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^{1}H NMR Investigation of the Tetrahydrofuran Replacement by Phosphine Ligands on $MoCl_3(THF)_3$. A Trans Effect

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The reactions of *mer*-$MoCl_3(THF)_3$ with the phosphine ligands (L) PPh_xMe_{3-x} (x = 0, 1, 2, 3), PPh_xEt_{3-x} (x = 0, 1, 2), and PR_3 (R = *n*-Pr, *n*-Bu) have been investigated in $CDCl_3$ or CD_2Cl_2 by paramagnetic ^{1}H NMR spectroscopy. In all cases, a trans effect is shown by the data: the THF ligand trans to chloride is replaced much more rapidly than the two THF ligands trans to each other, to produce the observed *mer,trans*-$MoCl_3(THF)_2L$ intermediates. The reaction with PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, and PEt_2Ph proceeds to the tris(phosphine) mononuclear derivatives *mer*-$MoCl_3L_3$. For the bulkier $PEtPh_2$ and PPh_3 systems, the *mer,trans*-$MoCl_3(THF)_2L$ intermediates completely lose THF but do not yield the corresponding tris(phosphine) derivatives; instead, they yield dinuclear products. The most nucleophilic among the above phosphines and $P(n\text{-Pr})_3$ and $P(n\text{-Bu})_3$ react with the chlorinated solvents to displace chloride anions, which generate the *trans*-$[MoCl_4(PR_3)_2]^-$ anions. The latter ions have also been obtained independently from $[MoCl_4(THF)_2]^-$ and the appropriate phosphine.

Introduction

$MoCl_3(THF)_3$ is a widely used starting material for the preparation of molybdenum complexes in the +III and lower oxidation states.[1] The first step involved in any of the above transformations is usually exchange of the THF ligands, but no detailed studies of this reaction (in term of reactivity trends, stereochemistry, and mechanism) have been carried out. Since octahedral Mo(III) complexes have three unpaired electrons, the investigation of Mo(III) chemistry has been largely restricted to the characterization of isolated crystalline materials by magnetic and structural methods.

We have recently observed that, in spite of the large paramagnetism, ^{1}H NMR spectrometry can be successfully applied to the investigation of the structure and reactivity of these complexes in solution. Notable observations have been as follows: (a) mononuclear MoX_3L_3 (X = Cl, Br, I; L = THF,[2] phosphine[3]) adopts exclusively the meridional configuration in solution; (b) mononuclear $MoX_3(THF)_3$ spontaneously loses THF in a noncoordinating environment to afford, in a sequential manner, edge-sharing bioctahedral $Mo_2X_6(THF)_4$ and face-sharing bioctahedral $Mo_2X_6(THF)_3$ compounds.[2] The opposite order of stability was observed for complexes of phosphine ligands: face-sharing bioctahedral $Mo_2X_6L_3$ complexes (L = monodentate phosphine) react with a stoichiometric amount of L to generate, sequentially, edge-sharing bioctahedral $Mo_2X_6L_4$ and mononuclear *mer*-MoX_3L_3;[3,4] edge-sharing bioctahedral $Mo_2Cl_6L_4$ compounds are metal-metal bonded when L = PMe_2Ph but they are nonbonded when L = PEt_3[3] and the corresponding bromide with L = PMe_2Ph is also nonbonded.[4]

We have now applied the ^{1}H NMR technique to the qualitative investigation of the THF substitution by phosphine ligands in $MoCl_3(THF)_3$. These studies, whose results are reported and discussed here, have revealed a previously unappreciated trans effect in ligand substitution for octahedral Mo(III).

Table I. ^{1}H NMR Resonances for Mononuclear Octahedral Mo(III) Complexes Containing THF and Phosphine Ligands[a,b]

compound	δ(α-H) THF ligands	δ(α-H) phosphine ligands
mer,tran-$MoCl_3(PMe_3)(THF)_2$	68	−35
mer,trans-$MoCl_3(PEt_3)(THF)_2$	66	−35
mer,trans-$MoCl_3(PPr_3)(THF)_2$	71	−36
mer,trans-$MoCl_3(PBu_3)(THF)_2$	66	−36
mer,trans-$MoCl_3(PMe_2Ph)(THF)_2$	71	−40
mer,trans-$MoCl_3(PEt_2Ph)(THF)_2$	72	−31, −52
mer,trans-$MoCl_3(PMePh_2)(THF)_2$	75	−42
mer,trans-$MoCl_3(PEtPh_2)(THF)_2$	73	−39
mer,trans-$MoCl_3(PPh_3)(THF)_2$	78	
mer-$MoCl_3(THF)_3$	56, 66	
mer-$MoCl_3(PMe_3)_3$		−17, −34
mer-$MoCl_3(PEt_3)_3$		−25, −31
mer-$MoCl_3(PMe_2Ph)_3$		−22, −41
mer-$MoCl_3(PEt_2Ph)_3$		−27, −37
mer-$MoCl_3(PMePh_2)_3$		−19, −43
trans-$[MoCl_4(THF)_2]^-$	72	
trans-$[MoCl_4(PMe_3)_2]^-$		−39
trans-$[MoCl_4(PEt_3)_2]^-$		−37
trans-$[MoCl_4(PPr_3)_2]^-$		−38
trans-$[MoCl_4(PBu_3)_2]^-$		−38
trans-$[MoCl_4(PMe_2Ph)_2]^-$		−39
trans-$[MoCl_4(PMePh_2)_2]^-$		−41
trans-$[MoCl_4(PEt_2Ph)_2]^-$		−33, −38
trans-$[MoCl_4(PEtPh_2)_2]^-$		−36

[a] Temperature = 287 ± 2 K. [b] Solvent = $CDCl_3$ or CD_2Cl_2.

Experimental Section

All operations were carried out under an atmosphere of dinitrogen by using standard Schlenk line techniques, and all glassware was pretreated with a 5% v/v solution of Me_2SiCl_2 in CCl_4. Solvents were dehydrated by conventional methods and distilled under dinitrogen prior to use. The $MoCl_3(THF)_3$ starting material was prepared by a slight modification of a literature procedure,[5] which consists of the reduction of $MoCl_4(THF)_2$ with metallic tin in THF. The literature procedure involves separation of the $MoCl_3(THF)_3$ precipitate from the excess tin by dissolution in CH_2Cl_2, followed by filtration and reprecipitation. Since we have recently shown[2] that the dissolution of $MoCl_3(THF)_3$ inevitably converts part of the orange mononuclear compound to purple dinuclear species, i.e. $Mo_2Cl_6(THF)_4$ and *anti*- and *gauche*-$Mo_2Cl_6(THF)_3$, we avoided the dissolution step and accomplished the separation by taking advantage of the large difference in density between the granular tin and the precipitated molybdenum product. Under gentle stirring with a magnetic stirring bar, the metallic tin remained at the bottom of the flask and the supernatant suspension of $MoCl_3(THF)_3$ was transferred into a new flask via a medium-sized (G15) cannula. The product was then collected by filtration, washed with THF, and dried under vacuum. The phosphine

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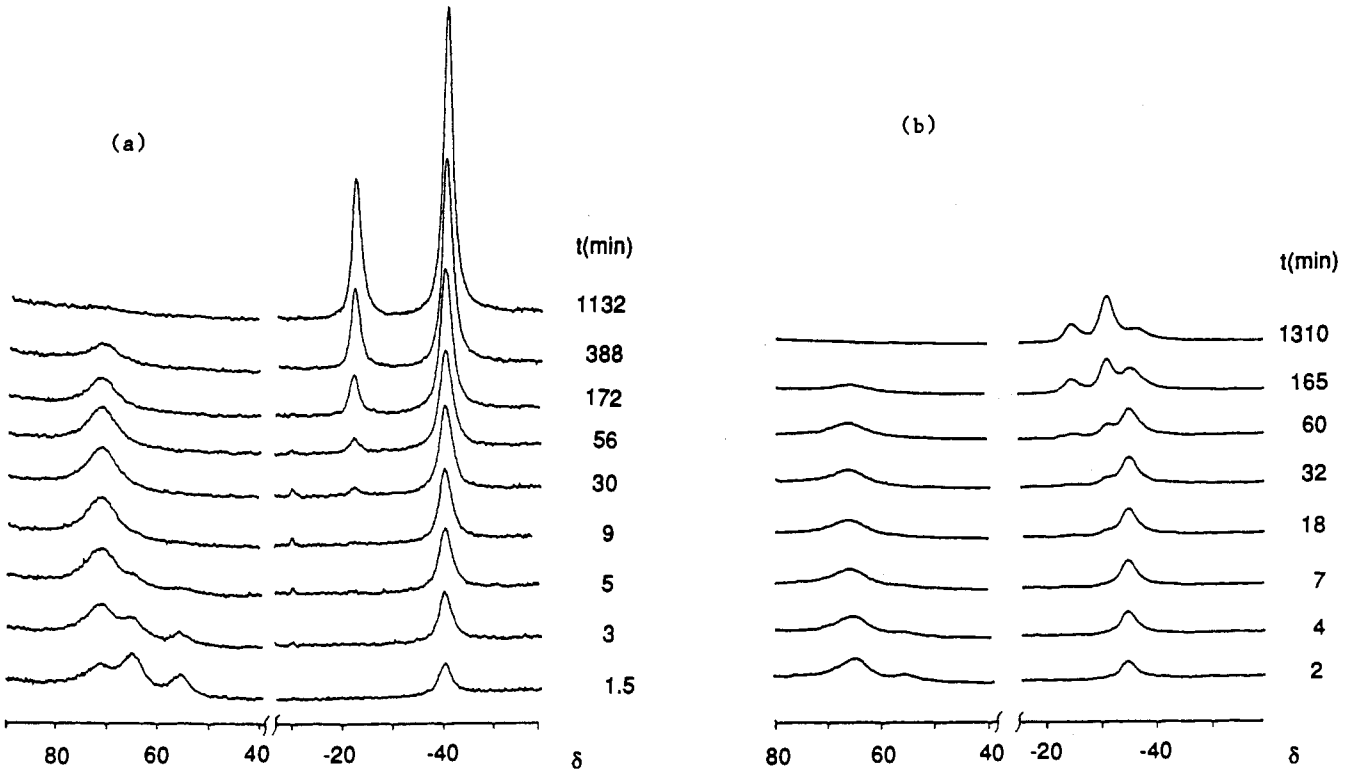


Figure 1. Time dependence of the ^1H NMR spectrum for the reaction of $MoCl_3(THF)_3$ with (a) PMe_2Ph and (b) PEt_3. Solvent = $CDCl_3$. Temperature = 293 ± 2 K.

ligands PMe_3, PEt_3, PPr_3, PBu_3, PMe_2Ph, $PMePh_2$, PEt_2Ph, and $PEtPh_2$ (Aldrich and Strem) were either purified by distillation or used as received, whereas PPh_3 was recrystallized from absolute ethanol.

Reactions of $MoCl_3(THF)_3$ with 3 equiv of Phosphine in the NMR Tube. The NMR experiments were run on a Bruker WP200 Fourier transform spectrometer. Each sample was prepared by dissolving a weighed amount (20–40 mg) of $MoCl_3(THF)_3$ in ca. 1 mL of $CDCl_3$ or CD_2Cl_2 and promptly transferring the solution via cannula into a 5-mm thin-walled NMR tube equipped with septum, which was then cooled to −78 °C. The stoichiometric amount (3 equiv) of the phosphine was added via a microsyringe. The tube was warmed to room temperature immediately prior to introduction into the NMR probe.

Preparation of $PPN^+[MoCl_4(THF)_2]^-$. $MoCl_3(THF)_3$ (510 mg, 1.22 mmol) was suspended in THF (10 mL) and treated with PPN^+Cl^- (699 mg, 1.22 mmol). The mixture was stirred at room temperature overnight, during which time the precipitated lightened in color. The pale salmon pink solid was collected by filtration, washed with *n*-heptane and vacuum dried. Yield: 976 mg (87%). Anal. Calcd for $C_{44}H_{46}Cl_4MoNO_2P_2$: C, 57.41; H, 5.04. Found: C, 57.33; H, 5.29. The compound is only sparingly soluble in THF and moderately soluble in CH_2Cl_2. The ^1H NMR spectral data in CD_2Cl_2 are reported in Table I.

Reaction of $PPN^+[MoCl_4(THF)_2]^-$ with PR_3 in the NMR Tube. Each sample was prepared by introducing the desired amount of $PPN[MoCl_4(THF)_2]$ in a 5-mm thin-walled NMR tube together with ca. 1 mL of CD_2Cl_2 and then adding the stoichiometric amount of phosphine (2 equiv) via a microsyringe. The NMR spectral data of the resulting $[MoCl_4(PR_3)_2]^-$ complexes are reported in Table I.

Reaction of $MoCl_3(THF)_3$ with $PEtPh_2$ in a 2:3 Ratio. $MoCl_3(THF)_3$ (319 mg, 0.76 mmol) was suspended in 10 mL of toluene and treated with $PEtPh_2$ (233 μL, 1.14 mmol). The mixture was refluxed for 90 min during which time the solution darkened. After filtration and cooling to room temperature, the solution was placed at −20 °C overnight, generating a small amount of an oily material, which was discarded. Heptane (10 mL) was diffused into the mother liquor, leading to the formation of a larger amount of oily material. After the mother liquor was decanted off, the oil was dissolved in CH_2Cl_2, followed by layering with *n*-heptane. An oil was again obtained. The solvents were stripped under vacuum, leaving approximately 400 mg of a brown glassy solid. The ^1H NMR spectrum of this material shows contamination by the various solvents used for the purification procedure and is consistent with this species being also formed in the reaction of $MoCl_3(THF)_3$ with $PEtPh_2$ in a 1:3 ratio (see Results). There is no sign of the presence of mononuclear, paramagnetic Mo(III) complexes.

Reaction of $MoCl_3(THF)_3$ with PPh_3 in a 2:3 Ratio. $MoCl_3(THF)_3$ (421 mg, 1.00 mmol) was treated with PPh_3 (396 mg, 1.51 mmol) in 10 mL of toluene at room temperature with stirring. The solution assumed a red/brown color, and the insoluble starting material was replaced by a darker precipitate. After 30 min the mother liquor was decanted off and the remaining solid repetitively washed with Et_2O and dried. A pale brown solid (280 mg) was obtained. When an identical reaction was carried out under reflux conditions, only oily materials were obtained. Neither the pale brown solid nor the oily materials analyzed correctly for $Mo_2Cl_6(PPh_3)_3$. ^1H NMR analysis showed that these materials were heavily contaminated with solvent of crystallization. However, the ^1H NMR and UV/vis spectra (λ_{max} = 246, 318 nm) of these materials are identical to those obtained from the reaction of $MoCl_3(THF)_3$ with 3 equiv of PPh_3 (see Results). There is no sign of the presence of mononuclear, paramagnetic Mo(III) complexes.

Results

NMR Monitoring of the $MoCl_3(THF)_3 + 3PR_3$ Reactions. The outcome of the reaction between $MoCl_3(THF)_3$ and 3 equiv of a small phosphine (L = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, and PEt_2Ph) is as described in the literature,[1b] that is the formation of the tris(phosphine) adduct $MoCl_3L_3$. Monitoring the reaction by NMR, however, reveals additional mechanistic features that were previously unappreciated. The NMR reactions were carried out either in $CDCl_3$ or CD_2Cl_2, the only two solvents in which the starting complex $MoCl_3(THF)_3$ dissolves appreciably. Our previous investigations[2,3] have revealed that mononuclear octahedral Mo^{3+} ($S = {}^3/_2$) complexes show resonances in the δ +50 to +70 region for the α-protons of coordinated THF ligands and in the δ −20 to −50 region for the α-protons of aliphatic chains of coordinated phosphines. These regions of the spectrum are therefore highly diagnostic for the solution behavior of the THF/phosphine exchange reaction in octahedral Mo(III) complexes. Figure 1 shows the salient changes of the ^1H NMR spectrum in these regions during the reaction of $MoCl_3(THF)_3$ with two representative phosphines, PMe_2Ph and PEt_3.

For both phosphine systems shown in Figure 1, the THF α-resonances of *mer*-$MoCl_3(THF)_3$ (at ca. δ 66 and 56 in a 2:1 ratio)[2] disappear quite rapidly at room temperature. In the PMe_2Ph case (Figure 1a), these are replaced by a single resonance at ca. δ 71 within ca. 9 min. At the same time, a single resonance appears at ca. δ −40.5. At longer reaction times (over ca. 19 h), the new resonance due to coordinated THF decreases in intensity, whereas the high-field region of the spectrum changes to ultimately

lead to the characteristic pattern[3] of *mer*-$MoCl_3(PMe_2Ph)_3$. There is an accidental overlap at ca. δ −41 between the phosphine proton resonance of the intermediate complex with one of the resonances of the final product.

It is clear that one intermediate complex accumulates substantially during the transformation from *mer*-$MoCl_3(THF)_3$ to *mer*-$MoCl_3(PMe_2Ph)_3$. Since only one type of THF ligand and one type of PMe_2Ph ligand are indicated by the NMR spectrum and integration indicates a THF:PMe_2Ph ratio of 2 and because it is reasonable to assume a meridional arrangement of the three chloro ligands (this arrangement is found both in starting material and product), the only possible structure for the intermediate is *mer,trans*-$MoCl_3(PMe_2Ph)(THF)_2$. The NMR spectrum also shows a decrease in intensity for the free PMe_2Ph resonances and an increase in intensity for the resonances of free THF as the reaction progresses. The β-H nuclei of coordinated THF in the intermediate *mer,trans*-$MoCl_3(PMe_2Ph)(THF)_2$ complex resonate at δ 8.2, and the coordinated phosphine phenyl protons for the same compound appear in the δ 9–15 region. In addition to the above changes, the accumulation of small but significant amounts of the edge-sharing bioctahedral $Mo_2Cl_6(PMe_2Ph)_4$ complex[3] at intermediate times is observed as diagnosed by the appearance of two peaks in a 1:1 ratio at δ 0.40 and 0.62 due to the inequivalent axial and equatorial phosphine methyl protons.[3] The final product, however, is pure *mer*-$MoCl_3(PMe_2Ph)_3$.

The PEt_3 system (Figure 1b) behaves in a manner identical to the PMe_2Ph system just described. In this case, the THF α proton resonance for the *mer,trans*-$MoCl_3(PEt_3)(THF)_2$ intermediate overlaps with the resonance at δ −66 due to the starting material. On the other hand, the phosphine α-proton resonance of the intermediate (at ca. δ −35) is separated from the resonances due the final *mer*-$MoCl_3(PEt_3)_3$ product (at ca. δ −25.5 and −32). In this case, resonances that could be assigned to the edge-sharing bioctahedral $Mo_2Cl_6(PEt_3)_4$ system were not observed, but the resonances of this compound would overlap with those of the final mononuclear product,[3] and thus we cannot exclude that minor amounts of this compound are present at intermediate times. On the other hand, the final spectrum reveals one extra resonance on the high-field side of the phosphine α-H region, in a position almost identical to that of the intermediate $(THF)_2$ complex (ca. δ −37). This signal cannot be due to residual $(THF)_2$ intermediate because the corresponding resonance due to the coordinated THF is no longer present. This resonance is due to the byproduct *trans*-$[MoCl_4(PEt_3)_2]^-$ ion, as will be shown later.

The reactions of $MoCl_3(THF)_3$ with PMe_3 and $PMePh_2$ follow a path identical to those discussed above for the PMe_2Ph and PEt_3 systems. The $[MoCl_4(PR_3)_2]^-$ byproduct is not observed with $PMePh_2$, while it is observed in minor amounts with PMe_3. When $PR_3 = PMe_3$, an additional small intensity signal at ca. δ −37 is observed at the very end of the substitution reaction (ca. 24 h). This signal is derived from a secondary reaction of *trans*-$[MoCl_4(PMe_3)_2]^-$ in the CD_2Cl_2 solvent as shown by a control experiment. We have not further investigated the identity of this product. At intermediate times, other low intensity signals are observed at ca. δ −10, 0, and −0.8. The last two resonances are due to $Mo_2Cl_6(PMe_3)_4$[6] whereas the former one may be due to an intermediate along the transformation of *fac,mer*-$MoCl_3(PMe_3)(THF)_2$ to $Mo_2Cl_6(PMe_3)_4$ (see Discussion). A low-intensity intermediate resonance at ca. δ −10 has also been observed for other phosphine systems.

When $PR_3 = PMePh_2$, the spectrum shows only the presence of *mer*-$MoCl_3(PMePh_2)_3$ after 24 h, but after 4 days a new, weak and very broad feature centered at ca. δ −35 is also visible. This accounts for less than 10% of the final product and is not due to the *trans*-$[MoCl_4(PMePh_2)_2]^-$ ion (see Table I). It could possibly be assigned to the isomeric *fac* complex. In addition, small resonances in the δ +1 to −1 region persist in the final solution. These signals may be assigned to a metal–metal-bonded edge-sharing bioctahedral tetrakis(phosphine) complex which, contrary to the PMe_3 and PMe_2Ph cases, remains in small proportions in equilibrium with the mononuclear tris(phosphine) complex presumably because of the larger steric requirements.

The reactions with $P(n\text{-}Pr)_3$ and $P(n\text{-}Bu)_3$ rapidly proceed to the *mer,trans*-monophosphine adducts, but further reaction results in the generation of solutions whose NMR spectra are consistent with the presence of the $[MoCl_4(PR_3)_2]^-$ anions as the prevalent species. We have run the same reactions in THF and replaced the solvent with $CDCl_3$ after 24 h followed by immediate recording of the NMR spectrum. In the case of $P(n\text{-}Pr)_3$, there is no significant variation of the results, while in the case of $P(n\text{-}Bu)_3$, although the $[MoCl_4[P(n\text{-}Bu)_3]_2]^-$ anion is still present in large quantities, there are at least two more paramagnetic species, one of which may be the tris(phosphine) monomer and the other could possibly be assigned to a nonbonded edge-sharing bioctahedral dimer (resonances at δ −28 and −31). Unambiguous assignments could not be made, however. A possible explanation of this reactivity is that dissociation of the phosphine from *mer*-$MoCl_3(PR_3)_3$ is facile allowing the reaction with the chlorinated solvent to take place rapidly for these phosphine ligands.

For $PR_3 = PEt_2Ph$, a complex spectrum is obtained after formation of the *mer,trans*-monophosphine adduct, showing resonances at δ −28, −33, −37, and −42. The resonance at δ −33 and part of the feature centered at δ −37 are due to *trans*-$[MoCl_4(PEt_2Ph)_2]^-$ (see Table I). Of the remaining resonances, we assign that at δ −28 and the rest of the δ −37 feature to the *mer*-$MoCl_3(PEt_2Ph)_3$ product based on relative intensities and on the position of the peaks relative to the corresponding peaks of similar compounds. The resonance at δ −42 remains unaccounted for. A possibility is an edge-sharing bioctahedral tetrakis(phosphine) complex which would have to lack a metal–metal bond. The difference between this complex and the metal–metal-bonded PMe_2Ph analogue would parallel the difference between the PMe_3 complex (bonded) and the PEt_3 complex (nonbonded).[3]

The reactions with bulkier phosphines ($PEtPh_2$ and PPh_3) proceed initially in the same manner as illustrated above for the other smaller phosphine ligands, but the final products are different. After conversion to the *mer,trans*-$MoCl_3L(THF)_2$ was complete, the resonances due to this intermediate complex decreased, but no resonance that could be assigned to a paramagnetic tris(phosphine) product grew to replace them. In the $PEtPh_2$ case, the final spectrum had no resonances upfield of ca. δ 0 that could be assigned to the phosphine methylene group in a paramagnetic complex, and in neither the $PEtPh_2$ nor the PPh_3 case were there resonances in the δ +9 to +15 region due to strongly paramagnetically shifted aromatic protons. There are, however, resonances in the δ +7 to +9 region indicating slight paramagnetic shifts for the aromatic protons. Thus, the final product(s) in each of these two cases is (are) diamagnetic or at most slightly paramagnetic. We know that the face-sharing complexes $Mo_2Cl_6L_3$ and metal–metal-bonded edge-sharing $Mo_2Cl_6L_4$ complexes are diamagnetic or only slightly paramagnetic due to the population of low-lying paramagnetic excited states.[3] Independent synthetic studies carried out with $MoCl_3(THF)_3$ and L in a 2:3 ratio (conditions known to give rise to the face-sharing complexes $Mo_2Cl_6L_3$ for other phosphines; see eq 1)[3] gave analytically impure

$$2MoCl_3(THF)_3 + 3L \xrightarrow{\text{toluene, } \Delta} Mo_2Cl_6L_3 \qquad (1)$$

materials which could not be obtained in a crystalline form and free of crystallization solvents. The material obtained for L = PPh_3 has ^1H NMR and UV/vis spectra identical to those of the final solution obtained from the same reaction carried out in a 1:3 Mo/PPh_3 ratio. For L = $PEtPh_2$, the compound synthesized according to eq 1 accounted only for some of the signals observed in the final solution during the NMR experiment with three phosphine equivalents. The remaining resonances may be due to the corresponding metal–metal-bonded edge-sharing bioctahedral complex, $Mo_2Cl_6(PEtPh_2)_4$.

(6) (a) This compound has been mentioned in the literature,[6b] but no NMR characterization was given. We have obtained this compound following the procedure reported recently for $Mo_2Cl_6(PMe_2Ph)_4$.[3] Details of this work will be reported in due course. (b) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347.

In the case of the $PEtPh_2$ reaction, the resonance at δ −39 due to the methylene protons or *mer,trans*-$MoCl_3(PEtPh_2)(THF)_2$ was initially replaced by a similar resonance centered at ca. δ −36 before formation of the final diamagnetic product. It is clear that a paramagnetic complex is accumulated as a second intermediate during the transformation of *mer,trans*-$MoCl_3(PEtPh_2)(THF)_2$ to $Mo_2Cl_6(PEtPh_2)_n$ (n =3, 4) but it was not possible to unambiguously identify this complex from the observed spectral changes. The reaction with PPh_3 was harder to interpret, due to the lack of phosphine aliphatic α-protons but a careful analysis of the δ 8.5–15 region (which contains the paramagnetically shifted phenyl protons) showed that, in analogy to the $PEtPh_2$ case, at least one additional paramagnetic intermediate is formed on conversion of *mer,trans*-$MoCl_3(PPh_3)(THF)_2$ to the diamagnetic final product. Again, the pattern observed does not allow the elucidation of the structure of the second intermediate(s).

None of the *mer,trans*-$MoCl_3L(THF)_2$ complexes have been isolated and the characterization relies fully on the ^1H NMR technique. Isolated materials of formula $MoCl_3L(THF)_2$ (L = phosphine) have been reported before[1b] (see also Discussion). The significant resonances of the intermediate *mer,trans*-$MoCl_3L(THF)_2$ and final *mer*-$MoCl_3L_3$ product are assembled in Table I. It is interesting to observe that the resonance for the THF α-H in *mer,trans*-$MoCl_3(THF)_2(PR_3)$ shifts downfield on increasing the phenyl substitution on the phosphine ligand.

Synthetic Studies and NMR Properties of the $[MoCl_4L_2]^-$ Anions. Since the above NMR experiments occasionally showed more resonances in the final solutions than expected for the formation of *mer*-$MoCl_3(PR_3)_3$, we considered the possibility for side reactions. It is known from the literature that certain tertiary phosphines can react with chlorinated hydrocarbons,[7] and complications due to this reactivity have been recently noted by us.[3] If the phosphine is able to displace chloride from the solvent with formation of phosphonium ions, then the phosphonium chloride salts might in turn add to the molybdenum compounds to afford salts with the $[MoCl_4(PR_3)_2]^-$ anion, which could be the source of at least some of the extra signals observed during the NMR monitoring of the exchange reactions. We have verified that some of the impurities correspond indeed to the $[MoCl_4(PR_3)_2]^-$ ions by generating these ions by an alternative pathway and by determining their NMR properties.

The reaction of $MoCl_3(THF)_3$ with 1 equiv of PPN^+Cl^- (PPN = Ph_3PNPPh_3) in CH_2Cl_2 proceeds rapidly to the pale pink PPN salt of $[MoCl_4(THF)_2]^-$ in good yield (eq 2).

$$MoCl_3(THF)_3 + PPN^+Cl^- \rightarrow PPN^+[MoCl_4(THF)_2]^- + THF \quad (2)$$

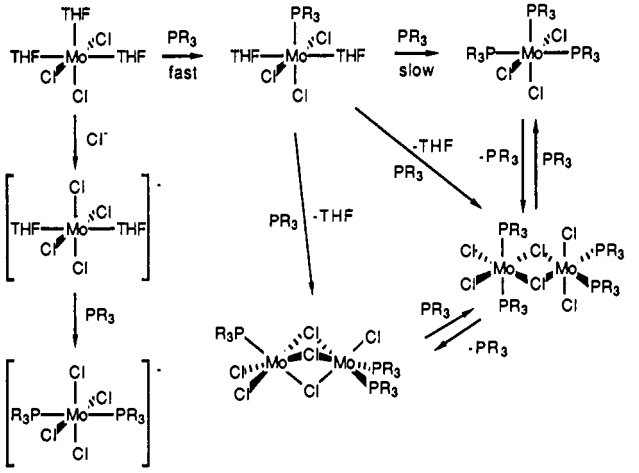
The stoichiometry of this reaction is confirmed by NMR monitoring, which shows the two resonances at ca. δ 55 and 65 for the THF α-H in *mer*-$MoCl_3(THF)_3$ to be replaced by a single resonance at δ 72 for the coordinated THF and by a resonance at ca. δ 3.8 for free THF (α-H), in a 2:1 ratio. The resonance for the β-H is observed at δ 1.1 for the coordinated THF ligand and at δ 1.9 for free THF. The reaction is complete within 12 min in CD_2Cl_2 at room temperature.

NMR shows that the two THF ligands in $[MoCl_4(THF)_2]^-$ are equivalent, in agreement with either a cis or a trans configuration, but a trans configuration is consistent with the solution structure of the phosphine complexes prepared during this study (vide infra) and with the solid-state structure reported for $PPh_4[MoCl_4(THF)_2]$.[8] The latter was prepared by a route alternative to that described here and was not characterized by NMR.

The reaction of $PPN^+[MoCl_4(THF)_2]^-$ with 2 equiv of PR_3 in CD_2Cl_2 results in the formation of *trans*-$[MoCl_4(PMe_3)_2]^-$ (eq 3). ^1H NMR spectral data of the products are collected in Table I. No coordinated THF remains at the end of the reactions as shown by the absence of resonances in the low-field (δ >20 and up to 100) region.

$$[MoCl_4(THF)_2]^- + 2PMe_3 \rightarrow [MoCl_4(PMe_3)_2]^- + 2THF \quad (3)$$

Scheme I



The trans configuration of the product is established by the single resonance obtained for PR_3 = PMe_3, PEt_3, $P(n\text{-}Pr)_3$, $P(n\text{-}Bu)_3$, PMe_2Ph, $PMePh_2$, and $PEtPh_2$ and by the two resonances in a 1:1 ratio obtained for PR_3 = PEt_2Ph (see Table I). A hypothetical *cis*-$[MoCl_4(PR_3)_2]^-$ ion is predicted to show one resonance only for PR_3 = PMe_3 or $PMePh_2$, but more resonances are expected for phosphine systems with diastereotopic protons (e.g. two resonances for PEt_3, PPr_3, PBu_3, and PMe_2Ph and four for PEt_2Ph). The trans configuration has been established by X-ray crystallography for the analogous $[PHEt_2Ph]^+[MoI_4(PEt_2Ph)_2]^-$ salt[9] and for other similar complexes of other metals [e.g. $MCl_4(PMe_2Ph)_2$ (M = W, Re, Os, Ir,[10] Tc[11])]. The positions of these signals also correspond to those of the extra signals (when these are observed) obtained during the NMR reaction between $MoCl_3(THF)_3$ and the corresponding phosphine ligand (see results of the NMR reactions described above and Table I).

Discussion

The NMR experiments illustrated above indicate a trans effect for the ligand substitution in octahedral *mer*-$MoCl_3(THF)_3$. The first substitution is much more rapid than the two subsequent ones and occurs selectively at the position trans to the chloride ligand, to give the *mer,trans*-$MoCl_3(THF)_2L$ intermediate.

The trans effect is a well-known phenomenon for ligand substitution in square-planar complexes but has been much less investigated for octahedral complexes,[12] and there have been no reports to date, to the best of our knowledge, of such an effect for substitutions in molybdenum complexes. The reported examples of the trans effect in octahedral substitution reactions indicate that the order of the trans-directing ability is the same as for square-planar substitution reactions. This is the case also for the system reported here. The first substitution occurs selectively at the position trans to a chloride ligand, which is higher than ethers in the trans-directing series. The second substitution occurs at a position trans to a THF ligand and is slower than the first substitution, but once this step has taken place, the last THF ligand to be replaced is now located trans to a phosphine ligand,

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which is known to have a strong trans-directing ability, and accordingly it is replaced at a much faster rate than the second THF ligand since no *mer,cis*-$MoCl_3(PR_3)_2(THF)$ intermediate has been observed with any of the phosphines utilized in this study. The high trans effect of phosphine ligands would suggest that, after the first THF ligand has been replaced, a fast substitution of the chloride trans to the phosphine should take place to generate the *trans*-$[MoCl_2(THF)_2(PR_3)_2]^+Cl^-$ system. We have no evidence that this process occurs in chlorinated hydrocarbons. Presumably this process is thermodynamically unfavorable, and we have not checked whether it would take place in a solvent with a higher dielectric constant.

The reactivity observed in these NMR investigations is summarized in Scheme I.

The transformation of *mer,trans*-$MoCl_3(THF)_2(PR_3)$ to *mer*-$MoCl_3(PR_3)_3$ deserves a further comment. The main pathway for this transformation is likely to involve exclusively mononuclear systems (classical dissociative or associative mechanism). The observed significant accumulation in a few instances of the edge-sharing dimer $Mo_2Cl_6(PR_3)_4$ could represent a minor, competitive pathway. Such a dimer is known to slowly transform to the mononuclear tris(phosphine) complex in the presence of free phosphine. It is quite possible that once the second phosphine ligand has coordinated to the metal, the high lability of the last THF ligand would make it possible to allow attack by either a third phosphine ligand or by a second molybdenum complex through its chloro ligands. While in the first case the mononuclear tris(phosphine) product is formed directly, in the second case an edge-sharing or face-sharing bioctahedral system would result as an intermediate. The fact that the intermediacy of a $Mo_2Cl_6L_3$ complex escapes our NMR detection is consistent with the results of a previous investigation where we have shown that, in the presence of excess phosphine, the transformation of $Mo_2Cl_6L_3$ to $Mo_2Cl_6L_4$ is fast, whereas the latter complex is transformed only slowly to the mononuclear $MoCl_3L_3$ molecule.[3]

For the system with the bulkier phosphines $PEtPh_2$ and PPh_3 (cone angle = 140° and 145°, respectively) NMR evidence seems to be most consistent with the formation of dinuclear $Mo_2Cl_6L_n$ (n = 3, 4) compounds. Presumably, the steric requirements of these phosphines do not allow the coordination of three of them around the metal center in a mononuclear complex. For the intermediate-size $PMePh_2$ and PEt_2Ph (both having a cone angle of 136°), the mononuclear system is formed but there is evidence for the presence of equilibrium concentrations of other species, presumably $Mo_2Cl_6L_4$. In addition to the steric requirements, the strength of the phosphine as an electron donor might also be responsible for these differences in reactivity.

The results presented in this paper allow us to reanalyze some previously published data in a new light. A number of $MoCl_3L(THF)_2$ derivatives have been described (for instance, L = $PEtPh_2$, PEt_2Ph, py), but details of their coordination geometry were not given.[1b] These compounds were obtained from $MoCl_3(THF)_3$ and the corresponding ligand in THF as solvent and precipitated by concentration and/or addition of a nonsolvent and/or cooling after short reaction times (ca. 1 h at room temperature).[1b] Our experiments indicate that products obtained under these conditions should have exclusively the *mer,trans* geometry.

The same report also describes a number of $MoCl_3(PR_3)_2(THF)$ derivatives (e.g. with PR_3 = $PEtPh_2$ and PMe_2Ph, the latter in two different isomeric forms). These derivatives were obtained, once again, from $MoCl_3(THF)_3$ and the appropriate phosphine after brief stirring at room temperature and precipitation from solution by one of the methods mentioned above.[1b] We have clearly shown in this work that bis(phosphine) mononuclear derivatives are not obtained under these conditions, and we therefore propose that the bis(phosphine) derivatives reported previously[1b] are in fact mixtures of *mer,trans*-$MoCl_3L(THF)_2$ and *mer*-$MoCl_3L_3$ (for L = $PMePh_2$) or mixtures of *mer,trans*-$MoCl_3L(THF)_2$ and $Mo_2Cl_6L_n$ (n = 3, 4) plus perhaps some interstitial THF when L = $PEtPh_2$. It was proposed[1b] that the failure to obtain tris(phosphine) derivatives in certain cases (e.g. $PEtPh_2$) was due to the steric bulk of the phosphine. Our NMR experiments show that complete conversion to the tris(phosphine) derivatives takes several hours at room temperature even for small phosphines such as PMe_3. When the steric bulk is increased on going to the $PEtPh_2$ and PPh_3 systems, the formation of the tris(phosphine) derivatives is no longer observed. However, mononuclear *bis(phosphine)* adducts are not the final product either. The only unambiguous $MoX_3L_2(THF)$ complexes that we are aware of are those with L_2 = bis(diphenylphosphino)ethane and X = Cl, Br, or I reported by us,[13] where the chelate effect contributes to the energetic stabilization. Incidentally, in a noncoordinating solvent, the latter complexes readily lose THF to afford the edge-sharing bioctahedral $Mo_2X_6(dppe)_2$ compounds.[14]

The earlier report[1b] also shows the isolation of two different forms of $MoCl_3(PMe_2Ph)_3$, assigned to *mer* and *fac* isomers. We observe only the *mer* compound after 24 h of monitoring in $CDCl_3$. After 4 days at room temperature a new, very broad signal at ca. δ −35 is noticeable which may well be assigned to a *fac* isomer, but the major species in solution is still *mer*-$MoCl_3(PMePh_2)_3$.

Conclusions

The present study demonstrates the usefulness of monitoring chemical reactions and contributes to further clarify the complex behavior of octahedral Mo(III) complexes. Basic facts such as the stereochemistry of MoX_3L_3 and $MoX_3LL'_2$ complexes *in solution* and a trans effect for ligand substitution reactions on octahedral Mo(III) complexes have gone undetected for over 15 years because of the lack of a structure-sensitive spectroscopic technique. We have now identified one such technique as paramagnetic ^1H NMR. Since our first report[2] on the ^1H NMR of Mo(III) complexes, the technique has been applied to the elucidation of another interesting aspect of the coordination chemistry of Mo, that is the dubious existence of "bond stretch" isomers for the $MoOCl_2(PR_3)_2$ class of compounds.[15] We anticipate yet more surprising results in our continuing investigation of Mo(III) coordination chemistry.

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