Phase-Transfer-Catalyzed Nucleophilic Reactions of Hydroxide Ions at Metal-Bound Carbon Monoxide Centers

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Abstract: Phase-transfer-catalyzed nucleophilic reactions of hydroxide ions with group 6B metal carbonyls ($M(CO)_{6-n}L_n$, where $n = 0$ or 1 and L = phosphine or phosphite ligands) are discussed. In the presence of $H_2{}^{18}O$, oxygen-18 enriched $M(CO)_{6-n}L_n$ species were afforded. These oxygen-exchange processes were monitored by both $\nu(CO)$ infrared spectroscopy and the small upfield shifts in the ^{13}C NMR resonances caused by oxygen-18. During the (PTC) oxygen-exchange reaction of OH^- with the $M(CO)_6$ species, slow formation of highly oxygen-18 labeled $\mu\text{-}H[M(CO)_5]_2^-$ derivatives was observed. Furthermore, when this process was carried out under a carbon monoxide atmosphere, hydrogen gas was produced catalytically; i.e., catalysis of the water-gas shift reaction occurred. The metal dependence of the oxygen-exchange process was found to be W > Mo > Cr, with phosphite-substituted derivatives being more reactive than their phosphine analogues. In substituted metal–carbonyl derivatives, where electronically different carbonyl ligands were present, the oxygen-exchange reaction was shown to occur preferentially at the more electrophilic carbon site, i.e., at the cis carbon monoxide ligands in $M(CO)_5L$ derivatives. Several of these thus formed stereoselectively oxygen-18 labeled species were demonstrated to simultaneously undergo intramolecular ligand rearrangement by a non-bond-breaking mechanism. The use of hydroxide ions under (PTC) conditions in the facile CO ligand substitution process in group 6B metal carbonyl complexes was investigated in a ^{13}CO atmosphere as well as in oxygen-18 enriched water. Both processes, CO ligand substitution and oxygen exchange, were greatly enhanced in the presence of phosphine ligands. This observation, coupled with the lack of metal hydride production from the reaction of hydroxide ions with phosphine-substituted metal–carbonyl derivatives, accounts for the quenching of catalytic activity by phosphine ligands during homogeneous catalyzed water-gas shift reactions involving mononuclear and cluster metal–carbonyl compounds.

Introduction

Nucleophilic reactions of hydroxide ion with transition-metal carbonyls provide a facile means for synthesizing metal hydride derivatives. Some illustrations are listed in eq 1–4.[2–6] The initial

$$Fe(CO)_5 + OH^- \rightarrow HFe(CO)_4^- \qquad (1)$$

$$2Cr(CO)_6 + OH^- \rightarrow HCr_2(CO)_{10}^- \qquad (2)$$

$$Mn(CO)_5PPh_3^+ + OH^- \rightarrow cis\text{-}HMn(CO)_4PPh_3 \qquad (3)$$

$$Ru_3(CO)_{12} + OH^- \rightarrow H_3Ru_4(CO)_{12}^- \text{ and } HRu_4(CO)_{13}^- \qquad (4)$$

step in these processes involves the nucleophilic addition of hydroxide ion to a carbonyl carbon atom to afford a hydroxycarbonyl intermediate; subsequent reactions lead to a metal hydride species and carbon dioxide. Recent reports of the isolations of $(C_5H_5)Re(CO)(NO)(CO_2H)$[7] and $(C_5H_5)Fe(L_2)(CO_2H)$ (where L = CO, PPh_3, or diphos)[8] from the reactions of hydroxide ion with $(C_5H_5)Re(CO)_{12}(NO)^+$ and $(C_5H_5)Fe(L_2)(CO)^+$, respectively, substantiate the intermediacy of metal derivatives containing the –COOH ligand.[9]

Although the reaction between OH^- and transition-metal carbonyls has been known for some time,[10] an upsurge of interest in it has been prompted in connection with its importance in the catalytic cycle of the *energy-important* water-gas shift reaction (eq 5) catalyzed by transition-metal carbonyl species.[11–17] Ap-

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (5)$$

plications of the water-gas shift reaction, where H_2O and CO serve as a source for hydrogen (i.e., the Reppe process[18]), to hydroformylation, hydrohydroxymethylation, and aminomethylation recently have received renewed attention.[12,19,20] Deeming and Shaw[21] reported over a decade ago reactions of the activated M–CO complexes ($IrCl_2(CO)_2L_2^+$, L = Me_2PhP or Me_2PhAs) with H_2O to provide the hydroxycarbonyl complexes $IrCl_2(CO_2H)(CO)L_2$. Pyrolysis of these derivatives at 160–180 °C in the solid state afforded CO_2 and $IrHCl_2(CO)L_2$. In a related process involving an activated metal–carbonyl derivative, oxygen exchange was demonstrated in $Re(CO)_6^+$ in the presence of $H_2{}^{18}O$, presumably by a pathway comprising reversible nucleophilic addition of OH^- to the carbon monoxide ligand with concurrent rapid proton transfer occurring in the [Re(COOH)] intermediate.[22] The analogous reaction between the less electron-rich $Mn(CO)_6^+$ species and $H_2{}^{18}O$ showed that metal hydride formation was concomitant with oxygen exchange, with metal hydride formation being slower than oxygen exchange.[23] We have conducted rather

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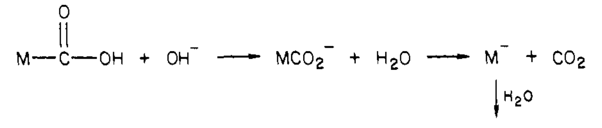
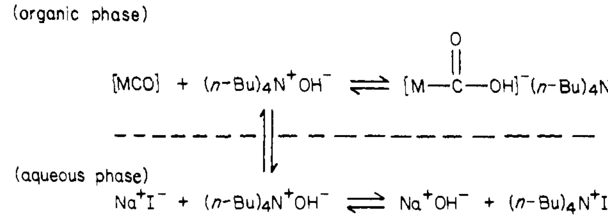
exhaustive studies of oxygen-exchange processes in substituted metal–carbonyl cationic derivatives and have made the following observations:[24-27] (1) The rate of oxygen exchange decreases as the number of electron-donating substituents on the metal increases, i.e., $M(CO)_6^+ > M(CO)_5L^+ \gg M(CO)_4L_2^+$. (2) In substituted metal–carbonyl derivatives, where there are two electronically different CO ligands, the oxygen atoms on the more electron-poor carbonyl ligands (i.e., CO groups with the larger CO stretching force constant or lower energy LUMO) exchanged faster. (3) The more electron-rich $L_n(CO)_{5-n}M(COOH)$ intermediates were less disposed to CO_2 elimination and M–H bond formation. (4) Metal hydride formation was enhanced over oxygen exchange as the basicity of the solution increased.

This latter observation was rationalized by a mechanism involving base deprotonation of the hydroxycarbonyl intermediate followed by release of CO_2 with hydrolysis of the reduced metal species (eq 6).[27] This process has been put forth previously to explain the reduction of Hg(II) to Hg(0) by carbon monoxide.[28]



$$\begin{array}{r} \mathrm{M{-}\overset{\overset{O}{\|}}{C}{-}OH + OH^- \longrightarrow MCO_2^- + H_2O \longrightarrow M^- + CO_2} \\ \downarrow \mathrm{H_2O} \quad\; \\ \mathrm{MH + OH^-} \quad (6) \end{array}$$

In neutral metal–carbonyl derivatives where the carbon atoms are less electrophilic, oxygen-exchange reactions with H_2O do not occur; however, as indicated in eq 1–4, these species do react with hydroxide ions. Because [MCOOH] intermediates are readily decarboxylated in the presence of excess OH^-, in order to observe oxygen-exchange processes in neutral metal–carbonyl derivatives, it is necessary to carry out these reactions in a biphasic system employing phase-transfer catalysis (⟨PTC⟩).[29] Under PTC conditions (eq 7), the hydroxide ion concentration is small in the organic phase, which contains the metal–carbonyl species, since OH^- is more highly hydrated than the halide ions; i.e., K_{eq} for eq 8 is $\sim 10^{-2}$.[30,31]



$$\begin{array}{l} \text{(organic phase)} \\ \mathrm{[MCO] + (\mathit{n}\text{-}Bu)_4N^+OH^- \rightleftharpoons [M{-}\overset{\overset{O}{\|}}{C}{-}OH]^-(\mathit{n}\text{-}Bu)_4N^+} \\ \text{- - - - - - -} \upharpoonleft\!\downharpoonright \text{- - - - - - - - - - - - - -} \quad (7) \\ \text{(aqueous phase)} \\ \mathrm{Na^+I^- + (\mathit{n}\text{-}Bu)_4N^+OH^- \rightleftharpoons Na^+OH^- + (\mathit{n}\text{-}Bu)_4N^+I^-} \end{array}$$

$$\underset{\text{organic}}{Q^+X^-} + \underset{\text{aqueous}}{OH^-} \rightleftharpoons \underset{\text{organic}}{Q^+OH^-} + \underset{\text{aqueous}}{X^-} \qquad (8)$$

In this paper we present our completed studies on PTC oxygen-exchange reactions of *neutral* metal–carbonyl derivatives with $H_2{}^{18}O$. Additional insight into reaction processes common to steps in the catalytic cycle of the water-gas shift reaction (WGSR) and into the use of hydroxide ions under PTC (eq 9) in the facile CO

$$M(CO)_6 + OH^- \xrightarrow[L]{\langle PTC\rangle} M(CO)_5L \text{ and } M(CO)_4L_2 \qquad (9)$$

ligand substitution processes in these metal–carbonyl derivatives will also be provided.[30,32,33]

Results and Discussion

The reactions of the group 6B metal–carbonyl derivatives with $H_2{}^{18}O$ were carried out under ⟨PTC⟩ conditions where the organic

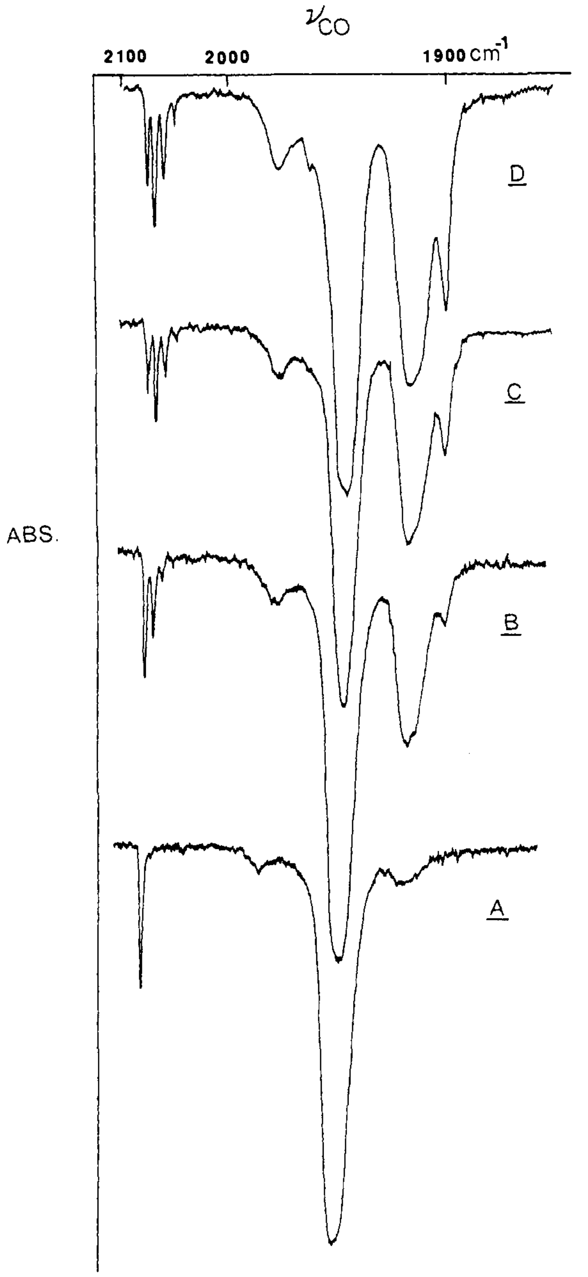


Figure 1. Infrared spectral traces in the ν(CO) region during the monitoring of oxygen-18 incorporation into $W(CO)_5PPh_3$ under ⟨PTC⟩ conditions (spectra observed in hexane solution): (A) $t = 0$; (B) $t = 10$ h; (C) $t = 22$ h; (D) $t = 32$ h.

phase consisted of the neutral carbonyl derivative in benzene and the aqueous phase consisted of NaOH (or KOH) with a small quantity of tetra-*n*-butylammonium iodide.[34,35] The oxygen-exchange process was monitored by noting the shifts in the ν(CO) bands in the infrared (see Figure 1). In general, these reactions (eq 10) were moderately slow, even at 72 °C, and required prolonged reaction periods (1–2 days), during which time problems arose from decomposition of the phase-transfer catalyst in basic

$$M(CO)_{6-n}L_n + {}^{18}OH^- \rightarrow M(CO)_{5-n}L_n(CO^{18}OH)^- \rightarrow M(CO)_{5-n}L_n(C^{18}O) + OH^- \qquad (10)$$

M = Cr, Mo, or W; L = CO, PPh_3, $P(OCH_2)_3CEt$, $P(OMe)_3$, $P(n\text{-}Bu)_3$, and $PPh(Bz)_2$

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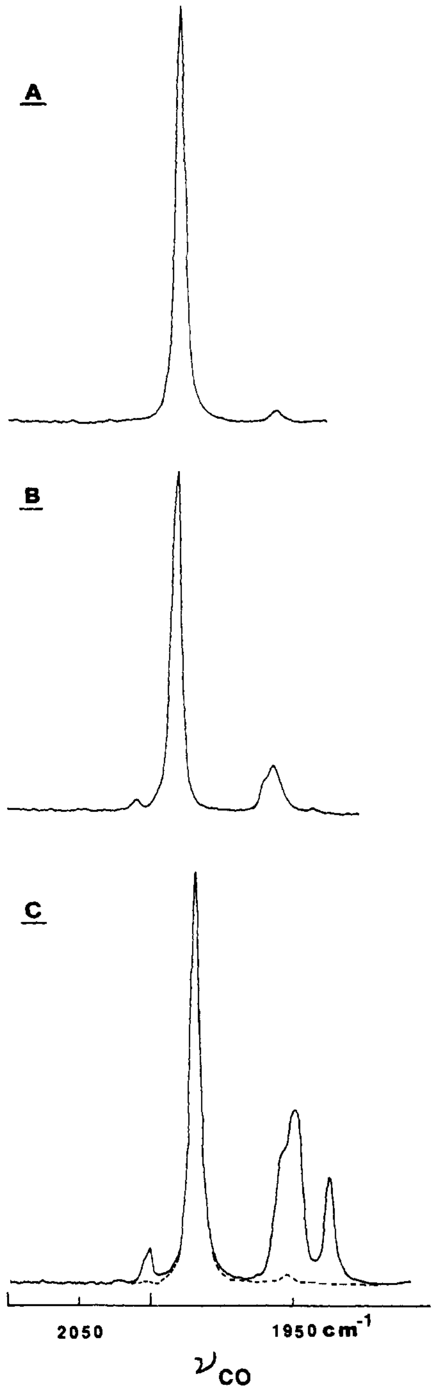

Figure 2. Relative rates of oxygen incorporation into the hexacarbonyl by (PTC) at 29 °C for identical concentrations of corresponding reactants over a 2-h reaction time: (A) $Cr(CO)_6$; (B) $Mo(CO)_6$; (C) $W(CO)_6$ ((---) natural abundance sample).

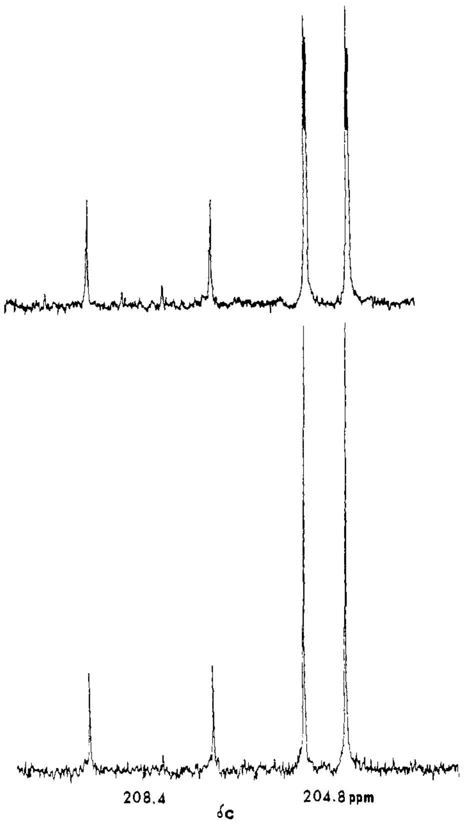

Figure 3. ^{13}C NMR spectra of $Mo(CO)_5P(OMe)_3$ in $CDCl_3$. Bottom view is the natural abundance spectrum of $Mo(C^{16}O)_5P(OMe)_3$, $\delta(C_{trans})$ 208.4 (J_{P-C} = 40.0 Hz) and $\delta(C_{cis})$ 204.8 (J_{P-C} = 13.7 Hz). Top view is the natural abundance spectrum of highly oxygen-18 enriched $Mo(CO)_5P(OMe)_3$. Approximately 50% of the C_{cis} resonance is shifted upfield by 0.040 ppm.

solution.[31] The relative rates of oxygen exchange increased markedly upon proceeding down the members of the homologous group 6B series, e.g., $W(CO)_6 \gg Mo(CO)_6 > Cr(CO)_6$ (see Figure 2 for relative rates of oxygen incorporation in this series at 29 °C).[36-38] In substituted metal–carbonyl derivatives where electronically different carbonyl ligands were present, it was possible to prepare stereoselectively oxygen-18 labeled derivatives, and in several instances, the reaction was completely stereoselective (vide infra). In all cases investigated, the oxygen-exchange rate is enhanced at the more electron-poor carbonyl ligand which is totally consistent with our earlier predictions regarding nucleophilic attack processes involving metal–carbonyl centers.[39] Although these reaction rates can be affected by the heterogeneity of the system and the distribution of the ions between the two phases, because of the variations in rates of oxygen exchange with the nature of the metal and phosphorus donor ligands as well as the stereoselectivity of the process, it appears that these factors are fast relative to the hydroxide addition reactions.

The use of infrared spectroscopy in the ν(CO) region coupled with restricted force field calculations has been extremely useful in assessing the stereochemistry of the carbonyl ligands which have undergone oxygen exchange.[24,26] However, for $M(CO)_5L$ derivatives it is difficult to observe small quantities of axial $C^{18}O$ species in the presence of a preponderance of equatorial $C^{18}O$ species.[40] For alleviation of this difficulty, the oxygen-18 isotope shifts on the natural abundance ^{13}C NMR spectra of the isotopically enriched metal–carbonyl derivatives were employed.[41] Table I lists the ^{18}O isotope upfield shift on the ^{13}C resonances in several of the group 6B metal–carbonyl species reported upon in this study.[42] As noted in Table I, these upfield shifts are small (0.61–0.67 Hz) at 15 MHz, but nontheless clearly observable (see Figure 3). The ^{18}O isotope shifts on the ^{13}C resonances of CO ligands cis or trans to the substituent ligand (L) in $M(CO)_5L$

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[36] A similar order has been observed previously for reactions involving nucleophilic addition of organomagnesium and organolithium reagents to carbon centers in metal-carbonyl species.[37,38]

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Table I. Oxygen-18 Isotope Shifts on the Natural Abundance ^{13}C NMR Spectra of M(CO)$_5$L Derivatives[a]

		σ(C)[b]		^{18}O isotope shift, Hz	
M	L	cis	trans	cis	trans
Cr	P(*n*-Bu)$_3$	217.8	221.6	0.61	0.61
Mo	CO	201.2		0.67	
	PPh$_3$	206.0	210.4	0.61	*c*
	P(OMe)$_3$	204.8	208.4	0.61	*c*
W	CO	192.0		0.61[d]	
	PPh$_3$	197.5	199.3	0.61	*c*
	P(OMe)$_3$	195.3	197.9	0.61	0.61

[a] Spectra were determined in CDCl$_3$ with the exception of W(CO)$_6$ which was measured in THF-d_8 at 15.03 MHz. [b] Chemical shifts are expressed in ppm relative to (CH$_3$)$_4$Si, with positive σ(C) values being at lower field than (CH$_3$)$_4$Si. [c] These samples were prepared stereospecifically labeled in equatorial positions only. [d] Isotope shift determined to be 2.68 Hz at 67.9 MHz.

species are of the same magnitude within the limits of experimental measurement.

Figure 3 illustrates the ^{13}C NMR spectrum of Mo(CO)$_5$P(OMe)$_8$ after extensive oxygen exchange with H$_2$^{18}O which indicates that *only* the equatorial (cis) carbonyl ligands have undergone oxygen exchange. Further, upon deconvoluting the resonances due to $\delta(C^{16}O)$ and $\delta(C^{18}O)$ with the assumption of symmetrical peak shapes (Lorentzian), the quantitative extent of oxygen-18 incorporation can be obtained; in this case 48% of the equatorial oxygen atoms were oxygen-18. Mass spectral analysis of this labeled species indicated it to be ~39% in oxygen-18 content. This would translate to labeling of 48% of the *equatorial* oxygen atoms. Infrared spectroscopy was consistent with these results, indicating ~50% of the equatorial oxygen atoms to be oxygen-18. Thus during this prolonged reaction period (2 days) required for ⟨PTC⟩ oxygen exchange of Mo(CO)$_5$P(OMe)$_3$ at 72 °C, oxygen incorporation was completely stereoselective. This fact also demonstrates the rigidity of the Mo(CO)$_5$P(OMe)$_3$ toward ligand rearrangement. It is conservatively estimated that it is possible to detect between 5 and 10% oxygen-18 incorporation at a particular CO ligand site by the oxygen-18 isotope shift of the ^{13}C resonance. In agreement with the above observations, *cis*-Mo(CO)$_4$(^{13}CO)P(OMe)$_3$, synthesized with stereochemical integrity from *cis*-Mo(CO)$_4$[NHC$_5$H$_{10}$]P(OMe)$_3$ and ^{13}CO,[43,44] exhibited only a small degree of CO scrambling (~6%, at least in part via a CO dissociation process) at 72 °C over a 2-day reaction period. Similarly, the Mo(CO)$_5$PPh$_3$ complex was shown to incorporate oxygen-18 highly stereoselectively in equatorial CO sites and also to be resistant toward ligand rearrangement at 72 °C.

On the other hand, the chromium and tungsten *cis*-M(CO)$_4$(^{13}CO)P(OMe)$_3$ species[45] have been observed to undergo more facile ligand rearrangements by means of a non-bond-breaking mechanism at temperatures similar to those employed in the oxygen incorporation processes (eq 10). Figure 4 displays the ^{13}C NMR spectra of *cis*-Cr(CO)$_4$(^{13}CO)P(OMe)$_3$ and the statistical mixture of *cis*- and *trans*-Cr(CO)$_4$(^{13}CO)P(OMe)$_3$ obtained after 2.5 h in CDCl$_3$ solution at 60 °C. During this stereochemical nonrigidity no ligand dissociation occurred as noted by the lack of incorporation of free ^{13}CO into the M(CO)$_5$P(OMe)$_3$ species as well as no production of metal hexacarbonyl under the reaction conditions for isomerization. In an analogous manner the *cis*-W(CO)$_4$(^{13}CO)P(OMe)$_3$ complex underwent intramolecular ligand scrambling, however, much more slowly than the chromium derivative.[46] We, therefore, believe that in all cases investigated of OH$^-$ reacting with M(CO)$_5$L species where electronically different CO ligands are present the reactions occur stereoselectively at cis CO groups, with subsequent ligand scrambling occurring in many instances. This conclusion is boosted by the observation that in molybdenum derivatives where the barrier to ligand rearrangement by a non-bond-breaking process is highest, completely stereoselective oxygen-18 incorporation was noted.

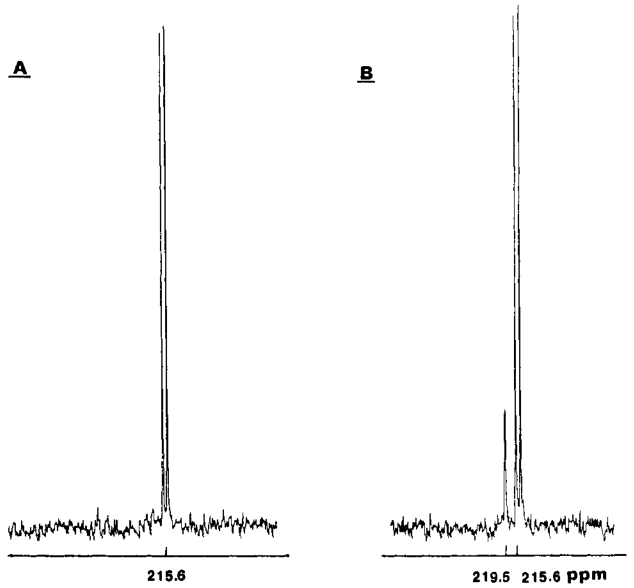

Figure 4. ^{13}C NMR spectra of Cr(CO)$_5$P(OMe)$_3$ in CDCl$_3$. (A) *cis*-Cr(CO)$_4$(^{13}CO)P(OMe)$_3$ prepared from *cis*-Cr(CO)$_4$[P(OMe)$_3$]Cl$^-$ and ^{13}CO in ethanol; (B) Cr(CO)$_4$(^{13}CO)P(OMe)$_3$ after 2.5 h at 60 °C, δ(C$_{\text{trans}}$) 219.5 (J_{P-C} = 4.4 Hz) and δ(C$_{\text{cis}}$) 215.6 (J_{P-C} = 21.0 Hz).

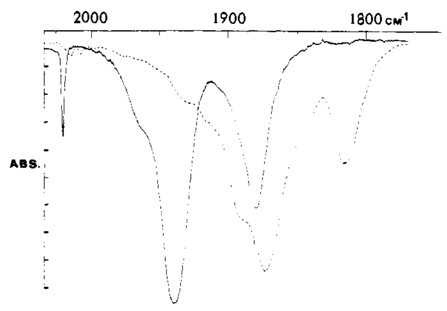

Figure 5. Infrared spectra in ν(CO) region in THF of μ-H[W(CO)$_5$]$_2$$^-$: (—) μ-H[W(C^{16}O)$_5$]$_2$$^-$; (---) highly oxygen-18 enriched μ-H[W(CO)$_5$]$_2$$^-$.

As depicted in eq 2, the reaction of Cr(CO)$_6$ with OH$^-$ is a synthetically useful reaction for preparing μ-H[Cr(CO)$_5$]$_2$$^-$ (i.e., in 80% yield).[3] Therefore, it would be anticipated that some metal hydride formation would accompany the oxygen-exchange process (eq 10) even though the OH$^-$ concentration in the organic phase is minimal. Indeed, highly oxygen-18 enriched μ-H[M(CO)$_5$]$_2$$^-$ derivatives were formed under ⟨PTC⟩ conditions, albeit rather slowly and in poor yields (Figure 5). The fact that the μ-H[M(CO)$_5$]$_2$$^-$ species are so highly enriched in oxygen-18 content (>75%) is indicative of the faster rate for oxygen incorporation into the M(CO)$_6$ complexes as compared with the rate of metal hydride and CO$_2$ production under ⟨PTC⟩ conditions. If the ⟨PTC⟩ reaction was carried out under 1 atm of carbon monoxide, these systems were observed to generate hydrogen with a low turnover rate, on the order of 1 week. No catalytic activity toward hydroformylation of 1-hexene to heptaldehyde was noted under these or more severe conditions (see Experimental Section). Upon phosphine or phosphite substitution of the M(CO)$_6$ species this secondary process leading to metal hydride production was not observed, although these complexes have been prepared by other routes.[47-49] For example, μ-H[Mo(CO)$_5$][Mo(CO)$_4$PPh$_3$]$^-$ and

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(45) The stereoselectivity labeled derivatives for chromium and tungsten were prepared from *cis*-M(CO)$_4$[P(OMe)$_3$]Cl$^-$ and ^{13}CO in ethanol. Darensbourg, D. J.; Baldwin, B. J.; Schenk, W., unreported work.

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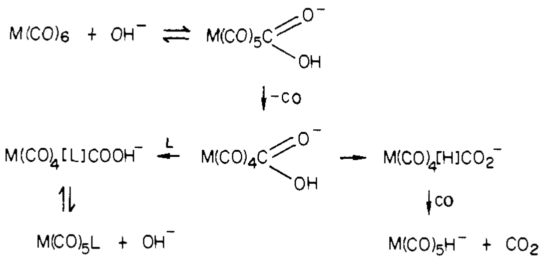
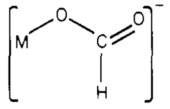
Scheme I



μ-H[Mo(CO)$_4$L]$_2^-$ derivatives have been prepared by thermal ligand substitution processes,[47,48] whereas μ-H[W(CO)$_5$][W(CO)$_4$PPh$_3$]$^-$ has been obtained by photochemical substitution of CO in μ-H[W(CO)$_5$]$_2^-$ by triphenylphosphine.[49] Hence the lack of formation of phosphine-substituted μ-H[M(CO)$_5$]$_2^-$ derivatives appears to be a kinetic effect and not a thermodynamic one.

In order to demonstrate further the reluctance of phosphine- or phosphite-substituted group 6B metal derivatives to proceed to hydride species in the presence of hydroxide ions, we have carried out a prolonged reaction of Cr(CO)$_5$P(OCH$_2$)$_3$CC$_2$H$_5$ with KOH in methanol in which the starting material was recovered unchanged. The Cr(CO)$_5$P(OCH$_2$)$_3$CC$_2$H$_5$ derivative was chosen for this study because P(OCH$_2$)$_3$CC$_2$H$_5$ is a small (cone angle 101°),[50] good π-acceptor ligand, and the group 6B and 7B metals decrease in their affinity for metal hydride formation with exclusion of CO$_2$ as one proceeds down the periodic table. This observation is consistent with the phosphine-substituted group 6B metal–carbonyl derivatives being poor catalysts for the water-gas shift reaction,[51] whereas the unsubstituted hexacarbonyls are very effective catalysts for the process.[14,15]

As we have discussed previously, the distinct possibility for the presence of an additional intermediate on the reaction pathway between hydroxide addition to the carbon center in MC≡O and M—H with concomitant CO$_2$ production involving a metal-complexed formate species exists (species I).[15] Certainly the reaction, M—OC(O)H → M—H + CO$_2$, has ample precedent in the literature.[52,53] Pertinent to this is the direct infrared spectral evidence, taken in conjunction with rate studies, which indicates that a surface formate ion is the reaction intermediate of the water-gas shift reaction on ZnO and MgO.[54] In any instance, whether metal hydride formation results from a M—COOH or M—OC(O)H intermediate, this process should be retarded by the presence of electron-donating groups (e.g., phosphines) on the metal centers.



I

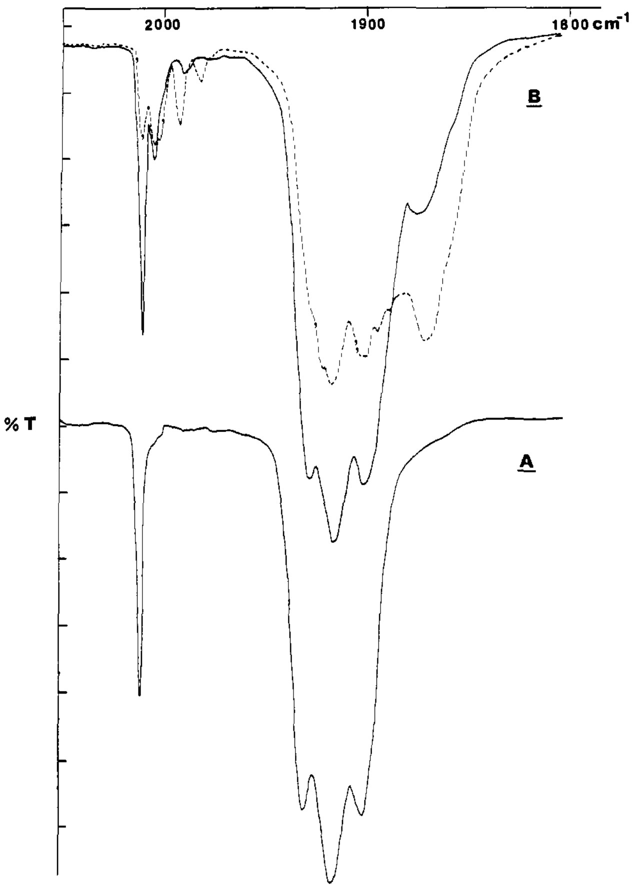


Figure 6. Infrared spectra in ν(CO) region in C$_2$Cl$_4$ of Mo(CO)$_4$(diphos): (A) natural abundance spectrum; (B) (–) ^{13}CO enriched during ⟨PTC⟩ ligand substitution process and (---) C^{18}O enriched during ⟨PTC⟩ ligand substitution process in H$_2$^{18}O.

Hui and Shaw[32] in an interesting related study have proposed the intermediacy of the anionic hydroxycarbonyl species, [M(CO)$_5$COOH]$^-$, in the facile phase-transfer catalyzed ligand substitution reactions of the group 6B metal hexacarbonyls with phosphines. These researchers propose the transient COOH ligand to labilize the dissociation of CO ligands. Brown and Bellus, during a more general discussion of base catalysis of ligand substitution processes in metal carbonyls, have characterized the –COOH group as a cis-labilizing ligand.[33] The relevant Scheme I proposed by Brown and Bellus is indicated below where the left-hand pathway incorporates the previous proposal of Hui and Shaw.

In order to obtain information germane to the mechanism depicted in Scheme I, we have carried out ligand substitution reactions of Mo(CO)$_6$ with 1,2-bis(diphenylphosphino)ethane and with ^{13}CO under identical basic ⟨PTC⟩ conditions at 29 °C. Mo(CO)$_4$(diphos) was obtained in 74% purified yield,[55] whereas the mono-^{13}CO-substituted species Mo(CO)$_5$(^{13}CO) accounted for only 10% of the Mo(CO)$_6$ (i.e., an enhancement of 1.7 times that of natural abundance). These observations strongly suggest that the rate of formation of substituted species is highly dependent on the nature of the incoming ligand (L), with phosphine substitution occurring much more rapidly than oxygen exchange or ^{13}CO substitution; features not accountable for by Scheme I. However, consistent with the above Scheme I, the rate of oxygen exchange was found to be greater than the rate of ^{13}CO incorporation in the Mo(CO)$_6$ species.

Further evidence for a more intimate involvement of the incoming phosphine ligand during ligand substitution and oxygen-exchange reactions was obtained when the Mo(CO)$_4$(diphos) preparation was carried out under a ^{13}CO atmosphere or in oxygen-18 enriched water. When the reaction was run under a ^{13}CO atmosphere the ^{13}CO content of the Mo(CO)$_4$(diphos) derivative was 15–18 times that of natural abundance (see Figure 6). The ^{13}C NMR spectrum of this ^{13}C-enriched sample in the carbonyl region exhibited a quartet at 217.5 ppm and a triplet at 209.6 ppm of the same intensity ratio as that observed for a natural abundance sample, and thus the ^{13}CO was distributed randomly in the complex. However, the recovered unreacted Mo(CO)$_6$ was not

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(48) Darensbourg, M. Y.; Atwood, J. L.; Burch, R. R., Jr.; Hunter, W. E. *J. Am. Chem. Soc.* **1980**, *102*, 0000.

(49) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1979**, *18*, 18.

(50) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(51) Unpublished results from our laboratory.

(52) For example see: (a) Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 3896. (b) Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59.

(53) We have observed the following reaction in our laboratory; (C$_5$H$_5$)Fe(CO)$_2$OC(O)H → [(C$_5$H$_5$)Fe(CO)$_2$]$_2$ + H$_2$ + 2CO$_2$. J. A. Froelich and D. J. Darensbourg, unpublished results. Further studies of these type processes are in progress.

(54) Ueno, A.; Onishi, T.; Tamaru, K. *Trans. Faraday Soc.* **1970**, *66*, 756.

(55) Reference 32 reported an 87% yield for this reaction.

enriched in ^{13}CO, thereby ruling out phosphine enhancement of ^{13}CO incorporation into $Mo(CO)_6$ without concomitant phosphine substitution (i.e., the two processes are concerted).[56] Similarly, when the $Mo(CO)_4$(diphos) preparation was carried out in $H_2{}^{18}O$, the oxygen-18 content in the $Mo(CO)_4$(diphos) species (randomly distributed)[29] was much greater than the oxygen-18 content of $Mo(CO)_6$ which was subjected to the oxygen-exchange process under identical ⟨PTC⟩ conditions (see Figures 2 and 6). These observations suggest a direct involvement of the incoming phosphine ligand in the labilization of CO as well as in the oxygen-exchange reaction. Phosphine enhancement of the oxygen-exchange reaction was greater than that of ^{13}CO substitution, again suggestive of the intermediacy of the hydroxycarbonyl species in both processes. The once formed $Mo(CO)_4$(diphos) was found not to undergo carbon monoxide or oxygen exchange under the reaction conditions nor was either process noted in the presence of 1,2-bis(diphenylphosphino)ethane but in the absence of the quaternary ammonium salt.

Although we cannot offer at this time a mechanistic explanation for all these observations on the phase-transfer-catalyzed ligand-substitution processes, they are apparently more complex than simple CO labilization by the –COOH ligand. Work in progress to be reported in due course on these and related metal cluster species[57] will provide a better understanding of these phenomena.

Experimental Section

The metal hexacarbonyls (M = Cr, Mo, W) were obtained from Strem Chemicals, Inc., and used without further purification. Carbon monoxide (93.3% ^{13}C) and $H_2{}^{18}O$ (99.5% ^{18}O) were acquired from Prochem, B.O.C. Ltd., London. The phase-transfer catalyst, tetrabutylammonium iodide, was obtained from Aldrich Chemical Co., Inc. Benzene was distilled prior to use. The phosphine- and phosphite-substituted metal–carbonyl derivatives were prepared according to established procedures.[58] All manipulations were carried out in Schlenkware under a nitrogen atmosphere.

Phase-Transfer-Catalyzed Oxygen-Exchange Processes. The compounds investigated included the $M(CO)_5L$ derivatives, where M = Cr, Mo, or W and L = CO, PPh_3, $P(OCH_2)_3CEt$, $P(OMe)_3$, $P(n\text{-}Bu)_3$, and $PPh(Bz)_2$.

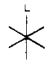
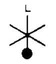
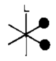
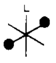
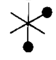
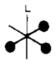
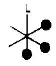
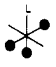
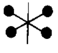
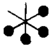
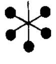
In a typical preparative scale reaction 1.0 g (2.19 mmol) of $Mo(CO)_5P(OMe)_3$ in 40 mL of benzene was added to 1.5 mL of $H_2{}^{18}O$ (99.5% ^{18}O) saturated with NaOH (preequilibrated) containing 0.10 g (0.27 mmol) of $(n\text{-}Bu)_4NI$. The resulting two-phase system was heated at 70 °C under nitrogen with vigorous stirring. The oxygen-exchange process was monitored by withdrawing samples at various time intervals and the solvent mixture removed in vacuo. The samples were redissolved in hexane, and the $\nu(CO)$ infrared spectra were recorded in 1.0-mm NaCl sealed solution cells. The reaction was cooled to room temperature, and the organic phase was separated, dried over $MgSO_4$, and filtered through Celite. The solvent was removed under vacuum to afford the clear liquid product.

In addition, several reactions were carried out on an infrared scale where the reagents were present to the extent of ~1/10 that employed in the preparative scale processes. Figure 1 illustrates an example of the infrared traces in the $\nu(CO)$ region noted during the monitoring of these oxygen-exchange processes.

Phase-Transfer-Catalyzed Ligand-Substitution Processes. A solution of 0.25 g (1 mmol) of $Mo(CO)_6$ and 0.40 g (1 mmol) of 1,2-bis(diphenylphosphino)ethane in benzene was added to 2 mL of H_2O containing 2 g of NaOH and 0.02 g of $(n\text{-}Bu)_4NI$. The reaction mixture was stirred rapidly under nitrogen at 29 °C for 2 h after which volatiles were removed under vacuum. The solid residue was recrystallized from dichloroethane and methanol to afford a 74% yield of $Mo(CO)_4$(diphos), mp 189–190 °C.

An analogous procedure was employed where the reaction was carried out in a ^{13}CO atmosphere (CO concentration in solution ~0.01 M) to afford a ^{13}CO-enriched sample of $Mo(CO)_4$(diphos). Similarly, the identical process was carried out in the absence of 1,2-bis(diphenylphosphino)ethane to provide low levels of ^{13}CO-enriched $Mo(CO)_6$. In addition, the reaction was carried out in $H_2{}^{18}O$ to afford highly oxygen-18 enriched $Mo(CO)_4$(diphos).

Table II. Observed and Calculated $\nu(CO)$ Frequencies for the Isotopic Species of $W(CO)_5P(OCH_2)_3Et$ with $C^{18}O$

isotope	geometry	frequencies,[a] cm⁻¹				
1		2083.9 (*2083.9*)	1964.3 (*1964.0*)	1996.6	1960.1	1960.1 (*1958.4*)
2		2079.9	1920.7	1996.6	1960.1	1960.1
3		2075.7 (*2075.8*)	1989.7	1964.1	1927.3 (*1925.8*)	1960.1
4		2066.0 (*2067.8*)	1984.4	1964.0	1929.8	1924.6
5		2067.5 (*2067.8*)	1974.0	1954.3	1912.8 (*1911.3*)	1960.1
6		2071.3	1989.5	1930.7	1917.6	1960.1
7		2055.7 (*2055.9*)	1971.2	1954.3	1912.8	1960.1
8		2060.9	1984.4	1934.7	1924.6	1916.5
9		2062.6	1967.2	1918.3	1912.8	1960.1
10		2042.0	1956.3	1948.5	1912.8	1912.8
11		2049.7 (*2049.6*)	1965.7	1927.9	1912.8	1916.7
12		2033.6	1916.9	1948.5	1912.8	1912.8

[a] Observed frequencies are listed in parentheses directly below the calculated values. Italicized frequencies were employed as input in the force field fit ($k_1 = 15.79_4$, $k_2 = 16.10_9$, $k_c = 0.30_5$, $k_c' = 0.30_5$, $k_t = 0.59_7$).

Hydrogen Production and Hydroformylation Processes. Under ⟨PTC⟩ conditions, in the presence of a carbon monoxide atmosphere, the $M(CO)_6$ species were observed to generate hydrogen at 75 °C. Over a period of several days, the concentration of CO was shown to diminish with concomitant appearance of a hydrogen peak, detected by gas chromatography (using a 5A molecular sieve, 60/80 mesh column with argon as the carrier gas). This system was observed to possess a low turnover rate, on the order of 1 week, but was noted to be quite stable. Regeneration of the catalyst system was accomplished by a simple freeze–pump–thaw cycle followed by removal of the CO atmosphere. The rejuvenated system continued to produce hydrogen at approximately the same rate as the initial system.

Hydroformylation of 1-hexene by $Cr(CO)_6$ was attempted under ⟨PTC⟩ conditions at 75 °C and an atmosphere of carbon monoxide or in basic 2-ethoxyethanol at 250 psi and 170 °C. Following a 2-day reaction period, no heptaldehyde was detected by gas chromatography.

Infrared Measurements and Vibrational Analysis. The infrared spectra were recorded in 1.0 mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with an infrared data station. Generally spectra recorded were the average of four added repetitively scanned spectra employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water vapor spectrum below 2000 cm⁻¹ and against a CO spectrum above 2000 cm⁻¹.

Initial CO stretching force constants for the CO stretching region were calculated by using the $C^{16}O$ vibrational data. The trial force constants were refined by use of the $C^{18}O$ frequency data and an iterative computer program that adjusts a set of force constants common to a group of isotopically substituted molecules to give simultaneously a least-squares

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[56] This observation would appear to eliminate a process involving phosphine (or phosphine oxide impurities) assisted anionic metal hydride formation accompanied by CO_2 elimination. Subsequent reactions of the metal hydride anion with H_2O would lead to H_2 production (no H_2 was detected by GC during the preparation of $Mo(CO)_4$(diphos)) and unsaturated metal–carbonyl fragments which would be trapped readily by phosphines.

[57] The reaction reported in this paper may have common mechanistic features with phosphine substitution reactions involving metal cluster species in the presence of hydroxide bases. See, for example: Angoletta, M.; Malatesta, L.; Caglio, G. *J. Organomet. Chem.* **1975**, *94*, 99.

[58] Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959.

J. Am. Chem. Soc. 1980, 102, 4694-4703

fit between the observed and calculated frequencies for all molecules. The trial force constants were refined to reproduce the observed $C^{16}O$ and $C^{18}O$ vibrations to within an average of 0.8 cm^{-1}. Data typical of that obtained are provided in Table II for the various isotopic species of $W(CO)_5P(OCH_2)_3Et$.

^{13}C NMR Measurements. The ^{13}C NMR spectra were recorded on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in $CDCl_3$ solvent in 10-mm tubes. Spectra for determining the oxygen-18 shifted ^{13}C resonances resulted from the accumulation of 14000 transients employing a sweep width of 500 Hz (16K data block) with an acquisition time of 16.4 s, a pulse repetition rate of 17.0 s, and a flip angle of 90°.

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Synthesis and Electronic and Redox Properties of "Double-Cubane" Cluster Complexes Containing $MoFe_3S_4$ and WFe_3S_4 Cores

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, and the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received January 21, 1980

Abstract: The reaction system $MS_4^{2-}/3\text{-}3.5FeCl_3/9\text{-}12NaSR$ (M = Mo, W) in methanol or ethanol affords as principal products four "double-cubane" cluster anions, $[M_2Fe_6S_9(SR)_8]^{3-}$ (**1**), $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (**2**), $[M_2Fe_7S_8(SR)_{12}]^{3-}$ (**3**), and $[M_2Fe_7S_8(SR)_{12}]^{4-}$ (**4**), which are isolable as appropriate quaternary ammonium salts. Syntheses of cluster types **1** (M = W), **3**, and **4** are described together with spectroscopic and voltammetric properties of the four cluster types. All clusters exhibit isotropically shifted ^1H NMR spectra which serve as criteria for adequate purity, reveal from shift patterns contact and dipolar mechanisms at terminal and bridge substituents, respectively, and support the existence of single geometrical isomers in solution. Cluster types **1** and **2** form three-membered electron-transfer series in which individual $MFe_3S_4(SR)_3$ clusters are reduced in weakly coupled steps. Cluster type **3** affords a four-membered series in which the initial reduction is $Fe^{III} \rightarrow Fe^{II}$ in the $Fe(SR)_6$ bridge unit and subsequent reductions occur at individual clusters. Potential separations for the latter two steps (~0.10 V) more closely approach the statistical value of 36 mV than do those of types **1** and **2** (~0.19 V), owing to larger intercluster separations. The presence of Fe^{III} and Fe^{II} in the bridge units of type **3** and **4** clusters, respectively, is demonstrated by Mössbauer spectroscopy. From observations of narrow intervals of ^{57}Fe isomer shifts, hyperfine magnetic fields at Fe sites, terminal methylene proton contact shifts, and redox potentials of **1** and **2** it is concluded that the Fe_3 portions of MFe_3S_4 core units are electronically delocalized and, within and among all cluster types **1**–**4**, are virtually equivalent electronically. Core Fe isomer shifts are considered to accord best with the mean oxidation state $Fe^{2.67+}$. This conclusion, together with prior observations of a pronounced structural core similarity in all clusters, leads to the core formal electronic descriptions $[Mo^{4+}Fe^{3+}{}_2Fe^{2+}S_4]^{4+} + [Mo^{3+}Fe^{3+}{}_2Fe^{2+}S_4]^{3+}$ (type **1**) and $2[Mo^{3+}Fe^{3+}{}_2Fe^{2+}S_4]^{3+}$ (types **2**–**4**), thereby defining total oxidation levels of the cores in each cluster type. Full tabulations of Mössbauer spectral parameters and ^1H NMR isotropic shifts are presented together with representative Mössbauer and NMR spectra and cyclic voltammograms.

Introduction

The burgeoning interest in iron–molybdenum–sulfur complexes and their tungsten counterparts arises in large measure from recent spectroscopic studies[2-5] of the FeMo proteins of nitrogenase and the FeMo cofactor obtainable therefrom. The results of these investigations point to the existence of an Fe–Mo–S cluster as yet incompletely defined in terms of composition and structure and not encountered in any other biological system or as a product of chemical synthesis. Several laboratories are engaged in the synthesis of Fe–Mo–S cluster complexes in order to generate species of possible relevance to the biological cluster. To date, synthetic methods productive of Fe–Mo–S clusters have utilized as starting materials the tetrathiometalates MS_4^{2-} (M = Mo, W).[6] The general tendency of these ions to form heterometallic complexes via sulfide bridging has been demonstrated in other contexts,[6,7] especially by the research of Müller and co-workers.[6,7a]

The classes of Fe–M–S clusters (M = Mo, W) derived from tetrathiometalates are most simply organized in terms of cluster nuclearity: binuclear, $[(PhS)_2FeMS_4]^{2-}$,[8] $[Cl_2FeMS_4]^{2-}$,[9] $[S_5FeMS_4]^{2-}$;[8b] trinuclear, $[Fe(MS_4)_2]^{2-}$,[10] $[Fe(NO)(MS_4)_2]^{2-}$,[10]

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(1) (a) Stanford University; (b) Francis Bitter National Magnet Laboratory.

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(9) (a) D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Simopoulos, A. Kostikas, V. Pětrouleas, and V. Papaefthymiou, *J. Am. Chem. Soc.*, **102**, 1730 (1980); (b) P. P. Power and R. H. Holm, unpublished results.

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