a method similar to that reported by Tait and Busch for the synthesis of the nickel(II) analogues.[22] The synthesis of $Cu(\mathbf{9})(ClO_4)_2$ was done as follows: To a 100-mL methanolic solution containing 0.04 mol of both 1,3-propanediamine and HCl (added as the concentrated aqueous solution), cooled in an ice bath, was added dropwise 0.04 mol of 2,3-butanedione (biacetyl) with vigorous stirring. After addition of the biacetyl, the solution was removed from the ice bath and allowed to stand at room temperature. After about 30 min copper(II) acetate (0.02 mol) dissolved in 80 mL of MeOH was added and the solution was stirred for 12 h after which 0.04 mol of 70% $HClO_4$ was added dropwise and the solution was evaporated to about 50 mL on a rotary evaporator. When the solution stood, large, square, violet crystals formed, which were removed by filtration, washed with small portions of cold ethanol, and dried in vacuo over P_4O_{10}. The yield was 25%. An analogous procedure was employed for the synthesis of $Cu(\mathbf{8})(ClO_4)_2$. All the complexes analyzed satisfactorily for carbon, hydrogen, and nitrogen.

Electrochemistry. Conventional and differential pulse polarography studies were performed with use of a Metrohm Polarecord E 506 apparatus. CV measurements were carried out with the Electrochemolab system (Amel, Milan, Italy) by using a hanging mercury drop electrode (Metrohm). In any case the counterelectrode was a platinum electrode and the reference electrode (SCE) was separated from the solution by a bridge containing aqueous 0.1 M NaCl. Erba RPE methanol was employed without further treatment. Polarographic grade tetraethylammonium fluoborate (Erba, Milan) was kept over P_4O_{10} in vacuo for 1 day or more prior to use.

Registry No. $Cu(\mathbf{3})^{2+}$, 60836-37-5; $Cu(\mathbf{3})^{+}$, 80502-45-0; $Cu(\mathbf{6})^{2+}$, 60836-37-5; $Cu(\mathbf{6})^{+}$, 80502-46-1; $Cu(\mathbf{7})^{2+}$, 80502-47-2; $Cu(\mathbf{7})^{+}$, 80502-48-3; $Cu(\mathbf{8})^{2+}$, 80502-49-4; $Cu(\mathbf{8})^{+}$, 80502-50-7; $Cu(\mathbf{9})^{2+}$, 71170-97-3; $Cu(\mathbf{9})^{+}$, 80502-51-8.

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Molybdenum Nuclear Magnetic Resonance Studies of Trifluorophosphine Complexes

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The similarity of carbon monoxide and phosphorus trifluoride as ligands toward lower valent metals has been well documented.[1] During the characterization of the complexes, the NMR spectra of various species of the type $M(PF_3)_x(CO)_y$ have been examined in some detail.[2] These studies have utilized either the phosphorus-31 or the fluorine-19 resonance and occasionally carbon-13, but the central metal atoms have been little studied. The first two nuclei have inherently high sensitivity, but there are some limitations to ^{31}P and ^{19}F NMR. For instance, diphosphines of the type $Mo(PF_3)_2(CO)_4$ have an $AA'X_3X'_3$ second-order pattern that is not always totally resolved. The second-order coupling in the triphosphines and higher phosphines generally prevents one from obtaining much information from the spectra.

NMR and other spectroscopic studies generally support the original assumption[3] that CO and PF_3 are quite similar as ligands. However, recent results in some nuclear hot-atom studies[4] and investigations into photocatalysis[5] have clearly shown them not to be identical. These results have, in turn, led to our current efforts to determine the equilibrium constants in the scrambling reactions among species in systems such as $Mo(PF_3)_x(CO)_{6-x}$.

The recent availability of a versatile multinuclei spectrometer[6] has led us to attempt an in situ analysis by metal NMR. One immediate potential benefit is that all spectra would be first order. The two nuclei are ^{95}Mo and ^{97}Mo. Both nuclei have spin $^5/_2$ with reasonable abundances and similar receptivities, about twice that of carbon.

The line width of ^{95}Mo has been reported as 0.7 Hz for the octahedral $Mo(CO)_6$. A ^{97}Mo spectrum will be 132 times broader than that of ^{95}Mo owing to a difference of 11.4 in the quadrupole moments for the two nuclei.[7] Accordingly, only limited efforts were made to obtain ^{97}Mo spectra. If the PF_3 and CO ligands are as much alike as we suppose, then the $Mo(PF_3)_x(CO)_{6-x}$ species will have pseudo-O_h symmetry and will not be too broadened by the lower symmetry.

The chemical shift is expected to be a sensitive parameter. Estimates and measurements have indicated a chemical shift range of about 4000 ppm.[8] One example of the known sensitivity is the substitution of D_2O for H_2O as a solvent for Li_2MoO_4 and Na_2MoO_4, which results in a shift of 1 ppm in the ^{95}Mo resonance.[9] Substituting sulfur for oxygen in $MoO_4{}^{2-}$ causes a shift of 500 ppm for each substitution.[10]

After this investigation was completed, Schmidt and Rehder[11] published a report of some phosphine complexes of vanadium carbonyls. The shielding differences between the various PF_3 complexes, although small, is significant (10–20 ppm). Similarly, a report[12] of some phosphine complexes of molybdenum indicates significant chemical shifts are present when CO is replaced by $P(OCH_3)_3$ and $P(OC_2H_5)_3$.

This investigation concerns the study of the chemical shifts, coupling constants, and line widths of a series of $Mo(PF_3)_x(CO)_{6-x}$ species.

Experimental Section

The molybdenum compounds were prepared by literature methods[13] from $Mo(CO)_6$ and PF_3. The $Mo(PF)_x(CO)_{6-x}$ mixtures were made in quantities such that before gas chromatographic separation, preseparation was done on a 24-in. spinning-band distillation column under reduced pressure. By this technique, residual $Mo(CO)_6$ was quantitatively removed (left in the pot). Of the remaining species, only $Mo(PF_3)(CO)_5$ was obtained essentially pure. The higher phosphines (at least up to the tetraphosphines) were the more volatile with progressively lower volatility down to the hexacarbonyl. At constant pressure, the distillation temperature range was only about 6° for the seven compounds between $x = 4$ and 1.

^{95}Mo and ^{97}Mo were both observed in 25-mm NMR tubes generally with $CDCl_3$, C_6F_6, or cyclohexane as solvents. The SEMINOLE magnet operates at a field of 3.52 T, and ^{95}Mo was observed at 9.754 MHz and ^{97}Mo at 9.961 MHz. Pulse widths were 40–50 μs for a 90° flip. Chemical shifts were checked relative to $Mo(CO)_6$ dissolved in the same solvent as the sample. At the time this work was done, an internal lock and absolute frequency standard was not available. However, the drift of the solenoid was not significant.

Results and Discussion

The first sample run showed clear evidence that there is less chemical shift among the species than we expected. A neat,

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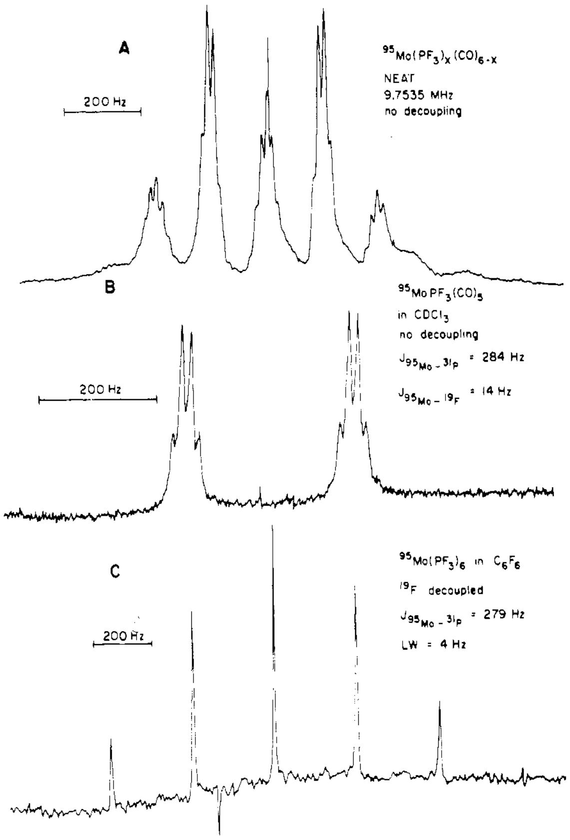

Figure 1. ^{95}Mo spectrum: A, neat mixture of Mo(PF$_3$)$_x$(CO)$_{6-x}$ species, approximate composition of 40% monophosphine, 35% *cis*-diphosphine, and 10% *trans*-diphosphine, plus others; B, ^{95}Mo(PF$_3$)(CO)$_5$ in CHCl$_3$; C, ^{95}Mo(PF$_3$)$_6$ in C$_6$F$_6$, ^{19}F decoupled.

unseparated mixture of Mo(PF$_3$)$_x$(CO)$_{6-x}$ (40% monophosphine, 35% *cis*-diphosphine, 10% *trans*-diphosphine, plus others) gives an overlapping spectrum as shown in Figure 1A. It is best interpreted as a doublet for the monophosphine and a triplet for the diphosphines in which molybdenum–phosphorus coupling is responsible for the major splittings. The molybdenum–fluorine coupling is observable but not clearly resolved in the mixture. In this sample, the doublet and triplet are almost superimposed on the same center and the *cis*- and *trans*-Mo(PF$_3$)$_2$(CO)$_4$ species are as one. One can imagine that spectral components can be seen for the less abundant species, but it is clearly not possible from this spectrum to do an in situ analysis of the mixture.

Both fluorine and phosphorus decoupling were done in an effort to sharpen the spectrum and possibly improve the resolution. Fluorine decoupling sharpens the basic doublet and triplet and shows clearly that minor components are present. However, even under these conditions, the spectral features overlap. Phosphorus decoupling produces a single peak of about 50-Hz line width at half-height. This width includes all of the fluorine coupling. The chemical shift between Mo(PF$_3$)(CO)$_5$ and Mo(PF$_3$)$_2$(CO)$_4$ can amount to only a few Hz at most.

In order to gain more information concerning the individual components, it was necessary to isolate them and run their spectra individually. Since many are solids at room temperature and/or available in only small quantities, they were run in solvents.

A typical coupled spectrum of ^{95}Mo(PF$_3$)(CO)$_5$ in CDCl$_3$ is shown in Figure 1B. The coupling of ^{95}Mo to ^{31}P is 284 Hz and to ^{19}F is 14 Hz. The spectrum is not as sharp as that of Mo(CO)$_6$ which has a line width of 1.2 Hz, but its doublet of quartet character is clearly seen. (Much of the line width of Mo(CO)$_6$ must be magnet inhomogeneity since a ^{97}Mo(CO)$_6$ spectrum reveals a line width of only 6 Hz).

Table I. ^{95}Mo–^{31}P Coupling Constants (Hz) for the Mo(PF$_3$)$_x$(CO)$_{6-x}$ Species

Mo(PF$_3$)(CO)$_5$	284	*mer*-Mo(PF$_3$)$_3$(CO)$_3$	290
cis-Mo(PF$_3$)$_2$(CO)$_4$	281	Mo(PF$_3$)$_6$	279
trans-Mo(PF$_3$)$_2$(CO)$_4$	288	MoP(OCH$_3$)$_3$(CO)$_5$	219
fac-Mo(PF$_3$)$_3$(CO)$_3$	290		

The *cis*- and *trans*-Mo(PF$_3$)$_2$(CO)$_4$ spectra show the expected triplet character caused by the large phosphorus coupling. The fluorine coupling makes it difficult to discuss the line widths clearly. However, the fluorine fine structure is seen in the C_{2v} cis isomer and it is not really resolved in the D_{4h} trans isomer. (The PF$_3$ group is being treated as a point.)

The triphosphine isomers were run fluorine decoupled to improve the signal to noise ratio since the difficulty in their preparation severely limited the sample size. Both give a quartet pattern expected of three equivalent PF$_3$ groups. The facial C_{3v} isomer has three equivalent phosphines, but the meridial C_{2v} isomer does not. In the later compound, there are two equivalent axial phosphines and one equatorial phosphine. However, the fluorine decoupled spectrum of *mer*-Mo(PF$_3$)$_3$(CO)$_3$ reveals no sign of the inequivalence. Again, there is very little chemical shift relative to Mo(CO)$_6$.

The fluorine-decoupled ^{95}Mo spectrum of Mo(PF$_3$)$_6$ shows clearly five lines of the expected heptet with the final two outside lines barely resolved from the base line. The shift relative to Mo(CO)$_6$ is <3.4 ppm upfield. This spectrum is shown in Figure 1C. Solubility of the complex presented a serious problem with C$_6$F$_6$ being the best solvent that we were able to find. The line width of this compound is a narrow 4 Hz, which is probably attributable to the compound's rigorous octahedral symmetry. The ^{97}Mo spectrum is an unresolved peak with a line width of 990 Hz. This is considerably greater than the anticipated 132-fold increase based upon the relative quadrupole moments. However, the unresolved phosphorus coupling almost certainly gives the additional width.

The ^{95}Mo–^{31}P couplings for the Mo(PF$_3$)$_x$(CO)$_{6-x}$ species are summarized in Table I. The coupling constants show more variation than the chemical shift values. We attempted to resolve the ^{97}Mo–^{31}P coupling in Mo(PF$_3$)(CO)$_5$, but the efforts were hampered by the added broadness of the ^{97}Mo spectra. With more fluid solvents such as cyclohexane and elevated temp., the ^{97}Mo–^{31}P couplings appear to be resolved and approximately 254 Hz, but the sample also disproportionated under the conditions we chose. Once the proper conditions are found, the ^{97}Mo–^{31}P coupling will almost certainly be seen.

In a final effort to put the very small chemical shift of the Mo(PF$_3$)$_x$(CO)$_{6-x}$ species in perspective, a different compound, MoP(OCH$_3$)$_3$(CO)$_5$, was run. This compound[14] is a liquid and quite miscible in solvents such as cyclohexane so large amounts can be used. The ligand trimethyl phosphite is different from trifluorophosphine in being both a better σ donor and a poorer π acceptor.[15] To us, the surprising feature is that the readily observed, sharp (7 Hz) doublet of the monophosphite is nearly centered on the singlet of Mo(CO)$_6$ in the same solvent. The chemical shift of the phosphite is no more than 1.5 ppm to low field. Whether the narrow range of chemical shift (of an estimated 4000-ppm range) represents a characteristic of organic phosphine-substituted molybdenum hexacarbonyls or merely an interesting coincidence, we are not prepared to say. The same similarity was found by Masters et al.[11] for monosubstituted triethyl phosphite but not for trisubstituted phosphite.

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It is not at all clear at this stage why these trifluorophosphine complexes should show so little difference in shielding as one varies either composition or structure. This is certainly contrary to the experience found with vanadium[11] and with cobalt[16] (in comparing $HCo(CO)_4$ with $HCo(PF_3)_4$).

In the process of doing the fluorine- and phosphorus-decoupling work, both the fluorine and phosphorus spectra of a $Mo(PF_3)_x(CO)_{6-x}$ mixture was run: it is still not possible to see the spectrum of the individual components resolved from one another. The chemical shift, though present, is still small relative to the spectral broadening caused by second-order interaction.

Conclusion

^{95}Mo NMR spectra can be readily run given adequate sample in solution and sharp enough lines. In our case 0.3–0.5 g of sample in 25 mL of solvent (about 0.05 M) is approaching the practical limit when pulsing overnight. In the case of $Mo(PF_3)(CO)_5$ or $MoP(OCH_3)_3(CO)_5$, where 5–10 g of sample was present, a crude spectrum can been seen in a single pulse. It is clear that in situ NMR analysis of a series of $Mo(PF_3)_x(CO)_{6-x}$ compounds *cannot* be done without use of additional techniques.

Registry No. $Mo(PF_3)(CO)_5$, 45322-05-1; *cis*-$Mo(PF_3)_2(CO)_4$, 45281-94-4; *trans*-$Mo(PF_3)_2(CO)_4$, 15282-05-0; *fac*-$Mo(PF_3)_3(CO)_3$, 15280-12-3; *mer*-$Mo(PF_3)_3(CO)_3$, 15280-14-5; $Mo(PF_3)_6$, 15339-46-5; $Mo[P(OCH_3)_3](CO)_5$, 15631-20-6.

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One-Electron Reduction of 18-Molybdodiphosphate and 18-Tungstodiphosphate Ions in Aqueous Solution. A Pulse Radiolysis Study

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Heteropoly electrolytes to molybdenum and tungsten with Keggin structure[1] (e.g., $[PW_{12}O_{40}]^{3-}$) and Dawson structure[2] (e.g., $[P_2W_{18}O_{62}]^{6-}$ and $[P_2Mo_{18}O_{62}]^{6-}$, henceforth designated as $(P_2W_{18}{}^{6-})$ and $(P_2Mo_{18}{}^{6-})$, respectively) are known to be capable of being reduced in distinct steps without decomposition. However, whereas the reduction of tungstates can be resolved into one-electron steps, the one-electron reduction of $(P_2Mo_{18}{}^{6-})$ has never been reported.

For the polarographic reduction of $(P_2Mo_{18}{}^{6-})$ in acidic solution, the polarographic waves are pH dependent and reduction is accompanied by protonation.[3] Cyclic voltammetry with sweep rates up to 120 V s^{-1} did not reveal intermediate (one, three, and five) electron reduction products.[3b] For $(P_2W_{18}{}^{6-})$, the polarographic work has shown that reduction is not accompanied by protonation; in these experiments, the one-electron heteropoly blue is stable in the absence of oxygen for hours. Now, electrodes are multielectron donors and the nearly simultaneous addition of two electrons is possible if the two steps have similar values of the redox potentials.

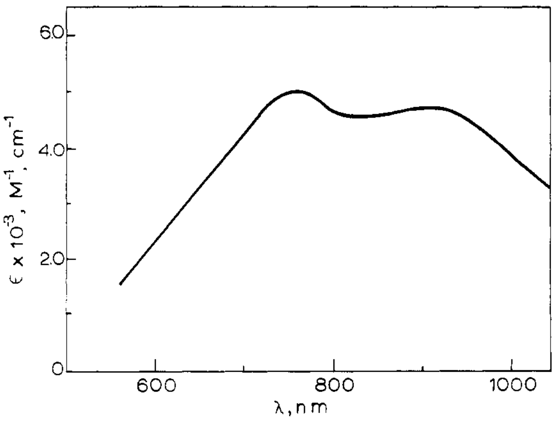

Figure 1. Spectrum of the one-electron reduction product from the reaction of $(CH_3)_2\dot{C}OH$ with $(P_2W_{18}{}^{6-})$ at pH 2 in 0.1 M $(CH_3)_2CHOH$.

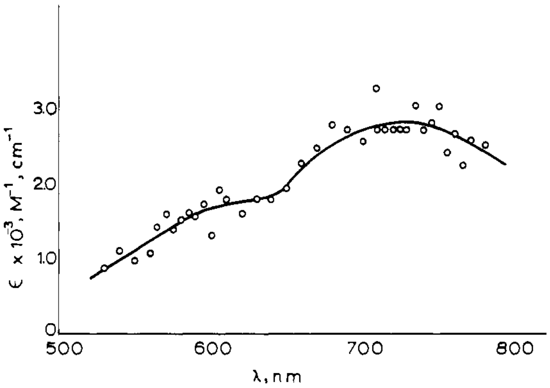

Figure 2. Spectrum of the one-electron reduction product from the reaction of $(CH_3)_2\dot{C}OH$ with $(P_2Mo_{18}{}^{6-})$ at pH 2 in 0.5 M $(CH_3)_2CHOH$.

The technique of pulse radiolysis permits the rapid generation of reducing agents that are capable of only one-electron transfer and the detection of the reduction products by optical spectrophotometry. In this way, the one-electron reduction product of $(P_2Mo_{18}{}^{6-})$ can be generated, characterized, and compared with that of $(P_2W_{18}{}^{6-})$. It should be noted that although the ESR spectrum of the one-electron blue from $(P_2W_{18}{}^{6-})$ has been recorded, no corresponding spectrum from reduced $(P_2Mo_{18}{}^{6-})$ in aqueous solution has been obtained.[4]

Experimental Section

Literature methods[5] were used for the preparation of $(P_2Mo_{18}{}^{6-})$ and $(P_2W_{18}{}^{6-})$; no dioxane was used in the recrystallizations in order to avoid the presence of adsorbed dioxane,[6] which interferes with the experiments. All chemicals were analytical grade, and distilled water was further treated by passage through a Millipore purification train.

The Febretron 705 pulse-radiolysis apparatus with optical absorption spectrophotometry detection at the U.S. Army Natick Research and Development Command, which delivers a 30-ns pulse of 2.3-MeV electrons, has been previously described.[7] Radiation dosimetry was performed with 0.1 M KSCN, taking ϵ_{500} 7.6 × 10^3 M^{-1} cm^{-1} for the $(SCN)_2{}^-$ radical.[8]

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