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Coupling Reactions of the Tetranuclear Rectangular Clusters $Mo_4Cl_8(PR_3)_4$. Phosphine Ligand Abstraction and Formation of the Condensation Products $[Mo_4Cl_8(PR_3)_2]_x$[1]

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Reaction of the tetrameric clusters $Mo_4Cl_8(PR_3)_4$ ($PR_3 = PEt_3$, $P(n\text{-}Pr)_3$, $P(n\text{-}Bu)_3$, and PMe_2Ph) with $Mo(CO)_4Cl_2$, or more conveniently with $Mo(CO)_6$, in refluxing chlorobenzene leads to phosphine abstraction and formation of the condensation products $[Mo_4Cl_8(PR_3)_2]_x$. Evidence obtained from reactivity and spectroscopic data indicates that these condensation products all have the same basic structure and retain the rectangular cluster units derived from $Mo_4Cl_8(PR_3)_4$ as essential components. Extended Mo–Mo bonding between the coupled tetrameric units is concluded to be unlikely. Because the compounds are crystalline and exhibit significant solubility in noncoordinating solvents, their formulation as dimers of tetramers, $[Mo_4Cl_8(PR_3)_2]_2$, is preferred over the alternative formulation as polymers, $[Mo_4Cl_8(PR_3)_2]_\infty$.

Introduction

Organic synthetic methods have long made it possible to form, at will, large molecules containing primarily carbon atom frameworks from small molecular building blocks, but this type of systematic chemistry has not been generally available in the synthesis of transition-metal compounds. The interest in catalysis and the modeling of adsorption sites on metal surfaces with metal clusters[2] has encouraged the development of more rational approaches to cluster synthesis, and a number of very large clusters have been formed.[3,4] Compounds containing metal–metal multiple bonds are logical precursors for the synthesis of large cluster species because of the potential for addition of atoms or molecules across the multiple bond. The addition of transition-metal atoms or molecular fragments to small cluster compounds to expand the size of the cluster has been successful in some cases;[5-7] however, stepwise formation of larger clusters from smaller precursors is poorly understood and deserves further research.

Since the initial discovery of tetranuclear rectangular clusters of molybdenum,[7] efficient methods for their synthesis by addition of the quadruply bonded dimers have been devised,[8] and related clusters $W_4Cl_8L_4$[9] and $Mo_2W_2Cl_4L_4$[10] have been prepared. During a study of potential reactions for addition of metal atoms to these electron-rich clusters we discovered reactions leading to abstraction of ligands from $Mo_4Cl_8(PR_3)_4$ and the subsequent condensation of fragments to form the compounds $[Mo_4Cl_8(PR_3)_2]_x$. The work reported here concerns the synthesis, reactions, and spectroscopic characterization of these interesting condensation products.

Experimental Section

Materials. The air-sensitive nature of the compounds that were prepared required the use of Schlenk techniques and dry solvents. Tetrahydrofuran was dried by stirring with sodium and benzophenone. Chlorobenzene was refluxed over CaH_2, and then it was distilled and stored under nitrogen. Acetonitrile and dichloromethane were dried with CaH_2 and then vacuum distilled onto outgassed molecular sieves for storage. Other solvents and phosphines were used as received. $AlCl_3$ was purified by sublimation through a sintered-glass frit. The $Mo[CO]_6$ was dried by storing in a desiccator containing $CaSO_4$ for several weeks before use. The starting material for the preparation of the tetranuclear clusters, $Mo_2(OAc)_4$, was synthesized according to literature procedure.[11] $Mo(CO)_4Cl_2$ was synthesized from $Mo(CO)_6$ and Cl_2 at -60 °C.[12] Chlorine was distilled from the cylinder into a trap where it was outgassed before being distilled onto the molybdenum hexacarbonyl. After gas evolution ceased, excess Cl_2 was distilled away and the product was allowed to warm to room temperature. The $Mo(CO)_4Cl_2$ of highest purity was obtained from preparations using dried $Mo(CO)_6$ and Cl_2 distilled from a fresh cylinder.

Samples to be analyzed were decomposed in an aqueous solution of KOH and H_2O_2. In those instances where the sample resisted decomposition by this method, the sample was mixed with powdered NaOH and heated in a nickel crucible until decomposed. Molybdenum analyses were accomplished by precipitation of $MoO_2(C_9H_6ON)_2$.[13] The chloride content was obtained by potentiometric titration of the solution with standardized $AgNO_3$. Carbon, nitrogen, hydrogen, and phosphorus analyses were performed by the Ames Laboratory Analytical Services.

Physical Measurements. A Beckman IR4250 spectrometer was used to measure the infrared spectra. The solution UV–visible spectra were recorded with a Cary 14 spectrometer. A Beckman DU spectrophotometer was used for measuring the reflectance spectra. The reference compound for the reflectance spectra was $BaSO_4$.

X-ray photoelectron spectra were obtained by grinding the sample in a drybox, spreading the powder on a strip of Ag–Cd alloy, and then transferring the strip directly into the attached AEI ES200B spectrometer. Al Kα radiation (1486.6 eV) was used to irradiate the sample. Nonmonochromatic radiation was used with a 4 × 4 slit setting. The electrostatic charge on the sample was kept constant by using an electron floodgun. Binding energies of resolved peaks were referenced to the C 1s signal, which was taken to be 285.0 eV. Data reduction and spectrum resolution computations were accomplished with APES,[14] a computer program developed in this laboratory to resolve XPS spectra, with use of a previously described procedure.[15]

Synthesis. $Mo_4Cl_8[PR_3]_4$. The tetrameric clusters were synthesized from $Mo_2(O_2CCH_3)_4$ with use of $AlCl_3$ in THF and the appropriate phosphine. The previously published method,[8] using a $Mo_2(OAc)_4$:$AlCl_3$:PR_3 mole ratio of 2:4:4, gave approximately a 50% yield, but if the amount of $AlCl_3$ used was doubled, yields of close to 80% were achieved,[16] according to the equation

$$2Mo_2(OAc)_4 + 8AlCl_3 + 4PR_3 \rightarrow Mo_4Cl_8(PR_3)_4 + 8AlCl_2(OAc)$$

In the reactions using PEt_3, $P(n\text{-}Pr)_3$, or $P(n\text{-}Bu)_3$, any of the dimer $Mo_2Cl_8(PR_3)_4$ formed as a secondary product is efficiently removed by washing the product with methanol. However, with PMe_2Ph some $Mo_2Cl_4(PMe_2Ph)_2$ cocrystallizes with the tetranuclear compound in the synthesis of $Mo_4Cl_8(PMe_2Ph)_4$. A visible spectrum of the product indicated that about 2% of the dinuclear compound was present. Dissolving the tetrameric cluster in CH_2Cl_2 and reprecipitating it by adding hexane

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(2) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(3) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225.

(4) Schmid, G.; Pfeil, R.; Boese, R.; Bandermann, F.; Meyer, S.; Calis, G. H. M.; van der Velder, J. W. A. *Chem. Ber.* **1981**, *114*, 3634.

(5) Chisholm, M. H.; Errington, R. J.; Folting, K.; Huffmann, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2025.

(6) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, *155*, 162.

(7) McGinnis, R. N.; Ryan, T. R.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 7900.

(8) Ryan, T. R.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 2072.

(9) McCarley, R. E.; Ryan, T. R.; Torardi, C. C. *ACS Symp. Ser.* **1981**, *No. 155*, 41-60.

(10) Carlin, R. T.; McCarley, R. E., to be submitted for publication.

(11) McCarley, R. E.; Templeton, J. L.; Colburn, T. J.; Katovic, V.; Hoxmeier, R. J. *Adv. Chem. Ser.* **1976**, *No. 150*, 319.

(12) Colton, R.; Tomkins, J. B. *Aust. J. Chem.* **1966**, *19*, 1143.

(13) Elwell, W. T.; Wood, D. F. "Analytical Chemistry of Molybdenum and Tungsten"; Pergamon Press: New York, 1971; pg 41, 42.

(14) Luly, M. H. "APES, A Fortran Program to Analyze Photoelectron Spectra", USDOE Report IS-4694; Ames Laboratory: Ames, IA, 1979.

(15) Michel, J. B.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 1864.

(16) Beers, W. W.; McCarley, R. E. *Inorg. Chem.*, following paper in this issue.

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was necessary to remove the blue $Mo_2Cl_4[PMe_2Ph)_4$. The yield of pure material was about 75%. Anal. Calcd for $Mo_4Cl_8(PMe_2Ph)_4$: Mo, 31.46; Cl, 23.25; C, 31.50; H, 3.64. Found: Mo, 31.19; Cl, 23.03; C, 31.10; H, 3.77.

$[Mo_4Cl_8(PR_3)_2]_x$. The initial synthesis of $[Mo_4Cl_8(PEt_3)_2]_x$ resulted from the reaction between $Mo_4Cl_8(PEt_3)_4$ and $Mo(CO)_4Cl_2$ in a 1:1 mole ratio in refluxing chlorobenzene. After 24 h, filtration of the mixture separated a yellow-brown solid from the brown solution. Vacuum distilling the solvent from the filtrate left dark-brown and yellow solids, which were separated by extracting with acetonitrile. The infrared spectrum of the yellow solid indicated that it was $Mo_4Cl_8(PEt_3)_4$. Bands arising from CO ligands were prominent in the brown substance. Further characterization of the latter compound was not undertaken, but it was presumed to be $Mo(CO)_3Cl_2(PEt_3)_2$.[12]

The primary, insoluble product from the above reaction was purified by extended extraction with chlorobenzene. An analysis of the insoluble product indicated a composition close to $[Mo_4Cl_8(PEt_3)_2]_x$. Anal. Calcd: Mo, 42.47; Cl, 31.38; C, 15.95; H, 3.35. Found: Mo, 41.50; Cl, 30.14; C, 16.23; H, 3.37. It was evident that PEt_3 had been abstracted by $Mo(CO)_4Cl_2$ to promote condensation of the tetrameric compound. This suggested that other more convenient phosphine acceptors could be utilized for the same purpose. Subsequently, the reaction of $Mo(CO)_6$ was found to be effective. In a typical reaction 1.0 g (0.88 mmol) of $Mo_4Cl_8(PEt_3)_4$ and 0.23 g (0.88 mmol) of $Mo(CO)_6$ were refluxed in 20 mL of chlorobenzene for 2 h. After filtration and washing with chlorobenzene, the yellow $[Mo_4Cl_8(PEt_3)_2]_x$ was isolated in 78% yield. This compound is relatively insensitive to air but should be stored under nitrogen.

The syntheses of $P(n\text{-}Pr)_3$ and $PPhMe_2$ derivatives were performed by exactly analogous procedures starting with the respective tetramers $Mo_4Cl_8(PR_3)_4$ and $Mo(CO)_6$ in 1:1 mole ratios. However, analytical data and infrared spectra both indicated retention of chlorobenzene in the crystalline products, which was not removed under vacuum. Anal. Calcd for $Mo_8Cl_{16}[P(C_3H_7)_3]_4\cdot 1.24C_6H_5Cl$: Mo, 36.28; inorganic Cl, 26.82; C, 24.67; H, 4.30. Found: Mo, 35.82; inorganic Cl, 26.10; C, 24.34; H, 4.40. Calcd for $Mo_8Cl_{16}[P(CH_3)_2(C_6H_5)]_4\cdot 1.67C_6H_5Cl$: Mo, 36.98; inorganic Cl, 27.33; C, 24.32; H, 2.54; P, 5.97. Found: Mo, 37.30; inorganic Cl, 27.02; C, 24.54; H, 2.94; P, 6.36.

Results and Discussion

Synthesis. The initially observed reaction between $Mo_4Cl_8(PEt_3)_4$ and $Mo(CO)_4Cl_2$ led to abstraction of phosphine ligand from the tetramer with deposition of a sparingly soluble yellow-brown, crystalline solid from the refluxing chlorobenzene solution. Analytical data for this product indicated the simplest formulation $Mo_2Cl_4(PEt_3)$. Undoubtedly this compound is a condensation product resulting from loss of phosphine and interlinking of tetrameric cluster units through bridging chlorine atoms, as represented in eq 1. Assuming that the coordination number of

$$xMo_4Cl_8(PEt_3)_4 + xMo(CO)_4Cl_2 = [Mo_4Cl_8(PEt_3)_2]_x + xMo(CO)_3Cl_2(PEt_3)_2 + xCO \quad (1)$$

the Mo atoms remains unchanged in this process, the most likely structural consequence is the replacement of each abstracted phosphine by a Cl atom bridging from a second cluster unit to produce either the polymer $[Mo_4Cl_6Cl_{4/2}(PEt_3)_2]_\infty$ or the discrete molecular compound $Mo_8Cl_{16}(PEt_3)_4$. This result can be viewed as a continuation of the condensation process already established in the formation of the tetranuclear rectangular clusters from quadruply bonded dimers,[7-9] as shown in eq 2, where A is a

$$2Mo_2Cl_4(PR_3)_4 + 2A = Mo_4Cl_8(PR_3)_4 + 2A(PR_3)_2 \quad (2)$$

phosphine acceptor. The question regarding the extent to which the rectangular cluster units are preserved upon condensation, as opposed to more delocalized metal–metal bonding between units, is discussed below.

It was subsequently found that $Mo(CO)_6$ functions as a more convenient phosphine acceptor. In refluxing chlorobenzene (131 °C) the reactions follow the stoichiometry given in eq 3. This

$$xMo_4Cl_8(PR_3)_4 + xMo(CO)_6 = [Mo_4Cl_8(PR_3)_2]_x + xMo(CO)_4(PR_3)_2 + 2xCO \quad (3)$$

procedure resulted in deposition of insoluble products from the deep brown solution for the phosphine derivatives with $PR_3 = PEt_3$, $P(n\text{-}Pr)_3$, PMe_2Ph. These compounds each were verified to be crystalline by X-ray powder diffraction. In each case the Cl/Mo and PR_3/Mo ratios were appropriate for the formulation $[Mo_4Cl_8(PR_3)_2]_x$, but infrared spectra and complete analytical data show that chlorobenzene in nonintegral and perhaps variable amount is incorporated in the crystals of the compounds containing $P(n\text{-}Pr)_3$ and PMe_2Ph.

Attempts to adjust conditions during synthesis of these compounds for slower and larger crystal growth have thus far failed. Likewise, attempts to grow crystals by recrystallization and liquid-transport methods have not been successful. Such methods are hindered by the very low solubility in noncoordinating and nonreacting solvents, e.g. chlorobenzene and dichloromethane. An attempt to recrystallize $[Mo_4Cl_8(PEt_3)_2]_x$ from boiling 1,2-dichlorobenzene (180 °C) led to recovery of a dark brown insoluble solid from the brown solution. The infrared spectrum of this solid showed greatly reduced intensities for the bands arising from the PEt_3 ligands and in the region 200–400 cm^{-1} resembled the spectrum of β-$MoCl_2$.[17] An X-ray powder pattern also showed only the broad diffuse lines characteristic of β-$MoCl_2$. It thus appeared that the condensed compounds were unstable at higher temperatures. As shown below, this instability is enhanced in the more soluble $P(n\text{-}Bu)_3$ derivative.

In an effort to derive a more soluble product, the synthesis of $\{Mo_4Cl_8[P(n\text{-}Bu)_3]_2\}_x$ was attempted via several reactions between $Mo_4Cl_8[P(n\text{-}Bu)_3]_4$ and $Mo(CO)_6$ in chlorobenzene under various conditions. Reactions conducted in refluxing solvent afforded a dark brown precipitate and a brown solution. The brown solid proved to contain little phosphine ligand and exhibited an infrared spectrum in the region 200–400 cm^{-1} very close to that of β-$MoCl_2$.[17] Subsequent addition of *n*-hexane to the brown filtrate provided a yellow-brown precipitate that appeared to be a mixture of $Mo_4Cl_8[P(n\text{-}Bu)_3]_4$ and $\{Mo_4Cl_8[P(n\text{-}Bu)_3]_2\}_x$, based on infrared and UV–visible spectra. From these data we conclude that the soluble species $\{Mo_4Cl_8[P(n\text{-}Bu)_3]_2\}_x$ may be formed but at reflux temperature decomposition *via* phosphine redistribution subsequently ensues, as for example in eq 4. A subsequent reaction

$$\{Mo_4Cl_8[P(n\text{-}Bu)_3]_2\}_x = (x/2)Mo_4Cl_8[P(n\text{-}Bu)_3]_4 + 2x(\beta\text{-}MoCl_2) \quad (4)$$

between the tetramer and $Mo(CO)_6$ in 1:1 mole ratio was conducted at ca. 100 °C for 40 min, until the appearance of the first turbidity in the solution. The solution was then cooled and stripped of solvent under vacuum and the residue extracted with hexane. The hexane-insoluble material recovered in 38% yield provided an infrared spectrum in the region 200–400 cm^{-1} that matched closely the spectra of the derivatives $[Mo_4Cl_8(PR_3)_2]_x$ with $PR_3 = PEt_3$, $P(n\text{-}Pr)_3$, and PMe_2Ph. However, because of the phosphine redistribution reaction, efforts to grow crystals of this more soluble derivative have so far been rewarded solely with recovery of crystals of $Mo_4Cl_8[P(n\text{-}Bu)_3]_4$.

Reactions of $[Mo_4Cl_8(PEt_3)_2]_x$ with PEt_3. These reactions were explored to gain insight about the degree of interaction between cluster units, i.e. weak or strong intercluster metal–metal bonding, resulting from the condensation reaction. Indeed, one can visualize coupling of two tetrameric units with extended metal–metal bonding in much the same fashion as the coupling of dimeric units that produces these same rectangular cluster units. However, the evidence presented here indicates that no new metal–metal bonds are formed between the coupled units.

In hot chlorobenzene the condensed compound $[Mo_4Cl_8(PEt_3)_2]_x$ reacts with excess PEt_3 to form deep blue solutions of $Mo_2Cl_4(PEt_3)_4$ with characteristic, intense absorption bands at 588 and 330 nm.[18] This result is in agreement with the earlier observation that the rectangular clusters $Mo_4Cl_8(PR_3)_4$ undergo dissociative addition of phosphine with formation of dimers under the same conditions.[8] If this reaction is conducted with slow addition of PEt_3 to a refluxing chlorobenzene suspension of

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(17) β-$MoCl_2$ used for this spectrum was prepared as described in: Glicksman, H. D.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205.

(18) San Fillipo, J., Jr.; Sniadoch, H. J.; Grayson, R. L. *Inorg. Chem.* **1974**, *13*, 2121.

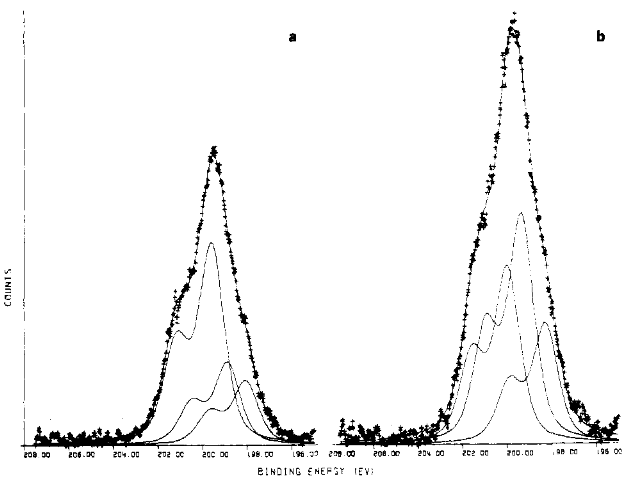

Figure 1. Cl $2p_{3/2,1/2}$ XPS of $[Mo_4Cl_8(PEt_3)_2]_x$: (a) scans 1–20; (b) scans 51–70. The sum of the resolved components is given by the solid line through the data points.

$[Mo_4Cl_8(PEt_3)_2]_x$, up to only a 2:1 mole ratio, the predominant product is $Mo_4Cl_8(PEt_3)_4$, isolated in 60% yield; notably $Mo_2Cl_4(PEt_3)_4$ was not detected in the reaction solution. Even at 25 °C, a reaction between PEt_3 and $[Mo_4Cl_8(PEt_3)_2]_x$ (2:1 mole ratio), conducted in chlorobenzene for 20 h, resulted in formation of the tetramer $Mo_4Cl_8(PEt_3)_4$, isolated in 55% yield.

These reactions suggest that the rectangular cluster units are essentially preserved in the condensed material. While the Mo–Mo bonds on the long edges of the rectangular cluster units are cleaved by reaction with excess phosphine at elevated temperature, this process is extremely slow at 25 °C. By analogy the reaction between PEt_3 and $[Mo_4Cl_8(PEt_3)_2]_x$ at 25 °C would not be expected to readily cleave Mo–Mo bonds if they were present in the bonding between tetrameric units of the condensed material. We conclude that the coupling of tetrameric units most likely occurs solely through Mo–Cl–Mo bridge bonding.

Spectroscopic Characterization. During collection of data for the Cl 2p XPS of $[Mo_4Cl_8(PEt_3)_2]_x$ the compound was observed to undergo decomposition in the X-ray source of the spectrometer. Figure 1 shows the Cl $2p_{3/2,1/2}$ spectra for scans 1–20 and 51–70 of the data collection. Resolution of these spectra into components from only two types of Cl atoms resulted in $2p_{3/2}$ binding energies of 199.5 and 198.4 eV for both data sets, with area ratios of 2.06/1.00 and 2.52/1.00 for the first and last data sets, respectively. However, the resulting fwhm of 1.5 eV for the resolved components was unacceptably large, suggesting a resolution with three types of Cl was more appropriate. The spectra resolved into three components, shown in Figure 1, provided an improved fit and a more acceptable fwhm of 1.3 eV for the resolved components. For scans 1–20, $2p_{3/2}$ binding energies of 199.6, 198.9, and 198.1 eV with area ratios of 2.72/1.51/1.0 were found; the corresponding values for scans 51–70 were 200.0, 199.3, and 198.3 eV in the area ratios 1.32/1.99/1.0. These data clearly demonstrate decomposition of the sample under irradiation in the spectrometer chamber.

The highest Cl $2p_{3/2}$ binding energy of 199.6–200.0 eV is appropriate for doubly bridging Cl atoms located over Mo–Mo-bonded edges of the cluster units. For reference, this type of doubly bridging Cl is found with BE's of 199.6 eV in $Mo_4Cl_8[P(n\text{-}Bu)_3]_4$[8] and 199.8 eV in $(Bu_4N)_2Mo_5Cl_{13}$.[19] The lowest BE of 198.1–198.3 eV corresponds to terminal Cl atoms, e.g. as found in $Mo_4Cl_8[P(n\text{-}Bu)_3]_4$ and $(Bu_4N)_2Mo_5Cl_{13}$ at 198.3 eV.[8,19] Tentatively the intermediate BE of 198.9–199.3 eV has been assigned to Cl atoms bridging nonbonded Mo–Mo separations. Notably this component grows to the greatest relative area as the decomposition progresses, as should be the case if loss of volatile phosphine ligand causes further coupling of cluster units through conversion of terminal to bridging Cl atoms. The fact that this middle component is resolved in data from the early scans indicates that this type of Cl must be present in the $[Mo_4Cl_8(PEt_3)_2]_x$ structure. Beyond this it is difficult to draw conclusions from the relative component peak area ratios because of the rather featureless shape of the spectrum and the progressive decomposition, both of which result in relatively large uncertainty in area ratios.

Table I. Electronic Absorption Band Maxima of $Mo_4Cl_8(PR_3)_4$ and $[Mo_4Cl_8(PR_3)_2]_x$

$Mo_4Cl_8(PEt_3)_4$[a]		$Mo_4Cl_8(PEt_3)_4$ (reflectance)	$Mo_8Cl_{16}(PEt_3)_4$ (reflectance)
λ, nm	ε, $M^{-1}\ cm^{-1}$	λ, nm	λ, nm
245	2×10^4	270	275
308	1.7×10^4	305	400
430	2.2×10^3	420	520
		675	620

$Mo_4Cl_8[P(n\text{-}Bu)_3]_4$[b]		$Mo_8Cl_{16}[P(n\text{-}Bu)_3]_4$[c]	$Mo_8Cl_{16}(PPr_3)_4$[d]
λ, nm	ε, $M^{-1}\ cm^{-1}$	λ, nm	λ, nm
248	2×10^4	282	300
312	2.8×10^4	288	350
435	3.5×10^3	360	420
685	100	420	

$Mo_4Cl_8(PMe_2Ph)_4$[d]		$Mo_8Cl_{16}(PMe_2Ph)_4$[d]	
λ, nm	ε, $M^{-1}\ cm^{-1}$	λ, nm	ε, $M^{-1}\ cm^{-1}$
310	2.2×10^4	304	3×10^4
430	2.4×10^3	420	5×10^3
680	50	550	7×10^2
		620	4×10^2

[a] Solution in THF. [b] Solution in hexane. [c] Solution in cyclohexane. [d] Solution in dichloromethane.

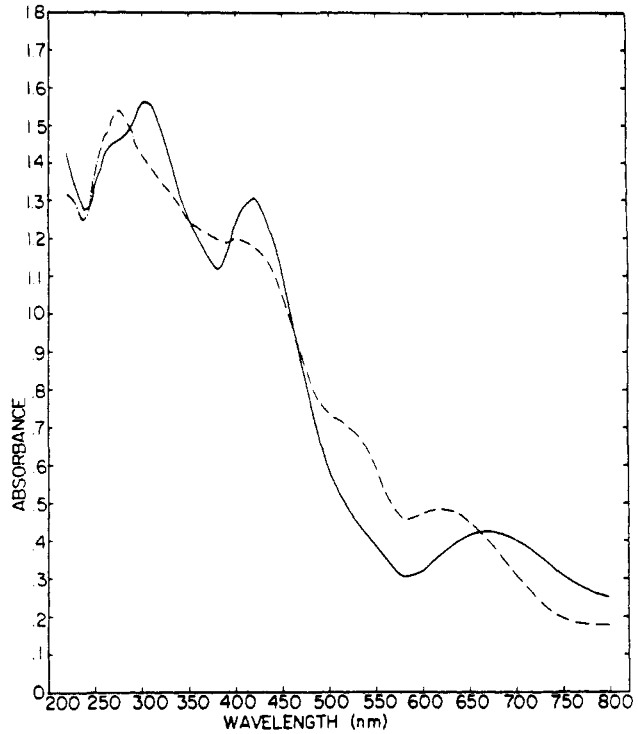

Figure 2. Reflectance spectra of $Mo_4Cl_8(PEt_3)_4$ (unbroken line) and $[Mo_4Cl_8(PEt_3)_2]_x$ (broken line).

Electronic absorption band maxima for the various phosphine derivatives of the tetramers $Mo_4Cl_8(PR_3)_4$ and their condensation products $[Mo_4Cl_8(PR_3)_2]_x$ are given in Table I. Because of low solubility only reflectance data were obtained for the PEt_3 derivatives. The comparison of the latter, given in Figure 2, shows the striking similarity of spectra for tetramer and its condensation product. There appears to be a close correspondence of principal bands, with those of $[Mo_4Cl_8(PR_3)_2]_x$ shifted to slightly lower

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(19) Beers, W. W.; McCarley, R. E., to be submitted for publication.

Table II. Infrared Absorption Frequencies for $[Mo_4Cl_8(PR_3)_2]_x$ in the Region 200–400 cm^{-1}

phosphine ligand	abs max, cm^{-1} ^{a}		
PEt_3	275 (m)	335 (m)	375 (s)
$P(n\text{-}Pr)_3$	280 (m)	330 (m)	375 (s)
$P(n\text{-}Bu)_3$	275 (m)	330 (m)	375 (s)
PMe_2Ph	280 (m)	335 (m)	380 (s)

^{a} Relative intensities are given in parentheses; s = strong, m = medium.

wavelength than those of the tetramers. An exception to this is noted in bands at 520 and 550 nm in spectra of $[Mo_4Cl_8(PEt_3)_2]_x$ and $[Mo_4Cl_8(PMe_2Ph)_2]_x$, respectively, which have no obvious counterparts in spectra of the corresponding tetramers. The blue shift of bands in spectra of the condensed compounds compared to those of the tetramers is understandable on the basis of substitution of bridging Cl atoms into coordination sites vacated upon loss of phosphine ligand. In an earlier study[8] of spectra of the tetramers $Mo_4Cl_8L_4$ it was found that absorption maxima underwent a blue shift with λ(max) in the order L = MeOH < RCN < PR_3, which is consistent with the shift observed here on loss of phosphine. Again, we infer from these spectra that the cluster units in $[Mo_4Cl_8(PR_3)_2]_x$ are closely related to, if not preserved rectangular units of, the type found in the tetrameric starting materials $Mo_4Cl_8(PR_3)_4$.

Infrared spectra of the condensation products in the region 200–400 cm^{-1} all exhibited the same unmistakable three-band pattern with the absorption frequencies listed in Table II. Since the spectra in this region are independent of phosphine ligand, the observed bands must all arise from Mo–Cl stretching vibrations. If the cluster units in the various derivatives were coupled via Mo–Cl–Mo bridge bonding in different ways, pronounced differences in these spectra should be observed. The virtually identical spectra thus lead to the conclusion that all of these derivatives have the same structure.

Conclusions. The bulk of evidence suggests that the tetrameric rectangular cluster units are retained in the condensed compounds $[Mo_4Cl_8(PR_3)_2]_x$, coupled together through Mo–Cl–Mo bridge bonding. Although this coupling might occur in different ways and result in isomeric forms, the derivatives discussed here all appear to possess the same basic structure. The reactions of $[Mo_4Cl_8(PEt_3)_2]_x$ with PEt_3 demonstrate that the rectangular cluster units can be regenerated under mild conditions, which suggests that new cluster units with extended metal–metal bonding are not involved in the condensed compound. This is corroborated by the great similarity in the electronic spectra of tetramer and corresponding condensed compound. It thus appears that the condensed compounds are composed of either a polymer of tetramers, $[Mo_4Cl_6Cl_{4/2}(PR_3)_2]_\infty$, or a dimer of tetramers, $[Mo_4Cl_6Cl_{4/2}(PR_3)_2]_2$. We believe the latter formulation is most likely correct because the compounds are microcrystalline and exhibit significant solubility in noncoordinating solvents, whereas insolubility and amorphous or semicrystalline character are properties commonly observed with polymeric structures. In the "dimer of tetramers" formulation two configurations of the coupled tetramers can be envisioned, as shown in Figure 3. Only one significant difference stands out between these two possible configurations, and that is the Mo–Mo distance between an atom of one cluster unit and the nearest-neighbor atoms in the adjacent unit. In the configuration with the metal atoms of the two rectangular units coplanar this distance will be shorter than when the planes of the two units are perpendicular. There are analogies to each of these configurations in known coupled dimeric species, viz. the rectangular cluster compounds $M_4Cl_8L_4$[7-9] as analogues to the coplanar dimer of tetramers and $Mo_4F_4(O\text{-}t\text{-}Bu)_8$[20] as analogues of the units coupled with their rectangular planes mutually perpendicular. The available evidence does not permit a choice between these possibilities, except perhaps the apparent lack of extended metal–metal bonding which is favored by the mutally perpendicular orientation of cluster planes.

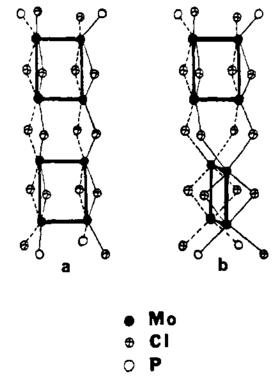

Figure 3. Proposed structures for $[Mo_4Cl_8(PR_3)_2]_2$: (left) coplanar tetrameric units; (right) perpendicular tetrameric units.

Finally, we might expect that the condensation process can be extended by further removal of phosphine ligands. Indeed, complete removal of ligands leads to β-$MoCl_2$, whose structure remains undetermined but which appears to be a metal–metal-bonded polymer.[17,21-23] The compounds discussed here appear to be the first members of the condensation chain $[(Mo_4Cl_8)_n(PR_3)_4]$, with $n = 2$. The end member with $n = \infty$ would resemble or be identical with β-$MoCl_2$. As noted above, material resembling the latter is obtained as a result of ligand redistribution upon prolonged heating of $[Mo_4Cl_8(PR_3)_2]_x$, R = Et, Bu. Further characterization of β-$MoCl_2$ produced in various ways will be the subject of a forthcoming paper.[16]

Registry No. $Mo_4Cl_8(PEt_3)_4$, 68568-88-7; $Mo_4Cl_8(PPr_3)_4$, 94499-56-6; $Mo_4Cl_8(PBu_3)_4$, 68568-89-8; $Mo_4Cl_8(PMe_2Ph)_4$, 94499-57-7; $Mo_8Cl_{16}(PEt_3)_4$, 94517-66-5; $Mo_8Cl_{16}(PBu_3)_4$, 94499-58-8; $Mo_8Cl_{16}(PPr_3)_4$, 94499-59-9; $Mo_8Cl_{16}(PMe_2Ph)_4$, 94499-60-2; $Mo(CO)_4Cl_2$, 15712-13-7.

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(20) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7100.
(21) Allison, G. B.; Anderson, I. R.; Sheldon, J. C. *Aust. J. Chem.* **1969**, *22*, 1091.
(22) Holste, G.; Schäfer, H. *J. Less-Common Met.* **1970**, *20*, 164.
(23) Hamer, A. D.; Walton, R. A. *Inorg. Chem.* **1974**, *13*, 1446.