OC)_3Mn(Nb_2W_4O_{19})]$ (**3**),[11] is prepared from **1** and $[(OC)_3Mn(NCC$-

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(11) (a) Anal. Calcd for $C_{51}H_{108}N_3MnNb_2W_4O_{22}$: C, 29.29; H, 5.20; N, 2.01; Mn, 2.63; Nb, 8.88; W, 35.16. Found: C, 29.35; H, 5.22; N, 2.02; Mn, 2.46; Nb, 8.72; W, 34.93. (b) IR (Nujol, 700–1000 cm^{-1}) 747 (s), 767 (sh), 808 (s), 824 (sh) [bridging oxygens], 887 (m) [cation], 912 (s), 922 (s), 957 (s), 974 (m) [terminal oxygens] cm^{-1}. IR (CH_3CN, 1850–2050 cm^{-1}) 1924 (s, br), 2031 (s) cm^{-1}.

(12) Camille and Henry Dreyfus Teacher-Scholar.

$H_3)_3](PF_6)$[5] by using conditions similar to those described above for the synthesis of 2. The anions of 2 and 3 are assumed to be isostructural on the basis of their extremely similar IR spectra.[6b,11b] Although compounds 2 and 3 are both stable toward atmospheric dioxygen and moisture, compound 3 alone is light sensitive. We are currently exploring its mechanism of photochemical decomposition.

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Hydrogen Evolution from Homogeneous Reaction Systems Containing Reduced Mo-Fe-S Clusters

Sir:

While there has recently been extensive research on light-driven hydrogen evolution systems,[1] the problem of effecting, and elucidating the molecular mechanism of, spontaneous hydrogen evolution from protic molecules in strictly homogeneous systems remains largely unresolved. In a biological context the prominent cases are the hydrogenase enzymes,[2] which, with one known exception,[3] contain Fe-S clusters as the only prosthetic groups. On the basis of core extrusion studies three such enzymes appear to contain 1-3 Fe_4S_4 sites,[4-7] and in another case EPR results indicate the presence of both Fe_4S_4 and Fe_2S_2 sites.[8] We describe here certain observations which may prove useful in designing and interpreting thermal hydrogen evolution systems of biological and abiological types.

Because those hydrogenases which operate in the H_2-evolving direction do so in the presence of reductants ($E_m \leq -400$ mV) sufficient to elicit EPR signals reasonably attributable to the $[Fe_4S_4]^{1+}$ core oxidation level in at least several enzymes,[2,5,8] reactions of the reduced cluster $[Fe_4S_4(SPh)_4]^{3-}$[9] with protic acids in aprotic media were investigated. In nearly all systems tested, weak acids such as HOAc present in stoichiometric to large excess amounts effected partial or complete oxidation to $[Fe_4S_4(SPh)_4]^{2-}$ (detected after addition of $Et_3N/PhSH$[10]) but gave no H_2 detectable by GC.[13] Stronger acids tended to decompose clusters. However, the system 2.0 mM $[Fe_4S_4(SPh)_4]^{3-}$ in *N*,*N*-dimethylacetamide (DMA) with initial PhSH/cluster molar ratios (*X*) of 240-480:1 afforded after 24 h 11-31% yields of H_2[11] on the basis of assumed reaction 1. While this system may be

$$2[Fe_4S_4(SPh)_4]^{3-} + 2PhSH \rightarrow 2[Fe_4S_4(SPh)_4]^{2-} + 2PhS^- + H_2 \quad (1)$$

regarded as a preliminary step toward development of a synthetic hydrogenase, the rather low yields obtained thus far encouraged an alternative approach to homogeneous H_2 evolution.

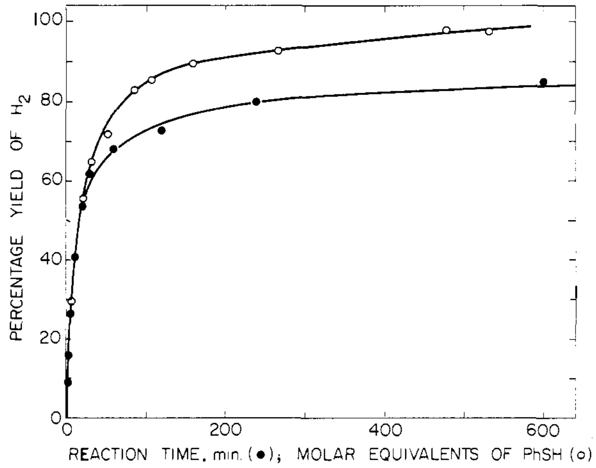

Figure 1. Percent yield of H_2 at ~25 °C from $(Et_4N)_5[Mo_2Fe_6S_8(SPh)_9]/PhSH$ reaction systems in DMA solutions as dependent upon initial PhSH/cluster molar ratios and time. (○) 1.02 mM $[Mo_2Fe_6S_8(SPh)_9]^{5-}$, ratios 0 to 532:1, sampled after 24-h reaction time. (●) 1.14 mM $[Mo_2Fe_6S_8(SPh)_9]^{5-}$, ratio 379:1, 0–600 min after thiol addition; reactions quenched by addition of 50 μL of a 1 M PhSSPh solution in DMA. The same abscissa applies to both curves.

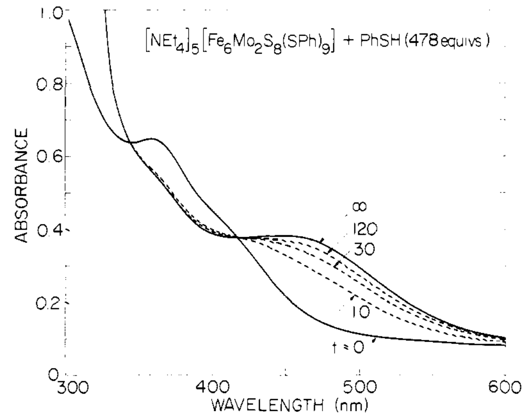

Figure 2. Absorption spectral changes accompanying H_2 evolution from a reaction system initially containing 1.02 mM $(Et_4N)_5[Mo_2Fe_6S_8(SPh)_9]$ (λ_{max} 358 (ϵ_M 62 600), ~405 nm, sh (ϵ_M 42 000)) and a PhSH/cluster molar ratio of 478:1. Spectra at various times *t* (min) after thiol addition are shown; the system at $t = 0$ contains no thiol. The spectrum at $t = \infty$ (~420 min) corresponds to that of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ (λ_{max} 347 (ϵ_M 53 000), 449 nm (ϵ_M 37 000)) measured separately, except that the 347-nm band is obscured by PhSH absorption.

Catalysis by hydrogenase of the exchange reaction $H_2 + HDO \rightleftarrows HD + H_2O$ has been widely interpreted as implicating an enzyme-bound hydride intermediate,[2,14] thus suggesting for more efficient H_2 evolution the utilization of a reactant molecule capable

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[1] See: M. Kirch, J.-M. Lehn, and J.-P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979), and references therein.

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