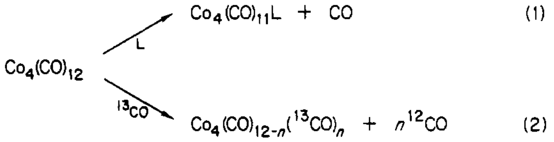
Results and Discussion

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 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]

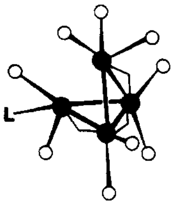


Figure 3. $Co_4(CO)_{12}L$ intermediate.

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

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

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Received May 31, 1984

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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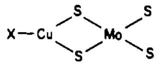
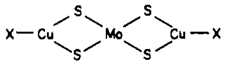
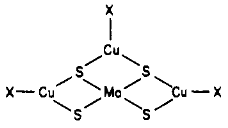
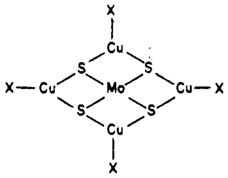
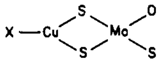
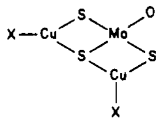
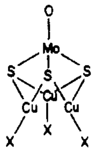
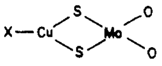
Table I. ^{95}Mo NMR Data for Cu-Mo-S Clusters

compd	δ(Mo)^d	solid-state struct	ref
$[Pr_4N]_2[(PhSCu)MoS_4]$	1903 (50)^a	 1	11
$[Pr_4N]_2[(NCCu)MoS_4]$	1864 (30)^a		9, 11, 13
$[Pr_4N]_2[(PhSCu)_2MoS_4]$	1700 (250)^a	 2	11
$[Ph_4P]_2[(BrCu)_2MoS_4]$	1632 (600)^b		this work
$[Pr_4N]_2[(ClCu)_2MoS_4]$	1618 (250)^b		this work
$[Pr_4N]_2[(NCCu)_2MoS_4]$	1616 (250)^a		13
$[Pr_4N]_2[(ICu)_3MoS_4]$	1282 (170)^a	 3	this work
$[Ph_4P]_2[(BrCu)_3MoS_4]$	1272 (250)^b		this work
$[Ph_4P]_2[(ClCu)_3MoS_4]$	1234 (200)^b		this work
$[Ph_4P]_2[(BrCu)_4MoS_4]$	910 (1400)^b	 4	this work
$[Ph_4P]_2[(ClCu)_4MoS_4]$	886 (1400)^b		this work
$[Et_4N]_2[(NCCu)MoOS_3]$	1198 (26)^a	 5	13
$[Ph_4P]_2[(PhSCu)_2MoOS_3]$	892 (100)^b	 6	this work
$[Ph_4P]_2[(ClCu)_3MoOS_3]$	474 (20)^c	 7	this work
$[Ph_4P]_2[(PhSCu)MoO_2S_2]$	611 (70)^b	 8	this work

^{a} In CH_3CN. ^{b} In DMF. ^{c} In CH_2Cl_2. ^{d} Relative to external 2 M Na_2MoO_4 in D_2O, effective pH 11; line widths in Hz in parentheses.

for the biological antagonism between copper and molybdenum that leads to copper deficiency in ruminant animals.[3,4]

Previous research has identified several different Cu-Mo-S clusters derived from reactions of $[MoS_4]^{2-}$ with copper compounds.[5-15] Such reaction products include anionic complexes of the general type $[(XCu)_nMoS_4]^{2-}$ ($n = 1$-4; X = CN, Cl, Br, I, SR)[8-11,13-15] and uncharged complexes such as $(PR_3)_3Cu_2MoS_4$[6,7] and $[Cu_3MoS_3](PPh_3)_3S$.[5,12] The solid-state structures of complexes of each type have been established by single-crystal X-ray structure determination. Raman and infrared spectroscopy have also been used to obtain information about the symmetry at the molybdenum atom in solid samples.[11,16] It has been more difficult, however, to establish the integrity and structures of Cu-Mo-S clusters in solution. Herein we show that anionic Cu-Mo-S complexes of the general formula $[(XCu)_nMoS_4]^{2-}$, with $n = 1$-4, can readily be distinguished from one another by ^{95}Mo NMR spectroscopy. These results substantially extend the previous reports of the ^{95}Mo NMR spectra of $[(XCu)MoS_4]^{2-}$ and $[(XCu)_2MoS_4]^{2-}$ ions (X = CN, SPh).[9,11,13]

Table I lists the ^{95}Mo NMR data for several diamagnetic $[(XCu)_nMoS_4]^{2-}$ complexes. Preparative details for the com-

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pounds[8-11,13-15,17] and the experimental procedures for obtaining the ^{95}Mo NMR spectra[18] have been described.

It has been previously established that $[(XCu)MoS_4]^{2-}$ complexes adopt structure **1** (see Table I) in the solid state.[8,9,11,13] In solution, such complexes give relatively sharp ^{95}Mo NMR signals near 1900 ppm with line widths of ~50 Hz.[9,11,13] $[(XCu)_2MoS_4]^{2-}$ complexes (structure **2**)[11,13] have ^{95}Mo NMR resonances in the 1600–1700 ppm range with line widths that are 200 Hz or greater.[11,13]

Here, we present the first ^{95}Mo NMR data for $[(XCu)_3MoS_4]^{2-}$ and $[(XCu)_4MoS_4]^{2-}$ clusters. The former adopt structure **3**[14,15] in the solid state and in solution show a chemical shift range of 1230–1280 ppm with line widths of ~200 Hz. The $[(XCu)_4MoS_4]^{2-}$ ions (**4**)[10] have ^{95}Mo NMR resonances near 900 ppm, and the lines are substantially broader (~1400 Hz) than any of the other Cu–Mo–S species.

The data in the table show that the molybdenum chemical shift decreases monotonically as additional CuX units are bound to the $[MoS_4]^{2-}$ core of the clusters. Thus, the molybdenum chemical shift of a $[(XCu)_nMoS_4]^{2-}$ cluster provides a direct measure of the number of CuX units in the cluster. Each successive addition of a CuX moiety to the $[MoS_4]^{2-}$ core results in a decrease in the chemical shift of the molybdenum nucleus by 200–400 ppm. smaller variations in the molybdenum chemical shift result from changing the nature of the X ligand attached to the Cu atom. The general variation of the shielding of the molybdenum nucleus with the X substituent on Cu seems to be SPh < I < Br < Cl ~ CN, although the data do not permit direct comparison of the effects of I and SPh.

The table also presents ^{95}Mo data for some Cu–Mo–S clusters derived from the $[MoOS_3]^{2-}$ and $[MoO_2S_2]^{2-}$ anions. Direct comparison of the ^{95}Mo chemical shifts of $[(PhSCu)MoS_4]^{2-}$ and $[(PhSCu)MoO_2S_2]^{2-}$ shows that the molybdenum nucleus is ~1300 ppm more shielded in $[(PhSCu)MoO_2S_2]^{2-}$. This shielding difference is very similar to that in the parent anions where $[MoO_2S_2]^{2-}$ is ~1150 ppm more shielded than $[MoS_4]^{2-}$.[13,19] The pair $[(ClCu)_3MoOS_3]^{2-}$ and $[(ClCu)_3MoS_4]^{2-}$ exhibits increased shielding of ~760 ppm for the oxo-containing complex. The line widths of the latter pair are also dramatically different, presumably reflecting the different structures (**7**[20] and **3**,[14,21] respectively) adopted by the two ions. Similar shielding differences occur for the pair $[(PhSCu)_2MoOS_3]^{2-}$ and $[(PhSCu)_2MoS_4]^{2-}$ (808 ppm) and for the pair $[(NCCu)MoOS_3]^{2-}$ and $[(NCCu)MoS_4]^{2-}$ (665 ppm[13]).

The ^{95}Mo NMR resonances of the $[(XCu)_nMoS_4]^{2-}$ anions are all much broader than those for $[MoS_4]^{2-}$. The presence of quadrupolar copper nuclei and the increased molecular mass of Cu–Mo–S clusters can both contribute to line broadening. However, the data in the table show that there is no simple correlation between the number of copper atoms in the complexes (n) and the line width. The complexes with $n = 2$ and 3 have similar line widths (170–600 Hz) that are much larger than complexes with $n = 1$ and much smaller than complexes with $n = 4$.

In summary, this work clearly demonstrates that ^{95}Mo NMR chemical shifts can be used to identify various $[(XCu)_nMoS_4]^{2-}$ ions in solution and hence is a simple direct probe for determining the CuX:MoS$_4$ ratio for unknown complexes in solution. This research also provides good evidence that the Cu–Mo–S clusters do not dissociate in solution because each complex gives only one ^{95}Mo resonance.

Related Cu(I) complexes are formed by $[MoO_yS_{4-y}]$ (y = 0–2) anions.[2] The nature of the S–Mo–O core (i.e., the value of y) for such species is readily established from their vibrational and electronic spectra.[11,16] The present work has established that the ^{95}Mo chemical shifts of $[(XCu)_nMoO_yS_{4-y}]^{2-}$ species clearly identify the value of n for a given value of y. Therefore, on the basis of the ^{95}Mo NMR spectrum and the vibrational and/or electronic spectra, it is possible to determine both y and n for such complexes. The ability to distinguish and identify Cu–Mo–S clusters in solution should be of considerable value in further developing the chemistry of such systems. Also, there now exists the exciting prospect of using a combination of ^{95}Mo NMR and other spectroscopies to characterize the Cu–Mo–S species that may be present when molybdenum induces copper deficiency in ruminants.[3,4] Such studies could be further enhanced by using ^{95}Mo-enriched samples to increase the sensitivity of the ^{95}Mo NMR measurements.

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Registry No. **2**·2PPh$_4$ (X = Br), 92787-47-8; **2**·2PPh$_4$ (X = Cl), 92787-49-0; **3**·2PPh$_4$ (X = I), 92787-51-4; **3**·2PPh$_4$ (X = Br), 92787-53-6; **3**·2PPh$_4$ (X = I), 85752-65-4; **4**·2PPh$_4$ (X = Br), 88433-65-2; **4**·2PPh$_4$ (X = Cl), 88433-62-9; **6**·PPh$_4$ (X = SPh), 92787-55-8; **7**·2PPh$_4$ (X = Cl), 86430-80-0; **8**·2PPh$_4$ (X = Cl), 92787-57-0; ^{95}Mo, 14392-17-7.

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A Dimeric Platinum(III) System Containing a Long Metal–Metal Bond. Crystal Structure of $K_4[Pt_2(P_2O_5H_2)_4CH_3I]\cdot 2H_2O$

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Earlier we found that binuclear platinum(III) species can be obtained readily by oxidative addition of halogens or methyl iodide to $[Pt_2(pop)_4]^{4-}$ (pop = $P_2O_5H_2^{2-}$).[2] Though fragmentation of alkyl halides in two-center oxidative additions has been observed before,[3] relatively few structural studies on the adducts have been performed. Here we wish to report the structure of $[Pt_2(pop)_4CH_3I]^{4-}$, which was obtained through the reaction of $[Pt_2(pop)_4]^{4-}$ with CH$_3$I; the structural results

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