Table II. Cyclic Voltammetry of Fe(II) Complexes Containing Cyano, 2,2′-Bipyridine, and/or 2,2′-Bipyrimidine Ligands

complex	solvent	$E_{1/2}$, V[a]	ΔE, mV[b]	ref
$Fe(CN)_6^{4-}$	H_2O[c]	0.174	123	*d*
$Fe(bpym)(CN)_4^{2-}$	H_2O	0.482	60	*d*
$Fe(bpym)_2(CN)_2$	H_2O	0.876	62	*d*
$Fe(bpy)_3^{2+}$	H_2O	0.825	64	*d*
		0.810	...	28
	DMF	1.07	75	*d*
		1.06	...	26
$Fe(bpym)_3^{2+}$	DMF	1.33[e]	100	*d*

[a] Potential estimated from average of oxidation and reduction waves for Fe(III/II) vs. SCE at 10 mV/s scan rate. [b] Peak-to-peak separation between oxidation and reduction waves for Fe(III/II) at 10 mV/s. [c] pH 7.00. [d] This work. [e] Irreversible.

formation of $[Fe(bpy)_2]_2(bpym)^{4+}$.[27]

The thermal instability of the $Fe(bpym)_3^{2+}$ complex does not appear to manifest itself in aqueous solutions of $Fe(bpym)_2(CN)_2$ and $Fe(bpym)(CN)_4^{2-}$. Neither of the last two ions undergo any appreciable decomposition in aqueous solution.

The cyclic voltammograms of the mixed-ligand complexes of Fe(II) with cyanide and 2,2′-bipyrimidine show single reversible waves when scanned from −0.3 to +1.2 V (vs. SCE) in aqueous solution. The $E_{1/2}$ values for $Fe(bpym)_{3-n}(CN)_{2n}^{(2-2n)+}$ (n = 1–3) and $Fe(bpy)_3^{2+}$ in aqueous solution and DMF are listed in Table II. In aqueous solution, the $E_{1/2}$ value of the Fe(III)/Fe(II) couple shifts anodically in the order $Fe(CN)_6^{4-}$ < $Fe(bpym)(CN)_4^{2-}$ < $Fe(bpy)_3^{2+}$ < $Fe(bpym)_2(CN)_2$ and is dependent on scan rate. The $Fe(bpym)_3^{2+}$ wave was not observable in aqueous solution due to the onset of solvent oxidation at more positive potential. Comparative electrochemistry of $Fe(bpym)_3^{2+}$ and $Fe(bpy)_3^{2+}$ was conducted in DMF/0.1 M TEAP. The single irreversible wave for the $Fe(bpym)_3^{3+/2+}$ couple at +1.31 V (vs. SCE) occurred 0.25 V more positive than for the $Fe(bpy)_3^{3+/2+}$ wave at +1.06 V (vs. SCE). Although both oxidation and reduction waves are observed in the voltammogram, the reduction peak is much smaller at all scan rates. The peak-to-peak separation of the oxidation and reduction waves was ∼100 mV at a scan rate of 10 mV/s and is larger at faster scan rates.

A comparison of the potential of the $Fe(bpym)_3^{3+/2+}$ couple with that of the $Fe(bpy)_3^{+/2+}$ couple shows that the relative delocalization of electron density toward the nitrogen aromatic ring systems and away from the metal is greater for bpym than for bpy. The 0.25-V increase in the reduction potential for $Fe(bpym)_3^{2+}$ shows that the Fe(III) complex of bpym is not as stable as the corresponding bpy analogue. In fact, the instability of the $Fe(bpym)_3^{3+}$ complex as shown by cyclic voltammetry suggests that the stability of $Fe(bpym)_3^{2+}$ is probably due predominantly to the π-acceptor ability of bpym. Since the structural difference in bpym and bpy is the substitution of a N atom for a CH group at a site remote to metal coordination, it is not surprising that the bpym ligand is more π-electron withdrawing.

The proton-decoupled ^{13}C NMR spectra for the Fe(II)–bpym complexes show the behavior characteristic of bpym functioning as a π-acceptor ligand. There have been previous reports describing the coordination of aromatic nitrogen heterocyclic ligands (L) to d^6 transition-metal centers such as $Fe(CN)_5L^{3-}$, $Ru(NH_3)_5L^{2+}$, $Ru(NH_3)_4L^{2+}$, or $M(CO)_4L$ (where M = Cr, Mo, W) and the effect of coordination on the ^{13}C NMR chemical shifts of the ligand.[1,3,28-32] Bonding between d^6 low-spin metal centers and the aromatic nitrogen heterocyclic ligand has been described as ligand σ donation to the metal in conjunction with metal π back-bonding to the ligand.[1,32,33]

In all Fe(II)–2,2′-bipyrimidine complexes studied, the α-carbon is shifted downfield with respect to the same α-carbon in the free ligand. This result is in agreement with other studies and appears to be independent of the π-back-bonding ability or anisotropic character of the nonaromatic nitrogen heterocyclic ligand. Downfield shifts of α-carbons and small downfield or upfield shifts of β-carbons are observed for the Fe(II)–bpym complexes. These are in general agreement with other systems where π back-bonding to the nonaromatic ligands was possible.[1,3] The γ-carbon in bpym continues to shift upfield vs. free ligand as each bpym ligand is replaced by two CN^- ligands. The net conclusion is that the combined σ-donor/π-acceptor properties of CN^- and bpym result in the heterocycle being a better electron acceptor for Fe(II) than the CN^- ligand. This interpretation is consistent with the electrochemical results as well, where increased numbers of bpym ligands lead to more positive reduction potentials.

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Registry No. $[Fe(bpym)_3](ClO_4)_2$, 92816-69-8; *cis*-$[Fe(bpym)_2(CN)_2]$, 92787-93-4; $K_2[Fe(bpym)(CN)_4]$, 92787-94-5.

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(27) Brewer, K. J.; Petersen, J. D., work in progress.

(28) Saji, T.; Aoyagui, S. *J. Electronanal. Chem. Interfacial Electrochem.* **1975**, *60*, 1.

(29) Figard, J. E.; Paukstelis, J. V.; Byrne, E. F.; Petersen, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417.

(30) Malin, J. M.; Schmidt, C. F.; Toma, H. E. *Inorg. Chem.* **1975**, *14*, 2924.

(31) Lavallee, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718.

(32) Ruminski, R. R.; Petersen, J. D. *Inorg. Chim. Acta* **1982**, *65*, L177.

(33) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 697.

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Ligand Substitution Processes in Tetranuclear Carbonyl Clusters. 8. Reactions of $Co_4(^{12}CO)_{12}/Co_4(^{13}CO)_{12}$ with Phosphorus Donor Ligands. Further Evidence for Cluster Integrity during Ligand Substitution Processes

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Received March 28, 1984

A possibile mode of reaction for ligand substitution processes involving polynuclear metal carbonyl derivatives is cluster fragmentation followed by recombination. Definitive experiments designed to probe this phenomenon in dinuclear metal carbonyls of the group 7B metals have recently been published. These include studies of thermal ligand substitution reactions involving $MnRe(CO)_{10}$ or a mixture of $Mn_2(CO)_{10}/Re_2(CO)_{10}$,[1] $^{185}Re_2(CO)_{10}/^{187}Re_2(CO)_{10}$,[2] and $Mn_2(^{13}CO)_{10}/Mn_2(^{12}CO)_{10}$.[3] In these dimeric species, thermal ligand substitution reactions were demonstrated to proceed via carbon

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(1) (a) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Chem.* **1982**, *21*, 1698. (b) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484. (c) Poe, A. *Inorg. Chem.* **1981**, *20*, 4029. (d) Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 4031.

(2) Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822.

(3) Coville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2499.

0020-1669/84/1323-4382$01.50/0

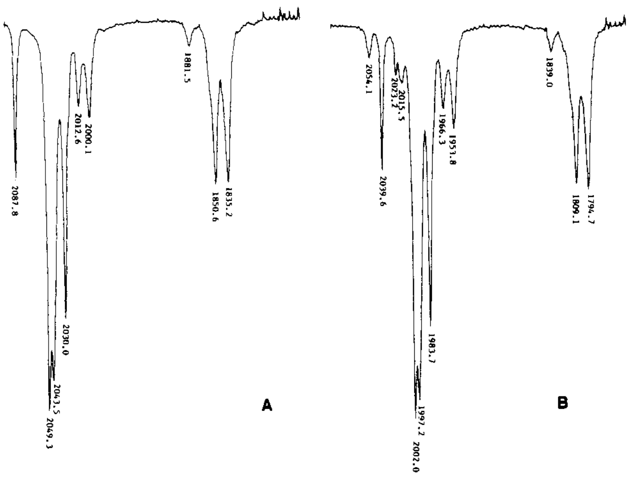

Figure 1. Infrared spectra in hexane in the ν_{CO} region: A, $Co_4(^{12}CO)_{11}P(OMe)_3$; B, $Co_4(^{13}CO)_{11}P(OMe)_3$. The peaks at 2054.1, 2023.2, and 2015.5 cm^{-1} are due to incompletely labeled cluster species.

monoxide dissociation from the intact dimer (Scheme I), as opposed to Scheme II, which entails metal–metal bond homolysis.

Scheme I

$$M_2(CO)_{10} \rightleftharpoons [M_2(CO)_9] + CO$$

$$[M_2(CO)_9] + L \rightarrow M_2(CO)_9L$$

Scheme II

$$M_2(CO)_{10} \rightleftharpoons 2[M(CO)_5]$$

$$[M(CO)_5] + L \rightarrow [M(CO)_4L] + CO$$

$$2[M(CO)_4L] \rightarrow M_2(CO)_8L_2$$

$$[M(CO)_5] + [M(CO)_4L] \rightarrow M_2(CO)_9L$$

We have for several years had a program under way in our laboratories aimed at defining mechanistic pathways for ligand substitutional processes involving tetranuclear metal carbonyl clusters.[4] Herein we report on an FT infrared spectroscopic investigation of the reaction of $Co_4(^{12}CO)_{12}/Co_4(^{13}CO)_{12}$ with an incoming phosphorus donor ligand to afford $Co_4(CO)_{11}L$ derivatives directed at assessing the importance of cluster fragmentation during ligand substitution. These studies are to be contrasted with the rapid carbonyl distribution process observed for a mixture of $Rh_4(^{12}CO)_{12}/Rh_4(^{13}CO)_{12}$ (<30 s at 25 °C in CH_2Cl_2), where cluster fragmentation or agglomeration is suggested.[5]

Experimental Section

All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line under an atmosphere of dry nitrogen. $Co_4(CO)_{12}$ and trimethyl phosphite were obtained from Strem Chemicals, Inc., and were used without further purification. Solvents were dried by refluxing over sodium benzophenone ketyl under nitrogen. Carbon monoxide (93 atom % ^{13}CO) was obtained from Prochem, BOC Ltd., London.

Synthesis of $Co_4(^{12}CO)_{11}L$ and $Co_4(^{13}CO)_{11}L$. The $Co_4(CO)_{11}L$ (L = $P(OMe)_3$ and PPh_3) derivatives were prepared from $Co_4(CO)_{12}$ and the corresponding phosphorus ligands as we have previously described.[4f] $Co_4(^{13}CO)_{12}$, employed in an analogous synthesis of the ^{13}CO-enriched derivatives, was synthesized from $Co_4(CO)_{12}$ (0.108 mol) in a 100-mL flask containing 50 mL of hexane and under a ^{13}CO atmosphere. The flask was heated at 45 °C in a constant-temperature bath for 3 days, being intermittently evacuated and backfilled with ^{13}CO. The samples were demonstrated to be pure by their infrared spectra. Figure 1 illustrates the infrared spectra in the ν_{CO} stretching region in hexane solution.

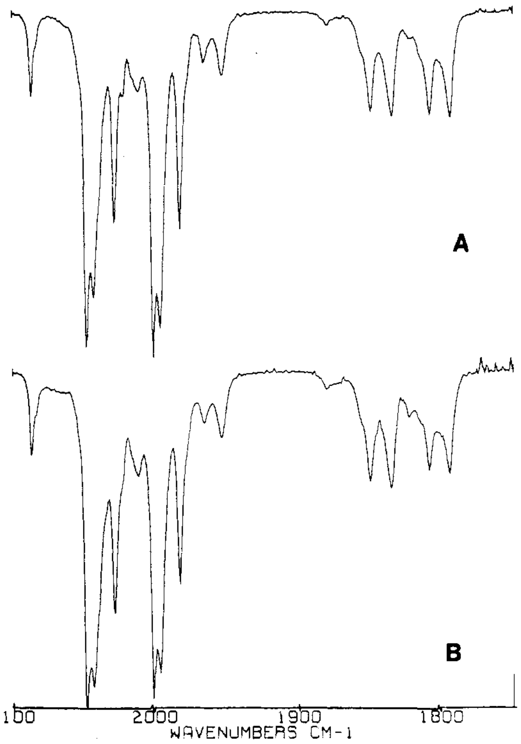

Figure 2. Infrared spectra in hexane in the ν_{CO} region of $Co_4(^{12}CO)_{11}P(OMe)_3/Co_4(^{13}CO)_{11}P(OMe)_3$ mixture: A, control experiment; B, reaction product from $Co_4(^{12}CO)_{12}/Co_4(^{13}CO)_{12}$ and trimethyl phosphite.

Reaction of $Co_4(^{12}CO)_{12}/Co_4(^{13}CO)_{12}$ with L. A hexane solution of ^{13}C-enriched $Co_4(CO)_{12}$ (0.0401 g in 15 mL) was added to a solution of $Co_4(^{12}CO)_{12}$ (0.0417 g in 10 mL) while both were maintained at 0 °C by means of an ice bath in order to minimize intermolecular ligand exchange. Following addition of 17 μL of trimethyl phosphite in 5 mL of hexane, the reaction mixture was stirred at 0 °C for 30 min. During this time period, complete formation of the $Co_4(CO)_{11}P(OMe)_3$ product was noted by infrared spectroscopy in the ν_{CO} region. Solvent was evaporated at reduced pressure, and the complex was purified by column chromatography on a silica gel column. Eluting the sample with hexane removed trace quantities of unreacted $Co_4(CO)_{12}$, and the desired product was obtained by eluting with a 10% (v/v) toluene/hexane solvent mixture. This entire purification and isolation process, i.e. solvent removal and chromatography, required ca. 3 h at ambient temperature. A 0.0346-g (36%) yield of purified product was obtained. Figure 2 contains an infrared spectrum in hexane of the $Co_4(CO)_{11}P(OMe)_3$ product.

Control Experiment between $Co_4(^{12}CO)_{11}P(OMe)_3/Co_4(^{13}CO)_{11}P(OMe)_3$. A 1:1 mixture of $Co_4(^{12}CO)_{11}P(OMe)_3/Co_4(^{13}CO)_{11}P(OMe)_3$ was allowed to stand in hexane solution at 0 °C for about 30 min and then at ambient temperature for 3 h, the exact conditions required for sample workup in the $Co_4(^{12}CO)_{12}/Co_4(^{13}CO)_{12}$ reaction with $P(OMe)_3$. Intermolecular scrambling of carbon monoxide ligands between the two metal cluster centers was monitored by infrared spectroscopy.

Infrared Spectral Measurements. Infrared spectra were determined on an IBM Instruments, Inc., Fourier transform IR/85 spectrometer in a 0.1-mm NaCl sealed cell. The spectra were measured at ambient temperature over the spectral range of 4000–400 cm^{-1} at a resolution of 2.0 cm^{-1} and a wavelength precision of ±0.01 cm^{-1} by employing a DTGS detector. The reported spectra represent an averaging of 100 scans requiring ca. 5 min acquistion time.

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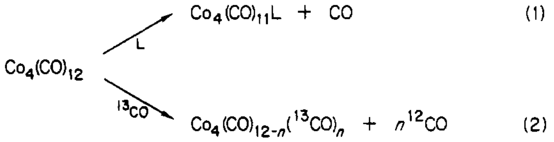
(4) (a) Darensbourg, D. J.; Incorvia, M. J. *J. Organomet. Chem.* **1979**, *171*, 89. (b) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, *19*, 2585. (c) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1981**, *20*, 1911. (d) Darensbourg, D. J.; Baldwin-Zuschke, B. J. *Inorg. Chem.* **1981**, *20*, 3846. (e) Darensbourg, D. J.; Baldwin-Zuschke, B. J. *J. Am. Chem. Soc.* **1982**, *104*, 3906. (f) Darensbourg, D. J.; Peterson, B. S.; Schmidt, R. E., Jr. *Organometallics* **1982**, *1*, 306.

(5) Heaton, B. T.; Longhetti, L.; Mingos, D. M. P.; Briant, C. E.; Minshall, P. C.; Theobald, B. R. C.; Garlaschelli, L.; Sartorelli, U. *J. Organomet. Chem.* **1981**, *213*, 333.

Results and Discussion

The reaction of dodecacarbonyltetracobalt with phosphorus ligands leading to the replacement of one carbonyl group, i.e. formation of $Co_4(CO)_{11}L$ derivatives, is known to readily occur at ambient temperature.[4a,6,7] In this instance the ligand substitution pathway is not governed via a CO-dissociative route as evidenced by quantitative intermolecular ^{13}CO-exchange studies involving the $Co_4(CO)_{12}$ species.[4f] For example, whereas reaction 1 takes place over a few minutes at room



$$Co_4(CO)_{12} \xrightarrow{L} Co_4(CO)_{11}L + CO \quad (1)$$

$$Co_4(CO)_{12} \xrightarrow{^{13}CO} Co_4(CO)_{12-n}(^{13}CO)_n + n\,^{12}CO \quad (2)$$

temperature, ^{13}CO incorporation into $Co_4(CO)_{12}$ (eq 2) occurs with a first-order rate constant of $3.27 \times 10^{-4}\ s^{-1}$ ($t_{1/2}$ = 35 min) at 40 °C. However, at higher CO pressures $Co_4(CO)_{12}$ undergoes fragmentation to dicobalt octacarbonyl, a process proposed to involve one to two additional CO ligands in the transition state.[8] Kinetics parameters for the related substituted-cluster fragmentation process, i.e. $Co_4(CO)_8[PPh_3]_4$ proceeding to $Co_2(CO)_6[PPh_3]_2$, have been reported by Huq and Poe.[9] This process was shown to proceed by three pathways involving phosphine or carbon monoxide dissociation and by spontaneous disruption of the tetranuclear species without a change in ligand composition.

It has been demonstrated by several research groups that the instantaneous reaction of $Co_4(CO)_{12}$ with a variety of phosphorus ligands to afford $Co_4(CO)_{11}L$ occurs in the absence of light, in the presence of radical traps, and in hydrocarbon solutions where particular care was taken to avoid trace oxygen impurities. We felt that it was of further importance to clearly establish whether or not cluster fragmentation is a key mechanistic feature of this rapid, kinetically difficult to access, ligand substitution process. The most definitive criterion for cluster disruption during ligand substitution is a metal isotope double-labeling experiment such as that described by Stolzenberg and Muetterties for the dimeric rhenium species.[2] Alternatively, if the proper control experiments are carried out, a ligand isotope double-labeling experiment will yield precisely the same mechanistic information. This is an important point since for many metals only one stable isotope is available; in addition, when multiple metal isotopes are accessible, the cost is often prohibitive.

The infrared spectra of $Co_4(^{12}CO)_{11}P(OMe)_3$ and $Co_4(^{13}CO)_{11}P(OMe)_3$, prepared from independent syntheses involving $Co_4(^{12}CO)_{12}$ or $Co_4(^{13}CO)_{12}$ and excess $P(OMe)_3$, respectively, in the ν_{CO} region are depicted in Figure 1. Figure 2 contains comparative infrared spectra of an equimolar mixture of $Co_4(^{12}CO)_{11}P(OMe)_3/Co_4(^{13}CO)_{11}P(OMe)_3$ obtained from (a) the control experiment, where the two independently synthesized samples were allowed to stand in solution for the time period required for the second method, and (b) the reaction of equal quantities of $Co_4(^{12}CO)_{12}$ and $Co_4(^{13}CO)_{12}$ with excess $P(OMe)_3$ followed by chromatographic purification. Qualitatively, it is apparent that these mixtures are quite similar. Quantitatively, this is seen to be the case as well, as revealed by careful examination of the difference spectra. As seen in the slight shoulder noted on the highest frequency ν_{CO} peak of the all-^{12}CO species in both spectra shown in Figure 2, there has been a small amount of carbonyl ligand scrambling between the two Co_4 units. This is to be expected on the basis of the known slow rate of intermolecular CO exchange that occurs in $Co_4(CO)_{11}P(OMe)_3$ at ambient temperature (eq 3).[4f]

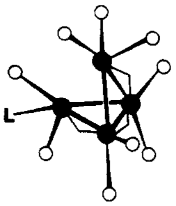


Figure 3. $Co_4(CO)_{12}L$ intermediate.

$$Co_4(CO)_{11}P(OMe)_3 + n\,^{13}CO \rightleftharpoons Co_4(CO)_{11-n}(^{13}CO)_nP(OMe)_3 + n\,^{12}CO \quad (3)$$

Observations identical with those reported for the $P(OMe)_3$ derivative were noted for the substitution reaction of $Co_4(CO)_{12}$ with triphenylphosphine. That is, an infrared spectrum taken within 5 min after mixing of the solution from the reaction of $Co_4(^{12}CO)_{12}/Co_4(^{13}CO)_{12}$ and 1 equiv of PPh_3 in hexane displayed essentially no CO scrambling among the two distinct Co_4 moieties. However, due to more facile intermolecular ligand exchange in this system, i.e., a statistical distribution of $^{12}CO/^{13}CO$ being seen in the Co_4 cluster within ca. 1 h (eq 4), we were unable to further purify the $Co_4(CO)_{11}PPh_3$ product for a more detailed spectral analysis.

$$Co_4(^{12}CO)_{11}PPh_3 + Co_4(^{13}CO)_{11}PPh_3 \rightleftharpoons 2Co(^{12}CO)_{11-n}(^{13}CO)_nPPh_3 \quad (4)$$

Conclusions

The ligand isotope double-labeling studies presented herein have conclusively shown that during the very rapid ligand substitution reactions of $Co_4(CO)_{12}$ with phosphorus ligands to afford $Co_4(CO)_{11}L$ derivatives *no* cluster fragmentation occurs. This result was demonstrated for two quite different incoming phosphorus ligands, $P(OMe)_3$ and PPh_3. Presumably the pathway for this substitution reaction is an interchange or associative process and may involve the intermediacy of species such as that shown in Figure 3.

Acknowledgment. The financial support of the Robert A. Welch Foundation is greatly appreciated.

Registry No. $Co_4(CO)_{12}$, 17786-31-1; $P(OMe)_3$, 121-45-9; triphenylphosphine, 603-35-0.

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(6) Cetini, G.; Gambino, O.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chem.* **1968**, *7*, 609.

(7) Labrou, D.; Poilblanc, R. *Inorg. Chim. Acta* **1972**, *6*, 387.

(8) Bor, G.; Dietler, H. K.; Pino, P.; Poe, A. J. *J. Organomet. Chem.* **1978**, *154*, 301.

(9) Huq, R.; Poe, A. *J. Organomet. Chem.* **1982**, *226*, 277.

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Direct Identification of Cu-Mo-S Clusters by ^{95}Mo NMR Spectroscopy

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The chemistry of Cu-Mo-S compounds has been of interest for over a century.[1] Recent studies of Cu-Mo-S clusters have been stimulated by general interest in $[MoS_4]^{2-}$ as a ligand for other metals[2] and by the implication that species derived from copper-thiomolybdate interactions may be responsible

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