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The $K_4Mo_2Cl_8$–NOCl, $Mo_2(C_2H_3O_2)_4$–NOCl, and $[(C_2H_5)_4N]_3Mo_2Cl_9$–NOCl Systems in Ethyl Acetate

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The behavior of the $K_4Mo_2Cl_8$–NOCl, $Mo_2(C_2H_3O_2)_4$–NOCl, and $[(C_2H_5)_4N]_3Mo_2Cl_9$–NOCl systems in ethyl acetate has been investigated. In every case, only products were found in which the molybdenum-molybdenum multiple bonds of the starting complexes had been cleaved. After appropriate work-up of the $K_4Mo_2Cl_8$–NOCl system immediately *after reaction, the complexes $K_2Mo(NO)Cl_5$ and $Mo(NO)Cl_3 \cdot 2(C_6H_5)_3PO$ were isolated. Infrared evidence indicated that these compounds were contaminated with species containing molybdenum–oxygen bonds, and indeed, extended reaction times resulted in marked decreases in the relative intensity of the absorption characteristic of the N–O stretch and increases in the intensities of those absorptions attributable to molybdenum-oxygen linkages. Reaction of NOCl with $Mo_2(C_2H_3O_2)_4$ gave, after treatment of the ethyl acetate solution with triphenylphosphine oxide, practically quantitative yields of $Mo(NO)Cl_3 \cdot 2(C_6H_5)_3PO$. Again, the compound was apparently contaminated with substances having molybdenum–oxygen bonds. It is worth noting that the initial reactions of NOCl with $K_4Mo_2Cl_8$ and $Mo_2(C_2H_3O_2)_4$ occurred with little oxidation of the dipositive molybdenum. The major products obtained after work-up of the $[(C_2H_5)_4N]Mo_2Cl_9$–NOCl system were $[(C_2H_5)_4N]_2Mo(NO)Cl_5$, $[(C_2H_5)_4N]$-$MoCl_4(H_2O)_x$ ($x = 1$–2), and $MoO_2Cl_2 \cdot 2(C_6H_5)_3PO$. It is proposed that $[(C_2H_5)_4N]_2Mo(NO)Cl_5$ is formed by reaction of a molybdenum(III) species with NO, the latter arising from the reduction of NOCl.*

Introduction

There appear to be no reports in the literature on the behavior of compounds containing strong metal–metal multiple bonds toward electrophiles. This paper describes the results of an investigation of the reactions of tetrapotassiumoctachlorodimolybdate(II), $K_4Mo_2Cl_8$, tetrakis(acetato)dimolybdenum, $Mo_2(C_2H_3O_2)_4$, and tris(tetraethylammonium)enneachlorodimolybdate(III), $[(C_2H_5)_4N]_3Mo_2Cl_9$, with nitrosyl chloride in ethyl acetate as solvent. In the first two compounds, the Mo–Mo bond order is 4 and in the last compound, 3.

Experimental

Chemicals

All gases and solvents were of the best grades purchasable and were purified before use by standard techniques. Tetrapotassiumoctochloromolybdate(II), $K_4Mo_2Cl_8$, was prepared as described by Brencie and Cotton [1]. Tetrakis(acetato)dimolybdenum was synthesized by a slight modification of the method of Stephenson, Bannister, and Wilkinson [2, 3]. Tris(tetraethylammonium)enneachlorodimolybdate (III), $[(C_2H_5)_4N]_3Mo_2Cl_9$, was made according to the procedure of Grey and Smith [4].

Chemical Analysis

Because of the reactivity of most of the complexes described in this work toward atmospheric moisture or oxygen, samples were always handled in an argon-filled glove bag. Molybdenum was determined gravimetrically as the 8-hydroxyquinolate [5], after decomposition of the compound by a mixture of concentrated nitric and perchloric acids; the decomposition converted the molybdenum to the +6 state. Samples containing organic ligands were fumed to dryness with concentrated nitric acid prior to treatment with the mixture of acids. Potassium was found gravimetrically as the tetraphenylborate according to the method of Sporek and Williams [6], the samples being brought into solution by means of concentrated hydrochloric acid. Chloride was analyzed for by potentiometric titration with standardized silver nitrate solution, after decomposition of the samples with 25–35% nitric acid. In those cases where decomposition did not occur readily, an excess of silver nitrate solution was added to the nitric acid solution and the mixture was kept in the dark for 10–12 hr. Then a known quantity of potassium chloride was added and the chloride remaining in solution titrated. Microanalyses for carbon, hydrogen, nitrogen, chlorine, and phosphorus on some of the compounds were performed by Chemalytics, Inc., of Tempe, Arizona.

Infrared Spectra

Infrared spectra of solid products were recorded on a Perkin–Elmer model 421 dual grating spectrophotometer. Essentially identical spectra were obtained for each compound in a Nujol mull and in a KBr disk.

Conductance Measurements

Data were obtained in nitromethane (reagent grade; Fisher Scientific Co.) as solvent with a Beckman conductivity bridge, model RC-16B2, and a stoppered flask-type conductivity cell. All solutions were prepared and transferred to the conductivity cell in an argon-filled glove bag. The cell constant was determined by measuring the resistance of a 0.0200 *M* potassium chloride solution, whose specific conductance is known to be 0.002768 ohm^{-1} at 25 °C.

General Reaction Procedure [3]

The apparatus for studying the various systems was constructed of Pyrex and its parts were connected by short sections of Tygon tubing. The reaction vessel was a 125-ml, 3-necked round-bottomed flask containing a Teflon-coated magnetic stirring bar and equipped with a central 24/40 and two 19/38 standard taper ground glass joints. The central joint was fitted with a tube in which was sealed a straight-bore stopcock to allow for exit of gases from the reaction vessel, and one of the other two joints was fitted with a bubbler tube for entry of gases (N_2 or Ar and NOCl) and the other with a ground glass stopper. The reaction flask was appropriately connected through the bubbler tube to sources of nitrogen or argon and nitrosyl chloride, to a pressure release bubbler containing mercury and mineral oil, and to a roughly calibrated trap for condensing the nitrosyl chloride. Prior to a run, all glassware was dried in an oven at 110 °C.

With a slow stream of nitrogen passing through the system, molybdenum complex and deaerated ethyl acetate were added to the reaction flask through the joint fitted with the ground glass stopper. The complex was suspended in the solvent with magnetic stirring and the nitrogen or argon was passed through the slurry for about 10 min. About 4 ml of nitrosyl chloride was then condensed in the trap (cooled by a Dry Ice–cellosolve mixture). The liquid nitrosyl chloride was permitted to warm to room temperature and 0.5–1 ml was swept out of the system by means of the nitrogen or argon stream. Then, nitrosyl chloride remaining in the trap was routed through the mixture of complex and ethyl acetate. Either immediately or within a very short time, reaction began, as evidenced by a change in color of the mixture. Enough nitrosyl chloride was introduced into the mixture to insure complete reaction (that is, until there appeared to be no further change in color). At that time, the reaction vessel was evacuated for several minutes *via* the exit tube to remove excess nitrosyl chloride and then was refilled with inert gas.

For the $K_4Mo_2Cl_8$–NOCl and $[(C_2H_5)_4N]_3Mo_2Cl_9$–NOCl systems the product mixture was filtered through a Schlenk-type filtration apparatus which had been attached to the reaction flask through the ground glass joint that had served for entry of inert gas and nitrosyl chloride. Filtrate and solid remaining on the filter disk were treated as described under the individual systems. In the case of the $Mo_2(C_2H_3O_2)_4$–NOCl system, where there appeared to be complete solution of products after reaction, the solution was transferred under a nitrogen atmosphere to a 125-ml pressure equalizing dropping funnel and then added dropwise with stirring to a solution of triphenylphosphine oxide in deaerated ethyl acetate. The light yellow–green precipitate which formed was filtered in a Schlenk tube, washed with ethyl acetate and then petroleum ether, and vacuum-dried for 2 hr.

The following quantities of reactants were used in the three systems investigated: $K_4Mo_2Cl_8$, 1.20–1.80 g (1.90–2.85 mmol)–NOCl, 0.5–1.5 ml (12–36 mmol)–ethyl acetate, 25 ml; $Mo_2(C_2H_3O_2)_4$, 1.39 g (3.24 mmol)–NOCl, 1.75 ml (41 mmol)–ethyl acetate, 25 ml–triphenylphosphine oxide, 3.73 g (13.4 mmol) in 70 ml of ethyl acetate; $[(C_2H_5)_4N]_3Mo_2Cl_9$, 0.80–1,20 g (0.89–1.33 mmol)–NOCl, 0.7–1.00 ml (17–24 mmol)–ethyl acetate, 40 ml.

Results and Discussion

The $K_4Mo_2Cl_8$–NOCl System

The pale green solid which was separated from the yellow–green ethyl acetate solution proved to be essentially potassium chloride which was contaminated with molybdenum-containing material. Approximately two mol (1.94–2.15) of potassium chloride were isolated for every mol of starting material.

Addition of petroleum ether to the ethyl acetate filtrate gave a bright golden-yellow solid and a yellow–green filtrate. The solid was extremely sensitive to atmospheric moisture but reacted only slowly with dry oxygen. It was insoluble in carbon tetrachloride and dichloromethane but reacted with donor-type solvents such as acetone, dimethylformamide, acetonitrile, and ethyl acetate to give yellow–green solutions and a solid which was identified as potassium chloride.

The infrared spectrum of the golden-yellow solid exhibited bands at 1787(vw), 1690(vs), 960(m), 617(w), 572(w), and 327–313 cm^{-1} (vs, db). The very strong band at 1690 cm^{-1} lies within the region in which the N–O stretching frequency of the coordinated nitrosyl ligand commonly occurs [7, 8]. The weak bands at 617 and 572 cm^{-1} are attributable to the bending and Mo–N stretching modes of the Mo–N–O moiety [7–9]. The very strong doublet at 327–313 cm^{-1} might represent the stretching frequencies due to Mo–Cl bonds [9, 10]. For the product isolated from various reactions the absorption band at 960 cm^{-1} varied in intensity relative to that of the N–O band from weak to (in some cases) very strong. This band is assigned to the Mo=O stretch [11] and is believed to arise from the presence of a contaminant. This point is discussed later.

On the basis of elemental analysis, the golden-yellow solid is assigned the formula $K_2Mo(NO)Cl_5$. *Anal.* Calcd. for $K_2Mo(NO)Cl_5$: K, 20.50; Mo, 25.15; Cl, 46.48. Found: K, 20.27 ± 0.18; Mo, 25.26 ± 0.04; Cl, 46.01 ± 0.11. Between 0.81 and 0.99 mol of the compound was isolated per mol of starting complex, $K_4Mo_2Cl_8$. Thus roughly half of the molybdenum available in the starting material was accounted for as $K_2Mo(NO)Cl_5$, and all of the potassium as this compound plus potassium chloride.

The yellow–green filtrate, left after separation of $K_2Mo(NO)Cl_5$, was added, under a blanket of argon, to a solution of triphenylphosphine oxide in an ethyl acetate-petroleum ether solution (1:1) A pale lime-green solid precipitated. The material (mp 273 °C after purification) appeared to be relatively stable to air, its color remaining unchanged after an exposure of two weeks. It exhibited strong or moderately strong infrared absorption bands at 1703(vs), 969(m), 939(m), 897(s), and 305 cm^{-1} (m, br), in addition to bands accounted for by the presence of triphenylphosphine oxide ligand [12]. The very strong band at 1703 cm^{-1} is undoubtedly attributable to the presence of the coordinated nitrosyl group and the broad absorption at 305 cm^{-1} could be due to Mo–Cl stretching. The band at 969 cm^{-1}, like that in the same region found in $K_2Mo(NO)Cl_5$, is believed to arise from a contaminant containing the Mo=O grouping. The two absorptions at 939 and 897 cm^{-1} are also in the region where one would expect the Mo=O stretching frequency to occur [13, 14] and can be assigned to MoO_2-containing species with the oxygen atoms occupying *cis* positions in an octahedral coordination sphere [14–16]. As the analyses immediately below indicate, the bands at 939 and 897 cm^{-1} probably are also due to the presence of impurities.

Elemental microanalysis of the lime-green solid corresponded well with the formula $Mo(NO)Cl_3\cdot 2(C_6H_5)_3PO$. *Anal.* Calcd: C, 54.81; H, 3.83; N, 1.77; Cl, 13.48; P, 7.85. Found: C, 55.02 ± 0.04; H, 3.78 ± 0.04; N, 1.92 ± 0.01; Cl, 12.82 ± 0.25; P, 8.45 ± 0.08. At least 0.7 mol of the complex was isolated per mol of starting compound in each experiment on the $K_4Mo_2Cl_8$–NOCl system.

The complex was quite soluble in acetone, chloroform, dichloromethane, acetonitrile, and nitromethane. Solutions in the latter two solvents changed color after several hours. Conductivity measurements in fresh nitromethane solutions (concentration range, 4×10^{-5}–1×10^{-4} *M*) gave an average molar conductance of 237 ohm^{-1} cm^2 mol^{-1} at 25 °C. This value falls within the range for 3:1 electrolytes in nitromethane [17].

Substances of the stoichiometry $Mo(NO)Cl_3\cdot 2(C_6H_5)_3PO$ have been reported previously. Davis, Johnson and Al-Obaidi [18] synthesized such a material by an initial reaction of $Mo_2(CO)_8Cl_4$ with liquid nitrosyl chloride at –40 °C, followed by treatment of the product obtained, $[Mo(NO)Cl_3]_n$, with a solution of triphenylphosphine oxide in benzene. There are major differences in solubility and air-sensitivity between their compound and ours. Their compound was only slightly soluble in organic compounds and very air-sensitive. Bencze *et al.* [19] prepared $Mo(NO)Cl_3\cdot 2(C_6H_5)_3PO$ (impure) by reductive nitrosation of molybdenum(V) chloride with nitric oxide in benzene solution in the presence of triphenylphosphine. The N–O stretching frequency reported for all three preparations is essentially the same, but neither of the two earlier reports gives information about the region in which Mo=O stretching absorptions would be expected.

There is additional strong evidence that the three absorption bands at 960–970, 939, and 897 cm^{-1} can indeed be attributed to Mo=O stretching. It has already been noted that the absorption at 960 cm^{-1} found in samples of $K_2Mo(NO)Cl_5$ from different experiments varied in intensity relative to that of the N–O band. Moreover, if $K_4Mo_2Cl_8$ were allowed to react for 5–7 days with *excess NOCl* and products were isolated in the usual manner, the intensity of the N–O stretching band at 1690 cm^{-1} (found in $K_2Mo(NO)Cl_5$) diminished strikingly in intensity and the band formerly at 960 cm^{-1} shifted to 970 cm^{-1} and its intensity increased dramatically. In one case, no absorption band was observed in the N–O stretching region and the only major feature of the infrared spectrum was a strong band at 970 cm^{-1}. Elemental analysis of the potassium-containing compound isolated for three separate reactions gave the following average atomic ratios: $K_{1.66}Mo_{1.00}Cl_{4.89}$ (the potassium, molybdenum, and chlorine content accounted for 90.3% of the product). In view of these results, there is little doubt that the molybdenum had been substantially oxidized from its original dipositive state. In two reactions of long duration, the molybdenum remaining in solution, after isolation of the potassium-containing material, was precipitated as the 2,2′-bipyridine derivative. In each instance, the infrared spectrum exhibited strong bands at 930 and 899 cm^{-1}, and no absorption was present that could be assigned to a nitrosyl ligand. On the other hand, when a short reaaction time was employed, the spectrum of the bipyridine derivative had a strong absorption at 1701 cm^{-1} and only bands of medium intensity at 930 and 899 cm^{-1}. Analysis of the gas above the reaction mixture after runs of 5–7 days duration showed the presence of nitric oxide, in addition to ethyl acetate, nitrosyl chloride, and nitrogen dioxide. A gas-phase spectrum of freshly fractionally distilled nitrosyl chloride showed the expected bands in addition to weak absorptions characteristic of NO_2. These results suggest that the formation of Mo=O containing species arises from an initial attack on coordinated NO by nitrosyl chloride. However, attack by NO_2 impurity is not ruled out.

A few final remarks regarding the $K_4Mo_2Cl_8$–NOCl system should be made. First, the solvent, ethyl acetate, plays an important role in the system. In contrast to the relatively rapid reaction in this solvent, the molybdenum complex reacts only slowly with liquid nitrosyl chloride in a sealed tube at room temperature (to give mainly $K_2Mo(NO)Cl_5$) and *not at all* with the oxyhalide in dichloromethane. This behavior calls to mind the considerable enhancement of the reactivity of dinitrogen tetroxide toward metals (*e.g.*, copper and zinc) when donor solvents such as ethyl acetate are used as media for reaction [20]. It has been proposed that such solvents promote the autoionization of the tetroxide

$$N_2O_4 \leftrightarrows NO^+ + NO_3^-$$

by solvating the nitrosonium ions, the species responsible for reaction with metals. One can visualize a similar enhancement of ionization of nitrosyl chloride in ethyl acetate.

Second, it is surprising that, with the metal in a low oxidation state and nitrosyl chloride a strong oxidant, initial reaction occurs without oxidation of the molybdenum(II); the reaction appears simply to be chloronitrosation with cleavage of the metal–metal bonds.

The $Mo_2(C_2H_3O_2)_4$–NOCl System

Reaction between tetrakis(acetato)dimolybdenum and nitrosyl chloride occurred immediately in ethyl acetate to give a dark green solution. The light yellow–green precipitate [4.631 g from 1.39 g of $Mo_2(C_2H_3O_2)_4$], which was isolated as described in the Experimental Section, was shown by infrared spectrum and mixed melting point to be $Mo(NO)Cl_3 \cdot 2(C_6H_5)_3PO$. Based on the weight of starting material, 90.5% of the molybdenum was recovered as the triphenylphosphine oxide adduct. Again, the compound appeared to be contaminated with oxomolybdenum species. And again, it is striking and surprising that in the initial reaction no oxidation of molybdenum(II) took place. Thus, both species, $K_4Mo_2Cl_8$ and $Mo_2(C_2H_3O_2)_4$, which contain molybdenum in the +2 oxidation state and metal–metal quadruple bonds undergo chloronitrosation accompanied by cleavage of these bonds.

The $[(C_2H_5)_4N]_3Mo_2Cl_9$–NOCl System

The red-orange suspension of tris(tetraethylammonium)enneachlorodimolybdate(III) in ethyl acetate rapidly became yellow-green upon the introduction of nitrosyl chloride. The light yellow solid which formed was separated from a green solution and washed with deaerated dichloromethane. Yield: 0.34–0.46 g from 0.80–1.20 g of starting complex. The infrared spectrum of the material showed two strong bands at 1675 and 944 cm^{-1}, in addition to absorptions characteristic of the tetramethylammonium cation. The band at 1675 cm^{-1} is undoubtedly due to coordinated nitrosyl ligand; that at 944 cm^{-1}, which varied in relative intensity from one reaction to another, is assigned, as has been done previously for absorptions in that region, to Mo=O stretching.

Elemental analysis leaves little doubt that the light yellow solid is $[(C_2H_5)_4N]_2Mo(NO)Cl_5$ and indicates that any oxomolybdenum species present must be there in quite small amount. *Anal.* Calcd for $[(C_2H_5)_4N]_2Mo(NO)Cl_5$: Mo, 17.02; Cl, 31.44; C, 34.08; H, 7.17. Found: Mo, 17.5 ± 0.08; Cl, 31.65 ± 0.45; C, 34.32; H, 7.12. Cl/Mo ratio: 4.88. Yield: 30–40% based on starting complex.

Whereas conductivity information could not be obtained for $K_2Mo(NO)Cl_5$ (isolated from the $K_4Mo_2Cl_8$–NOCl system) because of its insolubility or decomposition in appropriate solvents, the conductivity of $[(C_2H_5)_4N]_2Mo(NO)Cl_5$ could be measured in nitromethane. In this solvent, the compound is appreciably soluble and decomposes only slowly. Three freshly prepared solutions of concentrations in the range of $1.5–3.4 \times 10^{-3}$ *M* gave molar conductances of 158, 169 and 150 ohm^{-1} cm^2 mol^{-1}, values well within the extremes for 2:1 electrolytes in the solvent [17].

Charge balance considerations dictate that in $[(C_2H_5)_4N]_2Mo(NO)Cl_5$ the Mo(NO) group must have a +3 charge. This raises the question of how tripositive molybdenum in $[(C_2H_5)_4N]_3Mo_2Cl_9$ can react with nitrosyl chloride without an apparent change in oxidation state. This can only happen if some of the molybdenum is oxidized and nitric oxide formed in the redox process is available for reaction with remaining starting complex.

The addition of petroleum ether to the green solution remaining after removal of $[(C_2H_5)_4N]_2Mo(NO)Cl_5$ gave a light green precipitate and a golden solution. Most of the green precipitate dissolved in deaerated dichloromethane to give a green solution from which a light-green solid (0.20–0.30 g) was obtained on the addition of petroleum ether. In addition to absorptions characteristic of the tetramethylammonium cation, the infrared spectrum exhibited strong or moderately strong bands at 3452(m) and 1612 cm^{-1}(s). The band at 1612 cm^{-1} is assigned to H–O–H bending [21] and that at 3452 cm^{-1} to the O–H stretching of water. These assignments are consistent with the analytical data cited below.

Analyses for molybdenum and chloride fit well the empirical formula $[(C_2H_5)_4N]MoCl_4 \cdot nH_2O$ (n =

1–2]. *Anal.* Calcd for n = 1: Mo, 24.9; Cl, 36.8. Calcd for n = 2: Mo, 23.8; Cl, 35.1. Found: Mo, 24.8 ± 0.06; Cl, 35.8 ± 0.3. Cl/Mo ratio: 3.90. Between 32 and 37% of the starting molybdenum was accounted for by the compound. The compound has been reported previously [22].

The golden solution left after separation of $[(C_2H_5)_4N]MoCl_4$ was treated with an ethyl acetate solution of triphenylphosphine oxide and a white precipitate formed. The infrared spectrum of the solid showed, in addition to absorption bands due to coordinated triphenylphosphine oxide, the following strong or moderately strong bands: 939(vs); 896(s); and 310 cm^{-1}(m). The first two absorptions, which have been referred to previously, are common for octahedral molybdenum complexes with two oxygen atoms occupying *cis* positions in the coordination sphere [14–16]. The band at 310 cm^{-1} can be assigned to Mo–Cl stretching.

Elemental analyses gave values which correspond well to the empirical formula $MoO_2Cl_2 \cdot 2(C_6H_5)_3PO$. *Anal.* Calcd: Mo, 12,71; C, 57.24; H, 3.97; Cl, 9.39; P, 8.21. Found: Mo, 13.05 ± 0.15; C, 56.03; H, 3.93; Cl, 9.82; P, 8.54. Mo:P:Cl:1.00:2.03:2.04. In two reactions, approximately 15% of the molybdenum was found as $MoO_2Cl_2 \cdot 2(C_6H_5)_3PO$. Thus a total of 77–92% of the starting molybdenum was recovered as the three compounds described in this section.

A compound of the same formula has been reported before [23]. It was described as being bright orange–yellow rather than white. It had a melting point of 216 °–218 °C, preceded by a color change from orange to colorless at 175°–185 °C; our material melted at 250°–252 °C. It was described as being insensitive to water; our compound changed to a light blue substance in that medium. The differences noted could be due to the fact that different isomers were obtained. Three isomers of $MoO_2Cl_2 \cdot 2(C_6H_5)_3PO$ are possible which have *cis*-dioxo ligands.

Some Final Observations

A word regarding the high stability of the $Mo(NO)Cl_3$ entity is in order. As already has been noted, it appears to be produced in polymeric form by the action of liquid nitrosyl chloride on $Mo_2(CO)_8Cl_4$ at –40 °C [18]. Our own work leaves little doubt that in solvated form it is present in ethyl acetate solution as one of the products of reaction of $K_4Mo_2Cl_8$ with nitrosyl chloride. Moreover, it is readily obtainable from $K_2Mo(NO)Cl_5$, one of the other products of that reaction. Thus, treatment of $K_2Mo(NO)Cl_5$ with ethyl acetate yields as a product potassium chloride, and addition of triphenylphosphine oxide to the resulting solution, after precipitation of unreacted potassium complex with petroleum ether, gives $Mo(NO)Cl_3 \cdot 2(C_6H_5)_3PO$ [3a]. Moreover, the latter compound is produced in 84% yield in reaction between $K_2Mo(NO)Cl_5$ and triphenylphosphine oxide in dichloromethane [3a]. The $Mo(NO)Cl_3$ species is certainly present in the solution resulting from reaction of $Mo_2(C_2H_3O_2)_4$ with nitrosyl chloride in ethyl acetate, for as we have shown in this paper, addition of the solution to one of triphenylphosphine oxide gives essentially quantitative yields of the adduct. In work not described in this paper, it has been found that a situation like that just described also exists when $K_4Mo_2Cl_8$ is permitted to react with nitrosyl fluoroborate in ethyl acetate [3b]. After removal of a precipitate consisting of potassium chloride and potassium fluoroborate, a practically quantitative yield of $Mo(NO)Cl_3 \cdot 2(C_6H_5)_3PO$ is obtained from the filtrate when it is added to a solution of the phosphine oxide in a mixture of ethyl acetate and petroleum ether.

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