voltammetric experiments, *i.e.*, much shorter than the polarographic drop life. The label "slow" implies a reaction with a half-life which is somewhat longer than the polarographic drop life, but much shorter than the time required for controlled-potential electrolysis. The existence of a "slow" chemical step complicates matters in that a statement of the effective over-all reaction differs for the polarographic and controlled potential electrolysis time scales. For polarographic and cyclic voltammetric conditions, reactions IIa–g are important and the over-all stoichiometry is given by reaction 8. For the times involved in controlled-potential electrolysis, all reactions in Mechanism II are important and the over-all process simplifies to reaction 9.

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# A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Derivatives of Group VI Metal Carbonyls[1,2]

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**Abstract:** The phosphorus-31 chemical shifts are reported for 25 compounds of the type $(R_nPh_{3-n}P)M(CO)_5$, where R is alkyl, *n* is 0, 1, 2, or 3, and M is Cr, Mo, or W. The $^{183}$W–$^{31}$P spin–spin coupling is observed for all the tungsten compounds, and a linear correlation exists between these coupling constants and the carbonyl stretching frequencies in the respective compounds. In addition, the novel compound *trans*-tributylphosphinetriphenylphosphinemolybdenum tetracarbonyl is described. Its $^{31}$P nmr spectrum exhibits phosphorus–phosphorus spin–spin coupling.

It has become evident in the past few years that $^{31}$P nmr studies can be of great value in the investigation of bonding and structure in coordination compounds. In the first paper in this field Meriwether and Leto[4] outlined various effects that may influence the chemical shift of phosphorus. Subsequent papers[5–18] have dealt with these effects and additional problems such as the influence of valency on chemical shift[11] or the effect of *cis–trans* isomerism on heavy metal–phosphorus coupling constants.[5,14,15,18]

In an attempt to provide additional pertinent information, monosubstituted tertiary phosphine complexes of the group VI metal carbonyls were investigated. These compounds are relatively easy to prepare and allow comparisons of variation in chemical shift with changing atomic weight of the metal while the valency and stereochemistry remain constant. The effect of changing the organic substituents on phosphorus can also be noted. In addition, useful information can be obtained from $^{183}$W–$^{31}$P spin–spin coupling constants.

## Experimental Section

The phosphorus-31 nmr measurements of concentrated dichloromethane solutions in 15-mm tubes were recorded with a Varian Associates DP60 nmr spectrometer. Calibrations were made using a 2-mm tube of 85% phosphoric acid inside the 15-mm sample tube. Chemical shifts are accurate to ±0.5 ppm and phosphorus–tungsten coupling constants to ±8 cps. Dilution of the solutions caused no noticeable chemical shift changes. Addition of excess tertiary phosphine to the solution of a complex compound resulted in an extra peak for the uncomplexed ligand with the same chemical shift as the pure ligand and no change in chemical shift of the complexed phosphine. This indicates that ligand exchange is not rapid enough to cause chemical shift averaging of complexed and free ligand. Several test solutions of the complexes were allowed to stand in air for 1 day. The nmr spectrum remained identical after this period. This indicates that paramagnetic impurities which might form on decomposition of the compounds do not noticeably affect the chemical shifts.

Proton nmr spectra were recorded of approximately 20% dichloromethane solutions with a Varian Associates A-60A spectrometer using tetramethylsilane as an internal reference.

The infrared spectra of the carbonyl region were obtained from cyclohexane solutions of the compounds with a Perkin-Elmer Model 621 double-beam spectrometer using a sodium chloride cell with sample thickness of 0.012 mm. The intense bands are accurate to ±1 cm$^{-1}$ and the weak bands to about ±5 cm$^{-1}$.

Microanalyses were performed by Galbraith Laboratories of Knoxville, Tenn., Midwest Microlabs of Indianapolis, Ind., and Dr. Franz Kasler of the University of Maryland.

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(2) Taken in part from the Ph.D. thesis of D. A. Wheatland, University of Maryland, 1967.

(3) National Institutes of Health Predoctoral Fellow, 1965–1967.

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**Table I.** Preparative Data

| Compound | Color | Mp, °C | Yield, % | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Calcd | Found | Calcd | Found |
| $Ph_2MePCr(CO)_5$ | Yellow | 90–92 | 60 | 55.1 | 55.2 | 3.3 | 3.2 |
| $Ph_2EtPCr(CO)_5$ | Yellow | 75–76 | 55 | 56.2 | 56.3 | 3.7 | 3.6 |
| $Ph_2(i\text{-}Pr)PCr(CO)_5$ | Yellow | 101–102 | 60 | 57.2 | 57.2 | 4.1 | 4.1 |
| $Ph_2BuPCr(CO)_5$ | Yellow | 100–102 | 71 | 58.1 | 58.2 | 4.4 | 4.3 |
| $Ph_2(t\text{-}Bu)PCr(CO)_5$ | Yellow | 89–90 | 60 | 58.1 | 58.0 | 4.4 | 4.5 |
| $PhBu_2PCr(CO)_5$ | Yellow | 67–68 | 75 | 55.1 | 55.2 | 5.6 | 5.7 |
| $Ph_2MePMo(CO)_5$ | Colorless | 87–88 | 30 | 49.6 | 50.4 | 3.0 | 3.0 |
| $Ph_2EtPMo(CO)_5$ | Colorless | 52–53 | 45 | 50.7 | 50.0 | 3.4 | 3.5 |
| $Ph_2PrPMo(CO)_5$ | Colorless | 72–73 | 76 | 51.7 | 51.9 | 3.7 | 3.6 |
| $Ph_2(i\text{-}Pr)PMo(CO)_5$ | Colorless | 92–93 | 65 | 51.7 | 51.9 | 3.7 | 3.8 |
| $Ph_2BuPMo(CO)_5$ | Colorless | 82–83 | 83 | 52.7 | 52.9 | 4.0 | 4.1 |
| $Ph_2(t\text{-}Bu)PMo(CO)_5$ | Colorless | 86–87 | 70 | 52.7 | 52.8 | 4.0 | 4.1 |
| $PhBu_2PMo(CO)_5$ | Dark brown | Liquid | 65 | 49.8 | 49.6 | 5.1 | 5.0 |
| $Bu_3PMo(CO)_5$ | Light brown | Liquid | 40 | 46.6 | 46.8 | 6.2 | 6.3 |
| $Ph_2MePW(CO)_5$ | Colorless | 98–99 | 75 | 41.3 | 41.4 | 2.5 | 2.7 |
| $Ph_2EtPW(CO)_5$ | Colorless | 59–60 | 40 | 42.4 | 42.5 | 2.8 | 3.0 |
| $Ph_2(i\text{-}Pr)PW(CO)_5$ | Colorless | 98–100 | 63 | 43.5 | 43.7 | 3.1 | 3.3 |
| $Ph_2BuPW(CO)_5$ | Colorless | 94–95 | 37 | 44.5 | 44.7 | 3.4 | 3.4 |
| $Ph_2(t\text{-}Bu)PW(CO)_5$ | Pale yellow | 93–94 | 65 | 44.5 | 44.3 | 3.4 | 3.4 |
| $PhBu_2PW(CO)_5$ | Yellow | 39–41 | 57 | 41.8 | 42.0 | 4.2 | 4.5 |
| $Bu_3PW(CO)_5$ | Yellow | Liquid | 70 | 38.8 | 40.0 | 5.2 | 5.3 |
| *trans*-$(Ph_3P)(Bu_3P)Mo(CO)_4$ | Yellow | 146–147 | 41 | 60.7 | 60.2 | 6.3 | 6.5 |

Triphenylphosphine and tributylphosphine were donated by M and T Chemicals, Inc., and Carlise Chemical Works, Inc., respectively. The other tertiary phosphines were prepared using standard Grignard reactions. *t*-Butyldiphenylphosphine was prepared by Davidoff.[19] Chromium and molybdenum hexacarbonyls were purchased from A. D. Mackay, Inc. Tungsten hexacarbonyl was purchased from the Pressure Chemical Co.

All compounds, with the exception of the mixed-ligand compound, were prepared by the method of Magee and co-workers.[20] It was observed that 1,2-dimethoxyethane could be used in place of diethylene glycol dimethyl ether (diglyme) for reactions involving molybdenum hexacarbonyl. The $Mo(CO)_6$ is more soluble and this solvent minimizes the sublimation of the carbonyl from the reaction medium, which is a well-known nuisance in this type reaction. Optimum conditions involved heating the metal carbonyl in the appropriate solvent almost to the boiling point and then injecting the tertiary phosphine through a serum cap on a side arm of the reaction flask. The progress of the reaction was followed crudely by collection of the CO evolved in a buret inverted in a beaker of oil. Reactions were carried out with a molar ratio of metal carbonyl:tertiary phosphine of 2:1. When the reactions were carried out in the suggested manner with diglyme as the solvent, it was qualitatively observed that the $Cr(CO)_6$ reacted the fastest, with $W(CO)_6$ quite a bit slower than $Mo(CO)_6$. Table I lists the compounds prepared and the colors, melting points, analytical data, and yields. The compounds are stable in air with the exception of the liquids which are moderately air stable. All compounds will decompose in $CH_2Cl_2$ solutions after several hours at room temperature. Samples of the solids stored in a vacuum desiccator over $CaCl_2$ showed no sign of decomposition after 4 or 5 months.

***trans*-Tributylphosphinetriphenylphosphinemolybdenum Tetracarbonyl.** $(Ph_3P)Mo(CO)_5$ (7.25 g, 14.5 mmoles) in 50 ml of diglyme was stirred magnetically and heated under $N_2$ in an oil bath to about 160°. $Bu_3P$ (2.9 g, 14.4 mmoles) was injected. Evolution of CO began after a few minutes and continued for several hours. When the evolution of CO ceased, the solvent was removed at reduced pressure and $CH_2Cl_2$ was added to the residue. Upon filtration, MeOH was added to the filtrate. Evaporation of the mixture to half-volume caused formation of 4.0 g (41%) of white crystals of $(Bu_3P)(Ph_3P)Mo(CO)_4$, which is assigned the *trans* stereochemistry from infrared measurements.

## Results and Discussion

The phosphorus-31 nmr data are recorded in Table II. The coordination chemical shift[18] is defined as $\delta_{\text{complex}} - \delta_{\text{free ligand}}$ and is negative (downfield) for all compounds in this study. In this discussion the absolute value of the coordination chemical shift will be used, and thus the coordination chemical shifts for the chromium compounds are roughly 18 ppm larger than those for molybdenum which are about 18 ppm larger than those for tungsten. The effects which can influence the chemical shift of phosphorus are summarized by Packer[6] as (a) a local diamagnetic term, (b) a paramagnetic term, (c) neighbor anisotropy effect, and (d) interatomic currents. The local diamagnetic term depends on the electron density around phosphorus and hence a good $\sigma$ donor would produce a large coordination chemical shift, whereas a good $\pi$ acceptor would result in a small coordination chemical shift. Since the tertiary phosphine series—$Ph_3P$, $Ph_2BuP$, $PhBu_2P$, $Bu_3P$—increases in $\sigma$-donor ability[21] and decreases in $\pi$-acceptor ability[22] in the order given, the coordination chemical shift should increase markedly in the same series of coordination compounds of chromium, for example. Such is not the case and the coordination chemical shifts for the chromium compounds, $(Ph_{3-n}Bu_nP)Cr(CO)_5$, are 61.3, 62.2, 61.5, and 62.5 for $n = 0$, 1, 2, and 3, respectively. Therefore, we conclude that the synergic effect causes equalization of $\sigma$- and $\pi$-bonding abilities for these various phosphines and/or that the diamagnetic term is not of major importance in determining the coordination chemical shift for these compounds. Evidence for the latter is the fact that tetraphenylphosphonium iodide has a $^{31}P$ chemical shift of $-23.2$ ppm *vs.* 85% $H_3PO_4$.[23] The positive charge on phosphorus in a phosphonium salt is expected to be greater than the positive charge on phosphorus in a coordination compound and thus the

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[23] S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, **70**, 581 (1966).

**Table II.** Phosphorus Nmr Data

| Compound | Chemical shift, ppm |  | Coord chem shift | $J_{W-P}$, cps |
|---|---|---|---|---|
|  | Free ligand | Complex |  |  |
| $Ph_3PCr(CO)_5$ | 6.0 | −55.3 | −61.3 |  |
| $Ph_2MePCr(CO)_5$ | 28.0 | −35.0 | −63.0 |  |
| $Ph_2EtPCr(CO)_5$ | 12.0 | −48.3 | −60.3 |  |
| $Ph_2(i\text{-}Pr)PCr(CO)_5$ | −0.2 | −59.5 | −59.3 |  |
| $Ph_2BuPCr(CO)_5$ | 17.1 | −45.1 | −62.2 |  |
| $Ph_2(t\text{-}Bu)PCr(CO)_5$ | −17.1 | −72.7 | −55.6 |  |
| $PhBu_2PCr(CO)_5$ | 26.2 | −35.3 | −61.5 |  |
| $Bu_3PCr(CO)_5$ | 32.3 | −30.2 | −62.5 |  |
| $Ph_3PMo(CO)_5$ | 6.0 | −37.5 | −43.5 |  |
| $Ph_2MePMo(CO)_5$ | 28.0 | −15.0 | −43.0 |  |
| $Ph_2EtPMo(CO)_5$ | 12.0 | −30.1 | −42.1 |  |
| $Ph_2PrPMo(CO)_5$ | 17.6 | −26.5 | −44.1 |  |
| $Ph_2(i\text{-}Pr)PMo(CO)_5$ | −0.2 | −43.2 | −43.0 |  |
| $Ph_2BuPMo(CO)_5$ | 17.1 | −26.9 | −44.0 |  |
| $Ph_2(t\text{-}Bu)PMo(CO)_5$ | −17.1 | −57.0 | −39.9 |  |
| $PhBu_2PMo(CO)_5$ | 26.2 | −17.6 | −43.8 |  |
| $Bu_3PMo(CO)_5$ | 32.3 | −12.2 | −44.5 |  |
| $Ph_3PW(CO)_5$ | 6.0 | −20.6 | −26.6 | 280 |
| $Ph_2MePW(CO)_5$ | 28.0 | 3.8 | −24.2 | 245 |
| $Ph_2EtPW(CO)_5$ | 12.0 | −12.1 | −24.1 | 240 |
| $Ph_2(i\text{-}Pr)PW(CO)_5$ | −0.2 | −26.3 | −26.1 | 240 |
| $Ph_2BuPW(CO)_5$ | 17.1 | −7.9 | −25.0 | 250 |
| $Ph_2(t\text{-}Bu)PW(CO)_5$ | −17.1 | −41.7 | −24.6 | 240 |
| $PhBu_2PW(CO)_5$ | 26.2 | 0.8 | −25.4 | 235 |
| $Bu_3PW(CO)_5$ | 32.3 | 6.4 | −25.9 | 200 |
| *trans*-$(Ph_3P)(Bu_3P)Mo(CO)_4$ | 6.0 ($Ph_3P$)<br>32.3 ($Bu_3P$) | −50.9<br>−22.0 | −56.9<br>−54.3 | $J_{PP}$ = 50 |

phosphonium salt should have the lower chemical shift if the local diamagnetic contribution is of major importance. The fact that the $^{31}P$ chemical shift of $(Ph_3P)Cr(CO)_5$ is −55.3 ppm *vs.* 85% $H_3PO_4$ supports the statement that the local diamagnetic term is not the most important effect.

The local paramagnetic term has been considered the major (indeed, the only) factor for determining the chemical shift of trivalent phosphorus compounds.[24,25] Briefly, this effect (a downfield shift) depends on orbital populations, electronegativities, and inversely upon the mean excitation energies, $\Delta E$.[25] Molecules having unfilled low-lying electronic states which can be mixed by the magnetic field with occupied energy levels will have small $\Delta E$'s and large paramagnetic shifts (other things being equal). Although ultraviolet measurements have not been obtained, the observation that the chromium compounds are yellow (see Table I), whereas nearly all the solid molybdenum and tungsten compounds reported are colorless, is qualitatively correct for this effect to be a contributing factor in the size of the chemical shift.

The neighboring anisotropy effect caused by heavy atoms is well known in the pmr of the hydrogen halides, in which the heavy iodine causes an upfield shift. This effect is qualitatively in the same direction as the chemical shifts in the Cr, Mo, and W and hence may be a contributing factor. Disregarding ring currents, it is concluded that the differences in chemical shifts in these series of compounds are mainly from differences in paramagnetic and anisotropy effects with the relative importance of these unknown at this time.

There is a significant trend in the coordination chemical shift with chromium in the series $Ph_2MeP$ (63.0), $Ph_2EtP$ (60.3), $Ph_2(i\text{-}Pr)P$ (59.3), and $Ph_2(t\text{-}Bu)P$ (55.6). This trend is not as clear in the molybdenum and tungsten series because the coordination chemical shifts are much closer together in these series and experimental errors could be as large as some of the differences in shifts. We attribute the trend to steric effects. In the uncomplexed phosphines, the bond angles are larger for those with bulky isopropyl and *t*-butyl groups resulting in unusually low chemical shifts for these bulky uncomplexed phosphines.[24] On complex formation, the phosphines approach tetrahedral configuration. This is less of a hybridization change for the phosphine with the bulky groups than for the less sterically hindered phosphines, *e.g.*, $Ph_2MeP$. Hence, $Ph_2MeP$ has the greatest coordination chemical shift.

Figure 1 is a plot of the $^{31}P$ chemical shifts (*vs.* $H_3PO_4$) of $(Ph_2RP)M(CO)_5$ for R = Me, Et, Pr, *i*-Pr, Bu, and *t*-Bu against the group contribution of R to the chemical shift of tertiary phosphine.[19,26] A relationship of this type also exists for quaternary phosphonium salts,[23] and this indicates that the effects of these organic groups on $^{31}P$ chemical shifts are in the same linear order for tertiary phosphines, quaternary phosphonium salts, and tertiary phosphine coordination compounds.

Tungsten-183 (nuclear spin $^1/_2$, natural abundance 14.3%) causes splitting of the phosphorus signal for those molecules containing $^{183}W$, and the total nmr signal consists of a large main peak, due to those molecules containing tungsten atoms with zero spin, flanked equidistant on each side by small satellites. The distances, $J_{W-P}$, between these satellites are given in Table II. It is seen that the size of $J_{W-P}$ is in the order $Ph_3P > Ph_2RP > PhR_2P > R_3P$. If spin–spin coupling is transmitted mainly through $\sigma$ bonds, one might expect the best $\sigma$ donor, *i.e.*, $R_3P$, to have the largest $J_{W-P}$. This could, but does not necessarily, imply that

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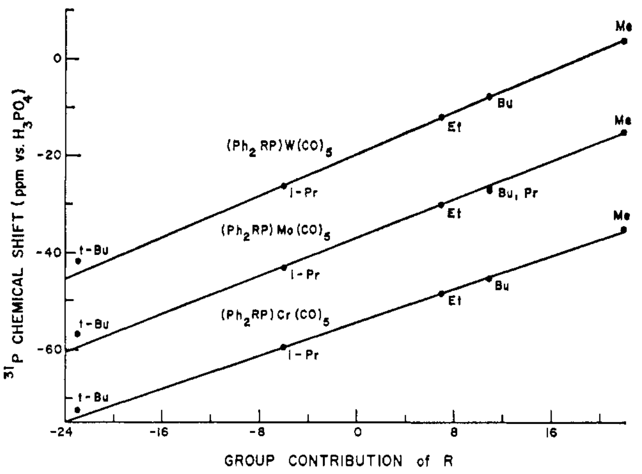

Figure 1. $^{31}P$ chemical shifts in $(Ph_2RP)M(CO)_5$ *vs.* group contributions of R: M = Cr, Mo, W; R = Me, Et, Pr, *i*-Pr, Bu, *t*-Bu.

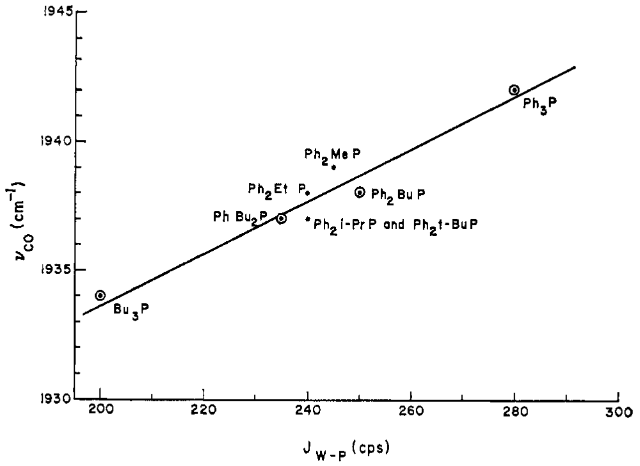

Figure 2. CO stretching frequencies *vs.* $^{183}W-^{31}P$ coupling constants in $(Ph_{3-n}R_nP)W(CO)_5$.

spin–spin coupling is also transmitted *via* $\pi$ bonds, since back-donation by tungsten 5d electrons to phosphorus would deshield the 6s bonding electrons of tungsten so that the Fermi contact mechanism could be more effective. At the same time phosphorus accepts electronic charge into the 3d orbital, but the shielding of the 3s bonding electrons by 3d electrons is not as important as the 5d shielding of the 6s electrons of tungsten, because the same principal quantum number is involved in the case of phosphorus.

Additionally, the synergic effect of a $\pi$ acceptor could cause increased $\sigma$ bonding and therefore increased coupling constants.

In any case, the size of $J_{W-P}$ appears to be a measure of the $\pi$-acceptor ability of the phosphorus compound, irrespective of the mechanism by which the coupling occurs.

The infrared spectra of the metal carbonyl stretching region for the compounds are reported in Table III. Agreement with published data[27-31] is good for strong intensity bands but differs up to 9 cm$^{-1}$ for the very weak $B_1$ frequency for $Ph_3PM(CO)_5$. The strongest band at about 1940 cm$^{-1}$ has been assigned previously[27] as the accidental superposition of the $A_1^{(1)}$ (*trans* CO stretching) and E (unsymmetric stretching of four coplanar CO's) modes in $Ph_3PM(CO)_5$. This accidental degeneracy is removed in (amine)$M(CO)_5$ compounds[28] with the $A_1^{(1)}$ moving to lower frequency, corresponding to the non-$\pi$-acceptor amine replacing the $\pi$ acceptor $Ph_3P$, and appearing as a shoulder on the strong-intensity E band. In the present compounds, $Ph_2RP$, $PhR_2P$, and $R_3P$ should be weaker $\pi$ acceptors than $Ph_3P$ and a shoulder on the low-frequency side of the E band might also be expected analogous to the amine compounds. This is observed in three cases (see Table III). In addition, the infrared spectra of all the new compounds have a well-defined shoulder on the high-frequency side of the strongest peak. This could arise because the unsymmetrical phosphine ligands cause a lifting of the degeneracy of the E modes.

Figure 2 illustrates the linear relationship between $J_{W-P}$ and the CO stretching frequency. Several points are circled only to emphasize the Bu series. The stretching frequency of the CO *trans* ($A_1^{(1)}$) to the phosphine would be most indicative of the relationship between the $\pi$-acceptor ability of the phosphine and the *trans* CO stretching frequency, but since this assignment is not certain for all compounds, the strongest peak is used in Figure 2 for consistency. This procedure seems valid because of the relationship of *cis*

**Table III.** Infrared Spectra in the Carbonyl Region

| Compound | CO stretching frequency,[a] cm$^{-1}$ | | |
|---|---|---|---|
| $Ph_3PCr(CO)_5$ | 2065 m | 1980 vw | 1940 vs |
| $Ph_2MePCr(CO)_5$ | 2064 m | 1981 w | 1947 sh, 1939 vs |
| $Ph_2EtPCr(CO)_5$ | 2064 m | 1981 w | 1947 sh, 1938 vs |
| $Ph_2$(*i*-Pr)$PCr(CO)_5$ | 2063 m | 1980 w | 1946 sh, 1937 vs |
| $Ph_2BuPCr(CO)_5$ | 2063 m | 1980 w | 1950 sh, 1937 vs |
| $Ph_2$(*t*-Bu)$PCr(CO)_5$ | 2063 m | 1980 w | 1944 sh, 1937 vs |
| $PhBu_2PCr(CO)_5$ | 2062 m | 1976 w | 1944 sh, 1936 vs, 1931 sh |
| $Bu_3PCr(CO)_5$ | 2062 m | | 1942 sh, 1933 vs |
| $Ph_3PMo(CO)_5$ | 2074 m | 1987 vw | 1950 vs |
| $Ph_2MePMo(CO)_5$ | 2074 m | 1985 w | 1951 sh, 1946 vs |
| $Ph_2EtPMo(CO)_5$ | 2073 m | 1985 w | 1952 sh, 1945 vs |
| $Ph_2PrPMo(CO)_5$ | 2073 m | 1985 w | 1951 sh, 1944 vs |
| $Ph_2$(*i*-Pr)$PMo(CO)_5$ | 2073 m | 1985 w | 1951 sh, 1944 vs |
| $Ph_2BuPMo(CO)_5$ | 2073 m | 1985 w | 1952 sh, 1944 vs |
| $Ph_2$(*t*-Bu)$PMo(CO)_5$ | 2072 m | 1985 w | 1948 sh, 1944 vs, 1939 sh |
| $PhBu_2PMo(CO)_5$ | 2072 m | 1982 w | 1949 sh, 1942 vs |
| $Bu_3PMo(CO)_5$ | 2070 m | | 1943 sh, 1938 vs |
| $Ph_3PW(CO)_5$ | 2075 m | 1981 vw | 1942 vs |
| $Ph_2MePW(CO)_5$ | 2073 m | 1979 w | 1947 sh, 1939 vs |
| $Ph_2EtPW(CO)_5$ | 2073 m | 1979 w | 1947 sh, 1938 vs |
| $Ph_2$(*i*-Pr)$PW(CO)_5$ | 2074 m | 1979 w | 1946 sh, 1937 vs |
| $Ph_2BuPW(CO)_5$ | 2073 m | 1978 w | 1947 sh, 1938 vs |
| $Ph_2$(*t*-Bu)$PW(CO)_5$ | 2072 m | 1979 w | 1944 sh, 1937 vs |
| $PhBu_2PW(CO)_5$ | 2071 m | 1975 w | 1944 sh, 1937 vs, 1933 sh |
| $Bu_3PW(CO)_5$ | 2070 m | | 1942 sh, 1934 vs |
| *trans*-$(Ph_3P)(Bu_3P)Mo(CO)_4$ | | 1894 vs | |

[a] m, medium; w, weak; vw, very weak; vs, very strong; sh, shoulder.

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and *trans* frequencies by interaction constants,[27] and because Van Hecke and Horrocks[22] found that the calculated CO stretching force constants parallel the raw frequency data for isosymmetric series.

It should be pointed out that there has been a recent attempt[32] to explain the variation of CO stretching frequencies of nickel carbonyl substituted with various trivalent phosphorus ligands as due entirely to $\sigma$ inductive effects, with the admitted exceptions of organic phosphites, $(RO)_3P$. Although the $\sigma$ bond is certainly important, there is considerably more support[22,29,31] for $\pi$ bonding also being an important factor. We feel our data support the $\pi$-bonding arguments.

The novel mixed ligand compound, $(Bu_3P)(Ph_3P)Mo(CO)_4$, has one strong CO band in its infrared spectrum and is therefore assigned as the *trans* isomer. The compound contains two nonequivalent phosphorus atoms and has the expected $^{31}P$ nmr spectrum consisting of a pair of doublets with $J_{P-P} = 50 \pm 10$ cps, which is in good agreement with the coupling constant (*ca.* 60 cps) calculated by Verkade,[33] *et al.*, from proton nmr spectra of *trans*-$L_2Mo(CO)_4$ where L is a constrained phosphite. We believe this is the first directly measured phosphorus–phosphorus coupling in a coordination compound containing mixed ligands.[14]

Proton nmr results are listed in Table IV. The resonance positions of the $\alpha$ and $\beta$ protons move downfield upon coordination as is expected from the greater electronegativity of phosphorus in the coordination compound than in the free phosphine. The chemical shift on coordination is not as great as on quaternization,[34] which is reasonable since phosphorus in a phosphonium salt should be more electronegative than in a coordination compound. Likewise, $J_{P-C-H}$ and $J_{P-C-C-H}$ in the coordination compounds are intermediate between those in the free phosphine and those in phosphonium salts.[34]

**Table IV.** Proton Nmr Data

| Compound | $\tau_\alpha$ | $\tau_\beta$ | $J_{P-H\alpha}$, cps | $J_{P-H\beta}$, cps |
|---|---|---|---|---|
| $Ph_2MeP$ | 8.49 | ... | 5.0 | ... |
| $Ph_2MePCr(CO)_5$ | 7.94 | ... | 6.8 | ... |
| $Ph_2MePMo(CO)_5$ | 7.91 | ... | 6.2 | ... |
| $Ph_2MePW(CO)_5$ | 7.72 | ... | 6.8 | ... |
| $Ph_2EtP$ | 8.07 | 9.02 | 1.5 | 16.5 |
| $Ph_2EtPCr(CO)_5$ | 7.50 | 8.98 | 7.5 | 17.5 |
| $Ph_2EtPMo(CO)_5$ | 7.52 | 8.98 | 7.5 | 17.5 |
| $Ph_2EtPW(CO)_5$ | 7.50 | 9.00 | 7.5 | 18.0 |
| $Ph_2(t\text{-}Bu)P$ | ... | 8.84 | ... | 12.3 |
| $Ph_2(t\text{-}Bu)PCr(CO)_5$ | ... | 8.67 | ... | 14.5 |
| $Ph_2(t\text{-}Bu)PMo(CO)_5$ | ... | 8.68 | ... | 14.0 |
| $Ph_2(t\text{-}Bu)PW(CO)_5$ | ... | 8.67 | ... | 14.5 |

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# The Solid-Phase *trans*-to-*cis* Isomerization of $[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$[1]

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**Abstract:** Studies were conducted which offer evidence that *cis*-$[Co(NH_3)_4Cl_2]IO_3$ is the product formed when solid *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ is heated. A kinetic study of this reaction gave $\Delta H^{\ddagger} = 52 \pm 6$ kcal mole$^{-1}$ and $\Delta S^{\ddagger} = 61 \pm 18$ cal mole$^{-1}$ deg$^{-1}$ for the dehydration process and $\Delta H^{\ddagger} = 46 \pm 6$ kcal mole$^{-1}$ and $\Delta S^{\ddagger} = 41 \pm 18$ cal mole$^{-1}$ deg$^{-1}$ for the isomerization. The isomerization is interpreted in terms of an aquation–anation reaction sequence.

The compound *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ has been found to readily undergo a distinct color change from green to dark violet during dehydration at temperatures near 110°.[3] On the basis of color and elemental analyses, Lobanov suggested that the product is *cis*-$[Co(NH_3)_4Cl_2]IO_3$. However, he did not eliminate the possibility that the violet substance is an iodato complex.

The present investigation was undertaken (1) to obtain further information which would allow a more definite structural assignment of this product, and (2) to determine the mechanism of the isomerization process. In seeking to accomplish the first goal, the spectral properties of the dark violet reaction product and a number of related substances were investigated. The visible spectra of *cis*-$[Co(NH_3)_4Cl_2]IO_3$ and other salts of *cis*-$[Co(NH_3)_4Cl_2]^+$ with colorless anions should be identical. However, few reliable spectra are available on compounds of this cation. It was therefore neces-

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