studies would support the proposed mechanism, the absence of cyclic tetramer will still remain unexplained.

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The Molybdenum Carbonyl–Phosphorus Trifluoride System

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The carbon monoxide groups in molybdenum hexacarbonyl are readily replaced by phosphorus trifluoride using either high temperature–high pressure or atmospheric pressure–ultraviolet irradiation conditions. By various means, all possible compositions for monodentate substitution, including three pairs of *cis* and *trans* isomers, were identified. Most of these isomers could be clearly isolated by preparative gas–liquid chromatography. Substitution studies of the various compounds clearly indicate that PF_3 is a slightly stronger *trans* labilizer than CO. The compounds are colorless liquids or solids, with good thermal and hydrolytic stabilities and frequently having volatilities greater than that of the parent hexacarbonyl.

Introduction

The substitution of phosphorus trifluoride for carbon monoxide of metal carbonyls has been studied for a number of the metals, with the nickel tetracarbonyl[1] and iron pentacarbonyl[2] systems being studied with the greatest thoroughness. In these studies, all possible compositions were prepared, isolated, and characterized. Other studies of PF_3 complexes have been made, especially by Kruck,[3-5] in which a limited number of the possible complexes were prepared.

This paper reports work done on one of the hexacarbonyls—molybdenum hexacarbonyl. While the work was in progress, Kruck[4] and Schmutzler[6] reported the preparation of chromium and molybdenum compounds of the type $M(PF_3)_6$ and $M(CO)_3(PF_3)_3$ by indirect means. Their work also showed clear evidence for other compounds.

The identification of all possible compounds in the $Mo(CO)_x(PF_3)_{6-x}$ system including three pairs of *cis* and *trans* isomers is presented in this report. The preparation and actual isolation of most of the complexes will be described and information will be reported concerning the mode of the substitution reactions.

Experimental

The phosphorus trifluoride used during the latter portion of the work was obtained from K and K Laboratories. It was purified before use by bubbling it through a 12-in. tower of water packed with glass beads. This material was then dried by vacuum distilling it from a trap cooled to −95°. The remainder of the PF_3 used was prepared as described previously.[2]

Two methods were used for the preparation of substituted products. One was a high pressure–high temperature synthesis and the other was an atmospheric pressure–ultraviolet light-induced reaction. In the former technique, the sample handling and recovery procedures were essentially as described earlier,[2] but somewhat simplified by the use of $Mo(CO)_6$, which is a stable solid of low volatility. The reactions were allowed to proceed for 8–18 hr. at temperatures ranging from 175 to 325°. The higher reaction temperatures produced products predominating in the higher substitution compounds, and the lower reaction temperatures yielded products with a lower degree of substitution. To obtain the totally substituted compound by this technique, it was necessary to heat the vessel to the higher temperature, then cool it frequently to −195° and remove the carbon monoxide by vacuum. Attempts to use higher reaction temperatures resulted in extensive decomposition.

The ultraviolet method is particularly well suited for the preparation of products with a low degree of substitution. In a typical reaction, about 0.7 g. of $Mo(CO)_6$ and 20 ml. of spectral grade pentane were placed in a 1-l. flask equipped with a standard taper joint at the top and a 35-mm. long by 30-mm. diameter extension at the bottom. The main function of the bottom extension was to allow a better exposure angle, but it also contained a magnetic stirring bar to mix the contents. The flask was closed with an adaptor containing a vacuum stopcock and a joint for connection to a vacuum system. The flask was evacuated at room temperature until about half of the solvent had vaporized. This resulted in the complete removal of the air and the degassing of the solvent. Phosphorus trifluoride was admitted until its partial pressure was about 500 torr.

The lower portion of the flask was irradiated at nearly the full intensity of an AH-6 ultraviolet lamp while the contents were being stirred. (The lamp contained a Pyrex velocity tube, and the irradiation vessel was made of Pyrex; so it appears that the far-ultraviolet is not important.) For the production of predominantly mono- and disubstituted materials, an irradiation time of 1.5–2 hr. was used, and for di- and trisubstituted materials, 3–4 hr. Higher substitution was readily produced, although at a progressively slower rate, by extensive irradiation with the evolved carbon monoxide being removed frequently at −195°. So long as the flask was adequately degassed and the PF_3 was pure, no noticeable decomposition appears to take place. The product from the irradiation was recovered by cooling the

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[1] R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).

[2] R. J. Clark, *ibid.*, **3**, 1395 (1964).

[3] Th. Kruck, *Chem. Ber.*, **97**, 2018 (1964).

[4] Th. Kruck and A. Prasch, *Z. Naturforsch.*, **19b**, 669 (1964).

[5] Th. Kruck, *Angew. Chem.*, **76**, 593, 787, 892 (1964).

[6] R. Schmutzler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 150.

flask to −30 to −40° and evaporating the pentane under high vacuum.

The individual species are recovered by preparative gas–liquid chromatography using an Aerograph Model A-700. The best conditions found were as follows: a copper column, 27 ft. × 0.25 in., packed with 15% Dow-Corning silicone diffusion pump fluid on 30/60 mesh Kromat FB; column temperature 85–95°; detector temperature no more than 130°; helium gas flow of 70 ml./min. The sample size depended upon the compounds being prepared. For the mono- and disubstituted materials, the peaks are sufficiently well separated that 20 μl. of the neat liquid could be used at one time. In the case of the compounds with a higher degree of substitution, the separation was worse, so that less than half as much material could be used. In addition, a solvent was necessary since the PF_3-rich compounds are solids. The best solvent found for them was Freon 112 ($C_2Cl_4F_2$).

When samples are trapped at −78°, they are inevitably contaminated by water. The compounds were dried by distilling the samples *in vacuo* into a tube containing P_4O_{10}. After being allowed to stand for 30 min., the samples were distilled into a trap, sealed off, and stored at −78° until used. Molecular Sieves 4A appeared to cause decomposition of the compounds and, therefore, could not be used as in other systems.[1,2]

The substitution studies in solution were performed in a small vessel of about 10-ml. capacity which could be evacuated, filled with ligand gas, closed off from the vacuum system, and loaded with solvent and compound through a septum. The compounds tested were previously isolated and dried. The solvent was an unidentified component of commercial heptane isolated by g.l.c. which came off the column between the penta- and hexacarbonyls. In a typical reaction, 10 μl. of compound and 150 μl. of solvent were used. Samples were removed after various time intervals and analyzed chromatographically.

The reactivity of these compounds in the gas phase toward either CO or PF_3 was tested by admitting 15 μl. of an isolated intermediate into an evacuated 1-l. flask and then pressurizing the flask to about 600 torr with ligand gas. The flask was irradiated and the contents isolated and analyzed by g.l.c.

Infrared spectra were taken in hexane solution on a Perkin-Elmer 221.

Rough density measurements and solvent stability tests were made as described previously.[2]

Only limited analytical data were obtained to act as a final confirmation of the infrared and chromatographic identification of the species. The analyses were carried out by the Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

Results

Molybdenum hexacarbonyl reacts with phosphorus trifluoride by either the high pressure or the ultraviolet irradiation methods to yield a number of products. These products are indicated by gas–liquid chromatography and all have a shorter retention time than the parent carbonyl.

The high pressure synthesis is well suited for the preparation of several gram quantities of mixed products predominating in the di- to tetrasubstitution range. It is, however, difficult to control this reaction in order to obtain different types of mixtures. The ultraviolet approach is more subtle and allows the synthesis of mixtures of species predominating in any desired range.

The species produced by either method are identified by several approaches. The general manner of their production by ultraviolet irradiation, when studied as a function of time, gives a fairly clear assignment of many of the compounds. This assignment is based on the rather obvious assumption that the replacement of the CO groups will be sequential and will result in first the monophosphine, then the disphosphines, etc. Thus, the first peak to show up during irradiation has the next-to-the-longest retention time and must be the monophosphine. Next, a pair of peaks appears with slightly shorter retention times and these must be the *cis*- and *trans*-diphosphines. This assignment approach can be continued throughout the series.

The retention time pattern shown with the molybdenum system conforms with the pattern shown in all other systems studied thus far. Hence, as the degree of PF_3 substitution increases, the retention progressively decreases. The retention times relative to the hexacarbonyl are shown in Table I.

TABLE I

PHYSICAL DATA ON $Mo(CO)_x(PF_3)_{6-x}$ COMPOUNDS

	ν C–O, cm.$^{-1}$	ν P–F, cm.$^{-1}$	M.p., °C.	Rel. retention time
$Mo(CO)_6$	1988[a]	. . .	145[a]	1.00
$Mo(CO)_5(PF_3)$	2104 m 2012 s 1990 s	904 w 874 m 865 w	5	0.60
cis-$Mo(CO)_4(PF_3)_2$	2087 s 2011 s 2014 s 1990 s	892 s 872 m 852 s	32	0.40
trans-$Mo(CO)_4(PF_3)_2$	1988 s	884 s 851 s	10	0.34
cis-$Mo(CO)_3(PF_3)_3$ (1,2,3)	2065 s 2012 s	908 s 888 m 875 m 852 s	64	0.30
trans-$Mo(CO)_3(PF_3)_3$ (1,2,6)	2075 m 2015 m 1990 m	908 m 892 s 872 m 850 s	42	0.27
cis-$Mo(CO)_2(PF_3)_4$	2048 s 2010 s	928 m[b] 892 s 875 w 849 s	. . .	0.20
trans-$Mo(CO)_2(PF_3)_4$	1989 s	*b*	. . .	0.19
$Mo(CO)(PF_3)_5$	2029 s	949 m 901 s 888 sh 846 s	45	0.23
$Mo(PF_3)_6$	. . .	902 s 845 s	196[c]	0.22

[a] Literature value. [b] The PF_3 regions for the *cis* and *trans* dicarbonyls were not resolved. [c] Th. Kruck, ref. 5.

The qualitative identification has been confirmed by a study of the infrared spectra. The carbonyl stretching frequencies are shown in Table I. The spectra of the compounds that correspond with previously known compounds are analogous to their well-characterized counterparts. Calculations made by Haas and Sheline[7] have shown that the spectra of the new compositions have the number of peaks that are expected on the basis of group theory. Furthermore, calculation of the frequencies to be expected for all of these compounds, using certain fixed *cis* and *trans* interaction constants, has shown internal consistency for all species having a standard deviation of only 0.8 cm.$^{-1}$ from the measured values.

(7) H. Haas and R. K. Sheline, to be published.

As a final confirmation, a limited amount of analytical data was obtained, which showed fairly good agreement with the expected percentages. *Anal.* Calcd. for $Mo(CO)_5(PF_3)$: C, 18.54; P, 9.56. Found: C, 18.76; P, 10.35. Calcd. for *cis*-$Mo(CO)_4(PF_3)_2$: C, 12.51. Found: C, 13.11. Calcd. for *trans*-$Mo(CO)_3(PF_3)_3$: C, 8.12; F, 38.52. Found: C, 7.86; F, 35.0. Calcd. for mixture of *cis*- and *trans*-$Mo(CO)_2(PF_3)_4$: C, 4.77. Found: C, 4.57. Calcd. for $Mo(CO)(PF_3)_5$: C, 2.13; P, 27.46; F, 50.55. Found: C, 1.97; P, 27.60; F, 50.58.

The compounds are colorless and are either liquids or solids which have, in general, low melting points. The species that are liquids are the pentacarbonyl and the *trans*-tetracarbonyl, with the *cis*-tetracarbonyl melting at 32°. The difficulty of separating the tetraphosphines in high purity precluded determining their melting points. Kruck and Prasch[4] have reported the melting point of $Mo(PF_3)_6$ to be 196°.

Vapor pressures have not been measured for these compounds, but the behavior of the purified species in a vacuum system clearly indicates that the volatility of the pentacarbonyl is much greater than that of the parent hexacarbonyl. The tetra- and tricarbonyls have roughly the same volatility as the pentacarbonyl, and then as the degree of substitution increases, the volatility becomes less. The totally substituted material can still be readily sublimed under high vacuum.

The compounds are moderately stable toward most general conditions. They are attacked by deoxygenated water only after several days, yielding first a blue solution and then, slowly, further darkish products. No noticeable reaction takes place in a few days in dry air. Nonhydroxylic solvents, like hydrocarbons or fluorocarbons, give stable solutions, but solvents like alcohol and acetone rapidly destroy the compounds without any apparent gas evolution. The moderate stability toward water is probably associated with the extreme insolubility of the compounds in this medium, as contrasted to their solubility behavior toward organic solvents. Thermal decomposition yields a black residue, but it has not been determined which of the many potential products, like metal and metal phosphides, are formed.

The general results of the irradiation of heptane solutions of the $Mo(CO)_x(PF_3)_{6-x}$ species in the presence of PF_3 are discussed below. Molybdenum hexacarbonyl, of course, yields first the monophosphine, followed successively in time by varying proportions of the diphosphines and triphosphines. A sample of the pure monophosphine yields, in the early stages, about 60% *cis*- and 40% *trans*-diphosphine, followed later by the tri- and tetraphosphines. A pure sample of *cis*-diphosphine yields roughly 60% *trans*-triphosphine and 40% *cis*-triphosphine in the early stages of reaction. The *trans*-diphosphine, as expected, gives a high yield of the *trans*-triphosphine—about 90%—but, in addition, some small percentages of *cis*-diphosphine and *cis*-triphosphine.

A small sample of pure monophosphine, sealed in a glass ampoule and freed of carbon monoxide or phosphorus trifluoride, disproportionates slowly. In 1 hr. perhaps 10% of the sample disproportionates, yielding the expected quantities of hexacarbonyl and mixed diphosphines. Similar results are found in solution. This disproportionation is much less rapid than the substitution in the presence of either CO or PF_3.

The behavior of the monophosphine toward CO and toward PF_3 was contrasted. It was found that carbon monoxide replaces a phosphine much less rapidly than the phosphine replaces a carbonyl group under similar conditions.

Finally, the ultraviolet reaction of the monophosphine in the gas phase with CO and PF_3 was studied qualitatively. The substitution was quite extensive and rapid. In the presence of PF_3, a mixture of di-, tri-, and tetraphosphines was produced in 30 min. A similar quantity of the monophosphine was converted almost completely to the hexacarbonyl in the presence of carbon monoxide in the same length of time. No sign of disproportionation was seen.

Discussion

The free substitution of phosphorus trifluoride into molybdenum hexacarbonyl extends the observations that have already been made in the nickel tetracarbonyl and iron pentacarbonyl systems. With these three compounds, all possible substitution compositions were obtained. This is the first time that all possible monodentate substitution compounds for a hexacarbonyl have been obtained. In addition, the unique feature of the identification and usually the isolation of the *cis* and *trans* isomers has been added.

The presence of isomers in the molybdenum system has an important bearing on observations made with other systems. With the tetrahedral nickel compounds, no isomerism is to be expected. However, with the pentacoordinated iron compounds, several isomers of each mixed composition are to be expected for either a trigonal bipyramid or square pyramid structure. These were not found.[2] Since the isomers in the hexacoordinated systems were so readily isolated, owing to clear differences in properties, support is given to the theory that the pentacoordinated compounds are undergoing a rapid internal rearrangement and are not just accidentally identical in properties.

The trends of physical properties of the molybdenum compounds generally conform to those found in the previous systems. In contrast to most ligands which substitute into metal carbonyls, PF_3 does not cause an increase in the melting point of the material and a decrease in the volatility. To the contrary, the insertion of the first PF_3 group markedly increases the volatility and decreases the melting point to the extent that the monophosphine becomes liquid. Many of the compounds are either liquids or low melting solids. The stability toward thermal degradation and toward various reagents is comparable to that of the iron and nickel systems.

The infrared patterns of these compounds correspond to analogous compounds reported in the literature, or to those predicted on the basis of group theory. The only points of immediate comparison are with the spectra of compounds reported by Schmutzler[6] and Kruck and Prasch.[4] These compounds are of the compositions $Mo(CO)_3(PF_3)_3$ and $Mo(PF_3)_6$. The former would be expected to be the *cis* isomer on the basis of the method of synthesis, but the reported spectrum has one too many bands. The presence of the extra band could be attributed to isomerization to some of the *trans* isomer which has roughly the spectrum reported. Alternately, the extra band could be explained by the presence of an impurity such as $Mo(CO)_6$, *trans*-$Mo(CO)_4(PF_3)_2$, or *trans*-$Mo(CO)_2(PF_3)_4$, any of which have a single band at about the position of the lowest frequency. Otherwise, the pattern obtained for the *cis*-tricarbonyl agrees well with the value reported by Kruck and Prasch,[4] with the values in this study shifted about 8 cm.$^{-1}$ to lower frequency, owing perhaps to a solvent shift. The spectrum of the *cis*-tricarbonyl used in calculations by Cotton[8] has the proper number of peaks, but these peaks are listed at considerably higher frequencies than those reported in this study. The pattern for $Mo(PF_3)_6$ in the P–F region agrees well with the values of Kruck and Prasch.[4] We also obtained a weak peak in the carbonyl region which is identical with the carbonyl peak for the pentaphosphine.

On comparing the carbonyl infrared frequencies obtained in this study to the rather extensive tables collected by Cotton,[8] it is found that the carbonyl frequencies for the PF_3 complexes always occur at higher frequencies than for any other complexes reported. This is consistent with the view that PF_3 is one of the strongest π-bonding ligands.

The substitution studies clearly show the PF_3 group to be a stronger *trans* labilizing group than carbon monoxide—at least under conditions of ultraviolet radiation. On a statistical basis, one would expect the monophosphine to yield 80% of the *cis*-diphosphine isomer and 20% of the *trans*-diphosphine. The fact that the *trans* isomer was formed in considerably greater than 20% yield points to a *trans* labilizing influence.

Similar results were evident from the study of the two disubstituted species. On a statistical basis, the *cis*-diphosphine would be expected to yield equal quantities of the *cis*- and *trans*-trisubstituted species. The actual yield of about 60% *trans*-triphosphine shows once again that the groups *trans* to the PF_3 are replaced slightly more easily than the ones *trans* to the carbonyl groups.

With the *trans*-diphosphine, only the *trans*-triphosphine should result. Better than 90% of the yield is this product. However, there is clear evidence for disproportionation since the appearance of *cis*-disphosphine and *cis*-triphosphine can result only from this source.

If the ability of a ligand to labilize the *trans* position is explained on the basis of π bonding,[9] one would then conclude that phosphorus trifluoride must have a slightly greater ability to π-bond to molybdenum than carbon monoxide. This conclusion is consistent with arguments made by Cotton.[8] It is also consistent with qualitative observations made on the basis of fluorine magnetic resonance shift data.[1] The calculations made by Sheline and Haas[7] also point to the conclusion that PF_3 π-bonds to a slightly greater degree than CO.

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[8] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[9] See, for example, F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.* **4** 429 (1962).