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Complexes of Trivalent Phosphorus Derivatives. II. Metal Carbonyl Complexes of Tris-(dimethylamino)-phosphine[1]

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Reactions of tris-(dimethylamino)-phosphine (Tdp) with the metal carbonyls $Ni(CO)_4$, $Co_2(CO)_8$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ yield the compounds $(Tdp)_2Ni(CO)_2$, $[(Tdp)_2Co(CO)_3][Co(CO)_4]$, $(Tdp)Cr(CO)_5$, $(Tdp)Mo(CO)_5$, and $(Tdp)_2W(CO)_4$, respectively. Reaction of either $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with tris-(dimethylamino)-phosphine yields a mixture of $(Tdp)Fe(CO)_4$ and $(Tdp)_2Fe(CO)_3$ which may be separated by fractional sublimation. Reactions of $C_7H_8M(CO)_4$ (C_7H_8 = bicyclo[2.2.1]heptadiene, M = Cr and Mo) and $C_7H_8M(CO)_3$ (C_7H_8 = cycloheptatriene, M = Cr and Mo) with tris-(dimethylamino)-phosphine yield the compounds $(Tdp)_2M(CO)_4$ (M = Cr and Mo). Reaction of $Hg[Co(CO)_4]_2$ with tris-(dimethylamino)-phosphine yields the compound $Hg[Co(CO)_3(Tdp)]_2$. Reaction of $C_5H_5V(CO)_4$ with tris-(dimethylamino)-phosphine yields the compound $C_5H_5V(CO)_3(Tdp)$. Reaction of $[C_5H_5NiCO]_2$ with tris-(dimethylamino)-phosphine yields a mixture of $(Tdp)_2Ni(CO)_2$ and $(C_5H_5)_2Ni$. Reactions of the halide derivatives $C_5H_5Fe(CO)_2I$, $C_3H_5Fe(CO)_3I$, $C_5H_5Mo(CO)_3I$, and $C_7H_7Mo(CO)_2I$ with tris-(dimethylamino)-phosphine yield the compounds $[C_5H_5Fe(CO)_2(Tdp)]I$, $(Tdp)_2Fe(CO)_3$, $C_5H_5Mo(CO)_2(Tdp)I$ (two isomers), and $C_7H_7MoCO(Tdp)I$. The proton n.m.r. spectra of these compounds are discussed.

Although numerous complexes have been obtained from the reactions between metal carbonyl derivatives and derivatives of tricovalent phosphorus where the phosphorus atom is bonded to carbon, oxygen, or halogens,[2-8] the reactions between metal carbonyl derivatives and tricovalent phosphorus derivatives with the phosphorus bonded to nitrogen do not seem to have been investigated.[8a] For this reason it seemed of interest to investigate the reactions between various metal carbonyl derivatives and a tris-(dialkylamino)-phosphine derivative with three nitrogen atoms bonded to the phosphorus atom in order to determine the effect of the presence of the three phosphorus–nitrogen bonds on the type of complexes produced.

Of the various possible tris-(dialkylamino)-phosphine derivatives tris-(dimethylamino)-phosphine[9] was selected for the following reasons: (1) It is easily synthesized from phosphorus trichloride and excess dimethylamine.[10] (2) Although it is a liquid it might be expected to form crystalline complexes readily freed from excess liquid tris-(dimethylamino)-phosphine. (3) Due to its relatively low molecular weight it might be expected to form some volatile complexes. Thus, sublimation might be a useful technique for the isolation of certain complexes. (4) The methyl groups should exhibit sharp resonances in the proton n.m.r. spectra of the complexes. This might permit the identification of various components in mixtures and might also give information concerning phosphorus–hydrogen and phosphorus–phosphorus coupling constants.

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 double-beam machine with sodium chloride optics. In addition, the metal carbonyl regions of selected compounds (Table I) were taken in Halocarbon oil mulls and recorded on a Perkin-Elmer Model 112 single-beam machine with calcium fluoride optics. Proton n.m.r. spectra were taken in carbon disulfide, chloroform, or benzene solutions on a Varian Associates Model A-60 machine (Table II). Hexamethyldisiloxane was used as an internal standard. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck Institut für Kohlenforschung, Mülheim (Ruhr), Germany; Schwarzkopf Microanalytical Laboratory, Woodside, New York; and Huffman Microanalytical Laboratory, Wheatridge, Colorado. Melting points were taken in capillaries and are uncorrected.

Materials.—Nickel tetracarbonyl was obtained from the International Nickel Co. Dicobalt octacarbonyl was obtained from Union Carbide Olefins, South Charleston, West Virginia. Iron pentacarbonyl was purchased from the Antara Division of General Aniline and Film. Chromium hexacarbonyl was purchased from the Diamond Alkali Corp., Painesville, Ohio. Molybdenum and tungsten hexacarbonyls were purchased from the Climax Molybdenum Company, New York, New York. The other metal carbonyl derivatives used in this work were prepared by published procedures or minor modifications thereof.

Tris-(dimethylamino)-phosphine was prepared from phosphorus trichloride and excess dimethylamine by the procedure of Burg and Slota.[10]

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[1] The paper, R. B. King, *Inorg. Chem.*, **2**, 199 (1963), should be considered as part I of this series.

[2] J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

[3] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

[4] W. Hieber and W. Freyer, *Ber.*, **91**, 1230 (1958); **93**, 462 (1960).

[5] Compare the similar reactions with $Fe_3(CO)_{12}$ and triphenylphosphine recently described by A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, **2**, 151 (1963).

[6] Compare T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

[7] W. Hieber and R. Breu, *Ber.*, **90**, 1259 (1957).

[8] A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).

[8a] NOTE ADDED IN PROOF.—Since this paper was accepted, some metal complexes of tris-(dimethylamino)-phosphine were described by H. Nöth and H. J. Vetter, *Ber.*, **96**, 1479 (1963). Most of their work was concerned with metal halide rather than with metal carbonyl complexes. However, they did report the complex $(Tdp)_2Ni(CO)_2$ also described in this paper, as well as the nickel carbonyl derivative $(Tdp)Ni(CO)_3$ not described in this paper. The melting point of $(Tdp)_2Ni(CO)_2$ appears to be very sensitive to impurities since the $(Tdp)_2Ni(CO)_2$ prepared by Nöth and Vetter melted at 69–74° and the two samples prepared in this work melted at 86–87° and 80–82°. All three of the samples gave excellent analyses.

[9] To minimize confusion and the use of several types of brackets tris-(dimethylamino)-phosphine will be abbreviated as Tdp in the formulas.

[10] A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

TABLE I

INFRARED SPECTRA OF TRIS-(DIMETHYLAMINO)-PHOSPHINE DERIVATIVES IN THE METAL CARBONYL REGION

(CaF_2 optics, Halocarbon oil mulls)

Compound	Metal carbonyl bands, cm.$^{-1}$
$(Tdp)_2Ni(CO)_2$	1929 (vs), 1992 (vs)
$[(Tdp)_2Co(CO)_3][Co(CO)_4]$	$[Co(CO)_4]^-$: 1877 (s) $[(Tdp)_2Co(CO)_3]^+$: 1970 (s), 1982 (s)
$(Tdp)Fe(CO)_4$	1930 (vs), 1969 (s), 2041 (s)
$(Tdp)_2Fe(CO)_3$	1871 (vs)
$(Tdp)Cr(CO)_5$	1932 (vs), 1978 (m), 2055 (s)
$(Tdp)Mo(CO)_5$	1938 (vs), 1983 (m), 2066 (s)
$(Tdp)_2Cr(CO)_4$	1868 (vs)
$(Tdp)_2Mo(CO)_4$	1885 (vs)
$(Tdp)_2W(CO)_4$	1870 (vs)
$Hg[Co(CO)_3(Tdp)]_2$	1936 (vs), 1974 (m)
$C_5H_5V(CO)_3(Tdp)$	1839 (s), 1853 (s), 1933 (s), 1953 (s)
$[C_5H_5Fe(CO)_2(Tdp)]I$	1987 (s), 1991 (sh), 2030 (s), 2037 (s)
$C_5H_5Mo(CO)_2(Tdp)I$	1869 (vs), 1940 (m), 1955 (s)
$C_7H_7MoCO(Tdp)I$	1915 (s)

TABLE II

PROTON N.M.R. SPECTRA OF TRIS-(DIMETHYLAMINO)-PHOSPHINE DERIVATIVES

(Chemical shifts given in τ values; J values in c.p.s.)

Compound	Methyl resonance	Other resonances
(A) Compounds with a doublet in the methyl region		
Tdp	7.56 (J = 8.9)	
$(Tdp)_2Ni(CO)_2$	7.53 (J = 9.3)	
$(Tdp)Fe(CO)_4$	7.35 (J = 9.6)	
$(Tdp)Cr(CO)_5$	7.74 (J = 10.1)	
$(Tdp)Mo(CO)_5$	7.75 (J = 10.2)	
$C_5H_5V(CO)_3(Tdp)$	7.78 (J = 8.4)	C_5H_5: 5.39 (unsplit)
$[C_5H_5Fe(CO)_2(Tdp)]I$	7.36 (J = 9.8)	C_5H_5: 4.53 (J = 1.0)
$C_5H_5Mo(CO)_2(Tdp)I$		
Isomer A:	7.35 (J = 9.0)	C_5H_5: 4.74 (J = 1.6)
Isomer B:	7.41 (J = 8.7)	C_5H_5: 4.67 (unsplit)
$C_7H_7MoCO(Tdp)I$	7.36 (J = 8.6)	C_7H_7: 4.79 (J = 2.5)
(B) Compounds with a triplet in the methyl region (Separation of outer peaks in c.p.s. given in parentheses)		
$[(Tdp)_2Co(CO)_3]$-$[Co(CO)_4]$	7.27 (10.5)	
$(Tdp)_2Fe(CO)_3$	7.35 (9.4)	
$(Tdp)_2Cr(CO)_4$	7.42 (9.7)	
$(Tdp)_2Mo(CO)_4$	7.33 (10.0)	
$(Tdp)_2W(CO)_4$	7.45 (10.2)	

Reaction between Nickel Tetracarbonyl and Tris-(dimethylamino)-phosphine.[8a]—A mixture of 6.0 ml. (6.0 g., 37 mmoles) of tris-(dimethylamino)-phosphine and 20 ml. of hexane was treated under nitrogen with 2.0 ml. (~2.6 g., ~15 mmoles) of nickel tetracarbonyl. An exothermic reaction occurred and much hexane was lost. After diluting the reaction mixture to its original volume with hexane, the reaction mixture was heated for ~15 min. After stirring overnight at room temperature it was filtered by gravity and the solvent was removed from the filtrate at ~30 mm. The mixture of oil and crystals which remained was treated with ~20 ml. of pentane and the solution filtered. Cooling in a −78° bath precipitated white crystals of the product. After a second recrystallization from pentane by this procedure the white crystalline product weighed 0.34 g. (~5% yield) and melted at 86–87°.

Anal. Calcd. for $C_{14}H_{36}N_6P_2NiO_2$: C, 38.1; H, 8.2; N, 19.0; P, 14.0. Found: C, 37.7; H, 8.4; N, 18.8; P, 13.7.

Infrared Spectrum.—Carbon–hydrogen bands at 2975 (w), 2900 (m), 2850 (m), 2815 (m), and 2775 (m) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1475 (sh), 1455 (m), 1270 (m), 1247 (w), 1185 (s), 1155 (m), 1140 (sh), 1055 (w), 960 (s), and 944 (s) cm.$^{-1}$.

Reaction between Dicobalt Octacarbonyl and Tris-(dimethylamino)-phosphine.[8a]—A mixture of 1.8 g. (~5 mmoles) of ~95% dicobalt octacarbonyl (containing ~5% of toluene) and 50 ml. of thiophene-free benzene was treated with 3.0 ml. (3.0 g., 18.4 mmoles) of tris-(dimethylamino)-phosphine. An exothermic reaction occurred with gas evolution. The reaction mixture was stirred for 18 hr. at room temperature. The reaction mixture was then filtered by gravity collecting the clear orange filtrate under nitrogen. Solvent was removed from this filtrate at ~30 mm. leaving yellow crystals. These were washed with six 20-ml. portions of pentane or hexane and sucked dry.

Traces of a red solid, possibly impure $[(Tdp)Co(CO)_3]_2$, may be isolated by cooling the pentane or hexane washings in a −78° bath followed by filtration. This material, characterized by a single band in the metal carbonyl region at 1930 cm.$^{-1}$, was obtained in insufficient quantities for further purification.

The crude yellow crystals of $[(Tdp)_2Co(CO)_3][Co(CO)_4]$ were purified by recrystallization from a mixture of dichloromethane and hexane to give 1.96 g. (61% yield) of yellow crystals which darkened on exposure to light or on heating above ~176°.

Anal. Calcd. for $C_{19}H_{36}N_6P_2Co_2O_7$: C, 35.6; H, 5.6; N, 13.1; P, 9.7; Co, 18.5; O, 17.5. Found: C, 35.8; H, 5.7; N, 13.7; P, 9.9; Co, 19.1; O, 18.4.

Infrared Spectrum.—Carbon–hydrogen bands at 2975 (w), 2875 (w), 2845 (sh), and 2790 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1475 (sh), 1458 (m), 1435 (sh), 1400 (w), 1273 (s), 1165 (s), 1055 (m), 963 (vs), and 765 (s) cm.$^{-1}$.

Conductivity.—A molar conductance of 155 ± 6 mhos was found by measurements on acetone solutions of several concentrations in the range 7.2×10^{-4} to 3.1×10^{-3} M.

Reaction between Triiron Dodecacarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 1.8 g. (3.6 mmoles) of triiron dodecacarbonyl, 3.0 ml. (3.0 g., 18.4 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of thiophene-free benzene was stirred 24 hr. under nitrogen at room temperature, the green color of the triiron dodecacarbonyl soon becoming yellow. The reaction mixture was then filtered. Solvent was removed from the filtrate at ~30 mm., leaving a liquid residue. This residue was treated with ~50 ml. of pentane and the solution filtered by gravity. The filtrate was cooled in a −78° bath. The resulting white crystals were filtered and sucked dry. The proton n.m.r. spectrum of the crude product indicated it to be a mixture of $(Tdp)Fe(CO)_4$ and $(Tdp)_2Fe(CO)_3$. This crude product weighed 2.0 g.

To obtain pure $(Tdp)Fe(CO)_4$ from this crude product it was sublimed at 50–60° (0.1 mm.) for 2 hr. The pale yellow sublimate, despite melting over the wide range 46–85°, was pure $(Tdp)Fe(CO)_4$ on the basis of n.m.r. and elemental analyses. A 0.63-g. portion of the crude product gave 0.25 g. of pure $(Tdp)Fe(CO)_4$ (22% yield based on triiron dodecacarbonyl).

Anal. Calcd. for $C_{10}H_{18}N_3PFeO_4$: C, 36.2; H, 5.4; N, 12.7; P, 9.4; O, 19.3. Found: C, 36.1; H, 5.5; N, 12.9; P, 9.5; O, 19.1.

Infrared Spectrum.—Carbon–hydrogen bands at 2975 (w), 2850 (m), 2825 (sh), and 2780 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1475 (w), 1458 (m), 1435 (sh), 1400 (vw), 1270 (m), 1175 (m), 1137 (sh), 1055 (w), 975 (sh), and 957 (vs) cm.$^{-1}$.

To obtain pure $(Tdp)_2Fe(CO)_3$ from this crude product, a 1.07-g. sample was sublimed at 100° (0.1 mm.). The first 0.22 g. of white sublimate was a mixture of $(Tdp)Fe(CO)_4$ and $(Tdp)_2Fe(CO)_3$ as demonstrated by its n.m.r. spectrum. Continuation of the sublimation at 100–120° (0.1 mm.) gave 0.34 g. (12.5% yield based on triiron dodecacarbonyl) of a pure white crystalline sublimate of $(Tdp)_2Fe(CO)_3$, m.p. 200–203°. The absence of $(Tdp)Fe(CO)_4$ was demonstrated by n.m.r.

Anal. Calcd. for $C_{15}H_{36}N_6P_2FeO_3$: C, 38.6; H, 7.7; N, 18.0; P, 13.3; Fe, 12.0; O, 10.3; mol. wt., 466. Found: C, 38.6; H, 7.8; N, 18.0; P, 13.1; Fe, 11.8; O, 11.5; mol. wt., 473.

Infrared Spectrum.—Carbon–hydrogen bands at 2985 (w, sh), 2860 (m), 2825 (sh), and 2775 (m) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1455 (m), 1400 (vw), 1265 (m), 1180 (s), 1138 (w), 1058 (m), 955 (vs), and 700 (vs) cm.$^{-1}$.

Reaction between Iron Pentacarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 2.0 ml. (2.9 g., 15 mmoles) of iron pentacarbonyl, 4.0 ml. (4.0 g., 24.5 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of ethylcyclohexane was refluxed for 21 hr. under nitrogen with magnetic stirring. The clear yellow reaction mixture was then allowed to cool to room temperature. Solvent was removed from the reaction mixture at ~0.1 mm., leaving a white crystalline residue. This residue was treated with 20 ml. of pentane and the solution filtered by gravity. The filtrate was cooled in a −78° bath. The crystals which separated were filtered and sucked dry to give 0.57 g. of white crystals determined by n.m.r. to consist of approximately equal quantities of $(Tdp)Fe(CO)_4$ and $(Tdp)_2Fe(CO)_3$.

Reaction between Molybdenum Hexacarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 2.64 g. (10 mmoles) of molybdenum hexacarbonyl, 2.0 ml. (2.0 g., 12.3 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of methylcyclohexane was refluxed 8 hr. under nitrogen with magnetic stirring. The reaction mixture became yellow and then black. After the reaction period was over, the reaction mixture was allowed to cool to room temperature and filtered by gravity. Solvent was removed from the filtrate at ~30 mm., leaving white crystals. These were dissolved in ~30 ml. of pentane and the solution filtered by gravity. Cooling the filtrate in a −78° bath caused white crystals to separate. These were filtered and sucked dry to give 2.0 g. (50% yield) of crude product, which was purified by two sublimations at 80–100° (0.1 mm.) to give 1.34 g. (33.5% yield) of pure white crystals of $(Tdp)Mo(CO)_5$, m.p. 152–154° dec.

Anal. Calcd. for $C_{11}H_{18}N_3PMoO_5$: C, 33.1; H, 4.5; N, 10.5; P, 7.8; O, 20.1. Found: C, 33.2; H, 4.5; N, 10.7; P, 7.5; O, 20.4.

Infrared Spectrum.—Carbon–hydrogen bands at 2975 (w), 2900 (m), 2850 (m), 2820 (m), and 2775 (m) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1460 (m), 1425 (w), 1400 (vw), 1259 (m), 1174 (s), 1145 (m), 1056 (m), 1005 (vw), 965 (s), 950 (vs), 795 (w), 754 (w), and 688 (s) cm.$^{-1}$.

Reaction between Chromium Hexacarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 2.2 g. (10 mmoles) of chromium hexacarbonyl, 2.0 ml. (2.0 g., 12.3 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of ethylcyclohexane was refluxed 24 hr. under nitrogen with magnetic stirring. From this reaction mixture 2.32 g. (65% yield) of crude $(Tdp)Cr(CO)_5$ was isolated in a manner completely analogous to the isolation of $(Tdp)Mo(CO)_5$ described above. Two sublimations at 90° (0.1 mm.) gave 1.97 g. (56% yield) of white crystalline $(Tdp)Cr(CO)_5$, m.p. 145° dec.

Anal. Calcd. for $C_{11}H_{18}N_3PCrO_5$: C, 37.2; H, 5.1; N, 11.8; P, 8.7. Found: C, 37.5; H, 5.2; N, 12.3; P, 8.0.

Infrared Spectrum.—Carbon–hydrogen bands at 2975 (sh), 2900 (w), 2850 (w), 2830 (sh), and 2775 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1470 (sh), 1455 (w), 1440 (sh), 1430 (sh), 1400 (vw), 1258 (w), 1170 (m), 1142 (w), 1055 (w), 965 (m), 950 (s), 691 (s), and 684 (s) cm.$^{-1}$.

Reaction between Tungsten Hexacarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 3.52 g. (10 mmoles) of tungsten hexacarbonyl, 2.0 ml. (2.0 g., 12.3 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of ethylcyclohexane was refluxed for ~21 hr. under nitrogen with magnetic stirring. From this reaction mixture 1.1 g. (29% yield) of crude $(Tdp)_2W(CO)_4$ was isolated in a manner completely analogous to that of $(Tdp)Mo(CO)_5$ described above. Two sublimations at 130° (0.1 mm.) gave 0.55 g. (14.5% yield) of yellow crystalline $(Tdp)_2W(CO)_4$, m.p. 153°.

Anal. Calcd. for $C_{16}H_{36}N_6P_2WO_4$: C, 30.8; H, 5.8; N, 13.5; P, 10.0; O, 10.3. Found: C, 30.6; H, 5.9; N, 13.7; P, 9.9; O, 11.4.

Infrared Spectrum.—Carbon–hydrogen bands at 2960 (w), 2880 (m), 2850 (m), 2815 (m), and 2775 (m) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1460 (m), 1430 (w), 1400 (m), 1260 (m), 1170 (m), 1145 (sh), 1056 (m), 960 (s), 945 (s), and 685 (m) cm.$^{-1}$.

Reaction between Bicyclo[2.2.1]heptadienechromium Tetracarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 1.28 g. (5 mmoles) of bicyclo[2.2.1]heptadienechromium tetracarbonyl,[11] 2.0 ml. (2.0 g., 12.3 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of methylcyclohexane was refluxed 21 hr. under nitrogen with magnetic stirring. From this reaction mixture 1.23 g. (50% yield) of crude $(Tdp)_2Cr(CO)_4$ was isolated in a manner completely analogous to the isolation of $(Tdp)Mo(CO)_5$ described above. Two sublimations at 130–160° (0.1 mm.) gave 0.60 g. (24.5% yield) of pale yellow crystals of $(Tdp)_2Cr(CO)_4$, m.p. 143–147° dec.

Anal. Calcd. for $C_{16}H_{36}N_6P_2CrO_4$: C, 39.2; H, 7.3; N, 17.1; P, 12.7; O, 13.1. Found: C, 39.0; H, 7.3; N, 17.4; P, 12.5; O, 14.0.

Infrared Spectrum.—Carbon–hydrogen bands at 2975 (w, sh), 2860 (m), 2830 (sh), and 2775 (m) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1473 (sh), 1460 (m), 1430 (w), 1400 (w), 1268 (m), 1170 (s), 1145 (sh), 1058 (m), 960 (s), 945 (s), and 687 (s) cm.$^{-1}$.

Reaction between Cycloheptatrienechromium Tricarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 1.14 g. (5 mmoles) of cycloheptatrienechromium tricarbonyl,[12] 2.0 ml. (2.0 g., 12.3 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of methylcyclohexane was refluxed 21 hr. under nitrogen with magnetic stirring, the red color of the cycloheptatrienechromium tricarbonyl gradually disappearing. From this reaction mixture 0.77 g. (42% yield) of crude $(Tdp)_2Cr(CO)_4$ was isolated in a manner completely analogous to the isolation of $(Tdp)Mo(CO)_5$ described above. Sublimation of a 0.40-g. sample of this crude product at ~150° (0.1 mm.) gave 0.21 g. (22% yield) of pale yellow pure $(Tdp)_2Cr(CO)_4$, m.p. 145° dec., identical with the material obtained above from the reaction between bicyclo[2.2.1]heptadienechromium tetracarbonyl and tris-(dimethylamino)-phosphine.

Anal. Calcd. for $C_{16}H_{36}N_6P_2CrO_4$: C, 39.2; H, 7.3. Found: C, 38.9; H, 7.5.

Reaction between Cycloheptatrienemolybdenum Tricarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 1.36 g. (5 mmoles) of cycloheptatrienemolybdenum tricarbonyl,[12] 3.0 ml. (3.0 g., 18.4 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of thiophene-free benzene was stirred for ~1 hr. at room temperature, the red color of the cycloheptatrienemolybdenum tricarbonyl disappearing rapidly in contrast to the analogous reaction with the chromium derivative described above. After the reaction period was over, solvent was removed from the reaction mixture at ~30 mm. The resulting dirty white residue was dissolved in ~30 ml. of dichloromethane and the brown solution filtered. After adding ~30 ml. of hexane, the reaction mixture was concentrated to a volume of ~25 ml. at 30 mm. The reaction mixture was filtered again. Cooling the filtrate in a −78° bath deposited a dirty white solid which was filtered after several minutes and sucked dry. The crude product was purified by two sublimations at 120–130° (0.1 mm.) to give 0.21 g. (10.5% yield) of pale yellow crystals of $(Tdp)_2Mo(CO)_4$, m.p. 147–148°.

Anal. Calcd. for $C_{16}H_{36}N_6P_2MoO_4$: C, 36.0; H, 6.7; N, 15.7; P, 11.6; Mo, 18.0; mol. wt., 534. Found: C, 35.7; H, 6.4; N, 15.5; P, 11.5; Mo, 17.9; mol, wt., 551.

Infrared Spectrum.—Carbon–hydrogen bands at 2975 (w),

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[11] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

[12] E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *ibid.*, 4559 (1958); J. D. Munro and P. L. Pauson, *ibid.*, 3475 (1961).

2900 (sh), 2860 (m), 2820 (sh), and 2780 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1460 (m), 1430 (w), 1400 (w), 1260 (m), 1172 (s), 1145 (m), 1055 (m), 960 (s), and 945 (s) cm.$^{-1}$.

Reaction between Bicyclo[2.2.1]heptadienemolybdenum Tetracarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 1.50 g. (5 mmoles) of bicyclo[2.2.1]heptadienemolybdenum tetracarbonyl,[13] 2.0 ml. (2.0 g., 12.3 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of methylcyclohexane was refluxed 1 hr. under nitrogen with magnetic stirring. From this reaction mixture 1.15 g. (43% yield) of crude $(Tdp)_2Mo(CO)_4$ was isolated in a manner completely analogous to the isolation of $(Tdp)Mo(CO)_5$ described above. Sublimation of a 0.60-g. sample of this crude product at 140° (0.1 mm.) gave 0.47 g. (34% yield) of pale yellow crystalline $(Tdp)_2Mo(CO)_4$, m.p. 148–150°, identical with the material obtained above from the reaction between cycloheptatrienemolybdenum tricarbonyl and tris-(dimethylamino)-phosphine.

Anal. Calcd. for $C_{16}H_{36}N_6P_2MoO_4$: C, 36.0; H, 6.7. Found: C, 35.5; H, 6.9.

Reaction between Cyclooctatetraeneiron Tricarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 0.61 g. (2.5 mmoles) of cyclooctatetraeneiron tricarbonyl,[14] 1.0 ml. (1.0 g., 6.1 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of ethylcyclohexane was refluxed 15 hr. under nitrogen with magnetic stirring. From this reaction mixture 0.27 g. (23% yield) of orange crystals of crude $(Tdp)_2Fe(CO)_3$, m.p. 191–200°, was isolated in a manner analogous to the isolation of $(Tdp)Mo(CO)_5$ described above.

The infrared and n.m.r. spectra of this sample of $(Tdp)_2Fe(CO)_3$ were identical with those of an authentic sample obtained from $Fe_3(CO)_{12}$ and tris-(dimethylamino)-phosphine.

Anal. Calcd. for $C_{15}H_{36}N_6P_2FeO_3$: C, 38.6; H, 7.7. Found: C, 39.4; H, 7.9.

Reaction between $Hg[Co(CO)_4]_2$ and Tris-(dimethylamino)-phosphine.—A mixture of 1.5 g. (2.76 mmoles) of $Hg[Co(CO)_4]_2$,[15] 1.5 ml. (1.5 g., 9.2 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of thiophene-free benzene was stirred at room temperature under nitrogen for 70 hr. Vigorous gas evolution seemed to occur immediately. After the reaction period was over the reaction mixture was filtered by gravity. Solvent was removed from the filtrate at ~30 mm., leaving a yellow crystalline residue. After one recrystallization from dichloromethane–hexane, 1.07 g. (48% yield) of yellow crystalline $Hg[Co(CO)_3(Tdp)]_2$ was obtained.

On standing or on heating to temperatures in excess of ~250° $Hg[Co(CO)_3(Tdp)]_2$ became black.

Anal. Calcd. for $C_{18}H_{36}N_6P_2Co_2HgO_6$: C, 26.6; H, 4.4; N, 10.3. Found: C, 26.2; H, 4.7; N, 10.2.

Infrared Spectrum.—Carbon–hydrogen bands at 2900 (sh), 2860 (w), and 2775 (sh) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1470 (sh), 1455 (w), 1270 (w), 1175 (m), 1055 (w), 965 (sh), 955 (s), and 697 (m) cm.$^{-1}$.

Reaction between Cyclopentadienylvanadium Tetracarbonyl and Tris-(dimethylamino)-phosphine.—A mixture of 0.5 g. (2.2 mmoles) of cyclopentadienylvanadium tetracarbonyl,[16] 2.0 ml. (2.0 g., 12.3 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of methylcyclohexane was refluxed 21 hr. under nitrogen with magnetic stirring. From this reaction mixture 0.32 g. (40% yield) of crude $C_5H_5V(CO)_3(Tdp)$ was isolated in a manner similar to that described above for $(Tdp)Mo(CO)_5$. After two sublimations at 90–100° (0.1 mm.), 0.30 g. (37.5% yield) of orange crystals of $C_5H_5V(CO)_3(Tdp)$, m.p. 187°, was obtained.

Anal. Calcd. for $C_{14}H_{23}N_3PVO_3$: C, 46.3; H, 6.3; N, 11.6; P, 8.6; mol. wt., 363. Found: C, 45.0; H, 6.5; N, 11.6; P, 8.5; mol. wt., 396.

Infrared Spectrum.—Carbon–hydrogen bands at 2900 (sh), 2850 (w), 2815 (sh), and 2775 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1463 (vw), 1444 (vw), 1423 (vw), 1265 (w), 1180 (m), 1165 (sh), 1060 (vw), 975 (m), 955 (s), 825 (w), 812 (w), and 692 (w) cm.$^{-1}$.

Reaction between Cyclopentadienylnickel Carbonyl Dimer and Tris-(dimethylamino)-phosphine.—A mixture of 1.5 g. (~5 mmoles) of cyclopentadienylnickel carbonyl dimer,[17] 3.0 ml. (3.0 g., 18.5 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of thiophene-free benzene was stirred 24 hr. under nitrogen at room temperature. The red color of the cyclopentadienylnickel carbonyl dimer disappeared rapidly. After the reaction period was over the reaction mixture was filtered by gravity, collecting the filtrate under nitrogen. Solvent was removed from the filtrate at ~30 mm., leaving a mixture of crystals and liquid. This residue was treated with ~30 ml. of pentane and the solution filtered by gravity, collecting the greenish filtrate under nitrogen. Cooling this filtrate in a −78° bath caused a mixture of green and white crystals to separate. These were removed by filtration and sucked dry.

The $(C_5H_5)_2Ni$ was removed from this mixture by sublimation at 50–70° (0.1 mm.) for 2 hr. to give 0.43 g. (46% yield based on $[C_5H_5NiCO]_2$) of green crystals of crude $(C_5H_5)_2Ni$. The residue from the $(C_5H_5)_2Ni$ sublimation was sublimed three times at 100–120° (0.1 mm.) to give 0.05 g. (2.3% yield) of $(Tdp)_2Ni(CO)_2$, m.p. 80–82°. The low yield was evidently a consequence of decomposition during these three sublimations.

The infrared spectrum of the $(Tdp)_2Ni(CO)_2$ obtained from this reaction was identical with that of the $(Tdp)_2Ni(CO)_2$ obtained from nickel tetracarbonyl and tris-(dimethylamino)-phosphine.

Anal. Calcd. for $C_{14}H_{36}N_6P_2NiO_2$: C, 38.1; H, 8.2; N, 19.0; P, 14.0. Found: C, 37.8; H, 8.1; N, 19.1; P, 13.8.

Reaction between Cyclopentadienyliron Dicarbonyl Iodide and Tris-(dimethylamino)-phosphine.—A mixture of 1.5 g. (5 mmoles) of cyclopentadienyliron dicarbonyl iodide,[18] 1.0 ml. (1.0 g., 6.1 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of thiophene-free benzene was refluxed 6 hr. under nitrogen with magnetic stirring. The black color of the $C_5H_5Fe(CO)_2I$ disappeared and a precipitate formed. After cooling to room temperature the precipitate was filtered and dried to give 1.6 g. (69% yield) of pale yellow $[C_5H_5Fe(CO)_2(Tdp)]I$, m.p. 234° dec.

Anal. Calcd. for $C_{13}H_{23}N_3PIFeO_2$: C, 33.4; H, 4.9; N, 9.0; P, 6.6; I, 27.2; O, 6.9. Found: C, 32.9; H, 5.1; N, 8.7; P, 6.6; I, 26.6; O, 8.1.

Infrared Spectrum.—Carbon–hydrogen bands at 3000 (w) and 2875 (w) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1480 (w), 1466 (w), 1460 (w), 1450 (w), 1425 (w), 1410 (w), 1270 (w), 1240 (vw), 1170 (w), 1138 (w), 1055 (vw), 1045 (vw), 1012 (vw), 1000 (vw), 970 (sh), 960 (m), 910 (vw), 895 (vw), 880 (w), 833 (w), 710 (m), and 700 (m) cm.$^{-1}$.

Conductivity.—A molar conductance of 164 ± 15 mhos was found by measurements on acetone solutions of several concentrations in the range 1.1×10^{-3} to 6.1×10^{-3} *M*.

Reaction between Cyclopentadienylmolybdenum Tricarbonyl Iodide and Tris-(dimethylamino)-phosphine.—A mixture of 0.93 g. (2.5 mmoles) of cyclopentadienylmolybdenum tricarbonyl iodide,[19] 0.5 ml. (0.5 g., 3.1 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of thiophene-free benzene was refluxed 21 hr. under nitrogen with magnetic stirring. After the reaction period was over the reaction mixture was allowed to cool to room temperature and then filtered. Solvent was removed from the red filtrate at ~30 mm., leaving a red solid residue which was washed with three 15-ml. portions of pentane and dried. The product was twice recrystallized from a mixture of dichloromethane and hexane to give 0.40 g. (31.5% yield) of red crystals,

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[13] R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

[14] T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960); M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

[15] W. Hieber, E. O. Fisher, and E. Böckly, *Z. anorg. allgem. Chem.*, **269**, 308 (1952).

[16] E. O. Fischer and S. Vigoureux, *Ber.*, **91**, 2205 (1958).

[17] E. O. Fisher and C. Palm, *ibid.*, **91**, 1725 (1958).

[18] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

[19] T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

m.p. 156–165°, which were identified by n.m.r. to be a mixture of two isomers of $C_5H_5Mo(CO)_2(Tdp)I$.

In a repeat preparation an attempt was made to separate the two isomers by chromatography in benzene solution on a 2 × 50 cm. alumina column. Extensive decomposition occurred. Only a single red band was observed. This band was eluted with benzene and the eluate evaporated at ~30 mm. After recrystallization from dichloromethane–hexane the resulting red crystals, m.p. 180–182° dec., were demonstrated by n.m.r. (see Fig. 2) to contain the two isomers of $C_5H_5Mo(CO)_2(Tdp)I$ in a greatly different ratio from that observed in the original preparation where chromatography was not used. This accounts for the significantly different melting points of the two samples. Unfortunately, the losses of material during the chromatography process were too large to permit isolation of one of the pure isomers by selective decomposition during repeated chromatography.

Anal. Calcd. for $C_{13}H_{23}N_3PIMoO_2$: C, 30.7; H, 4.5; N, 8.3; P, 6.1; I, 25.0. Found: C, 30.7; H, 4.3; N, 8.0; P, 6.0; I, 25.3.

Infrared Spectrum.—Carbon–hydrogen bands at 2860 (w), and 2775 (sh) cm.$^{-1}$; see Table I for metal carbonyl bands; other bands at 1455 (w), 1420 (sh), 1268 (w), 1175 (m), 1060 (w), 974 (m), 956 (s), 809 (w), and 691 (w, br) cm.$^{-1}$.

Conductivity.—A molar conductance of 1.5 ± 0.25 mhos was found by measurements on acetone solutions of several concentrations in the range 7.3×10^{-4} to 3.8×10^{-3} *M*.

Reaction between Cycloheptatrienylmolybdenum Dicarbonyl Iodide and Tris-(dimethylamino)-phosphine.—A mixture of 0.9 g. (2.5 mmoles) of cycloheptatrienylmolybdenum dicarbonyl iodide,[20] 0.5 ml. (0.5 g., 3.1 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of thiophene-free benzene was refluxed under nitrogen for 6 hr. with magnetic stirring. After the reaction period was over the reaction mixture was allowed to cool to room temperature. The reaction mixture was filtered. Solvent was removed from the yellow-black filtrate at ~30 mm. The resulting yellow-black residue was washed with three 15-ml. portions of pentane and sucked dry. The crude product was purified by repeated recrystallization from mixtures of dichloromethane and hexane. After two recrystallizations, 0.42 g. (33% yield) of brown crystalline $C_7H_7MoCO(Tdp)I$, m.p. 113° dec., was obtained.

This derivative appears to be unusually difficult to obtain pure, the carbon and nitrogen content being persistently low. Possibly the compound loses tris-(dimethylamino)-phosphine on drying.

Anal. Calcd. for $C_{14}H_{25}N_3PMoOI$: C, 33.3; H, 5.0; N, 8.3; P, 6.1; I, 25.2. Found: C, 30.5; H, 5.2; N, 7.3; P, 6.4; I, 26.1.

Infrared Spectrum.—Carbon–hydrogen bands at 2960 (sh, w), 2850 (w), and 2760 (w) cm.$^{-1}$; metal carbonyl band at 1910 (s) cm.$^{-1}$; other bands at 1490 (w), 1455 (w), 1428 (w), 1265 (w), 1238 (vw), 1175 (m), 1055 (w), 975 (m), 953 (s), 845 (vw), 797 (m), and 687 (w) cm.$^{-1}$.

Reaction between Allyliron Tricarbonyl Iodide and Tris-(dimethylamino)-phosphine.—A mixture of 1.54 g. (5 mmoles) of allyliron tricarbonyl iodide,[21] 1.0 ml. (1.0 g., 6.1 mmoles) of tris-(dimethylamino)-phosphine, and 50 ml. of thiophene-free benzene was stirred 72 hr. under nitrogen at room temperature. The brown color of the allyliron tricarbonyl iodide disappeared. After the reaction period was over the reaction mixture was filtered and solvent removed from the filtrate at ~30 mm. The resulting crystalline residue was treated with ~30 ml. of pentane and the orange solution filtered by gravity. Cooling the filtrate in a −78° bath caused the separation of pale orange crystals. These were filtered and sucked dry to give 0.30 g. (21% yield) of $(Tdp)_2Fe(CO)_3$, m.p. 198°.

The infrared and n.m.r. spectra of this product were identical with those of an authentic sample of $(Tdp)_2Fe(CO)_3$ obtained from triiron dodecacarbonyl and tris-(dimethylamino)-phosphine.

Anal. Calcd. for $C_{15}H_{36}N_6P_2FeO_3$: C, 38.6; H, 7.7. Found: C, 38.3; H, 7.7.

Other Reactions of Tris-(dimethylamino)-phosphine.—Sodium tetrachloropalladate(II) and tris-(dimethylamino)-phosphine gave a yellow precipitate in methanol solution which was demonstrated by n.m.r. and elemental analyses to be a mixture of at least two nonisomeric compounds. Cyclopentadienyliron dicarbonyl dimer and cyclopentadienylmolybdenum tricarbonyl dimer gave only brown amorphous decomposition products on refluxing with tris-(dimethylamino)-phosphine in xylene solution. Cyclopentadienylmanganese tricarbonyl was so inert that even on heating with excess tris-(dimethylamino)-phosphine to the boiling point of the latter (~160°) in the absence of solvents the manganese compound was recovered unchanged.

Discussion

A. General Properties of Tris-(dimethylamino)-phosphine Derivatives.—A characteristic feature of the derivatives of tris-(dimethylamino)-phosphine described above is the reluctance for more than two tris-(dimethylamino)-phosphines to be bonded to a single metal atom. Thus the reaction between tris-(dimethylamino)-phosphine and nickel tetracarbonyl yields $(Tdp)_2Ni(CO)_2$ rather than $(Tdp)_4Ni$ analogous to $(PCl_3)_4Ni$.[2] Somewhat more unusual, however, are the reactions of tris-(dimethylamino)-phosphine with the cycloheptatriene derivatives $C_7H_8M(CO)_3$ (M = Cr and Mo) to give the compounds $(Tdp)_2M(CO)_4$ (M = Cr and Mo) rather than the compounds $(Tdp)_3M(CO)_3$ (M = Cr and Mo) analogous to the compounds formed from the cycloheptatriene–metal tricarbonyl derivatives and all other trivalent phosphorus derivatives.[3]

This reluctance for more than two tris-(dimethylamino)-phosphines to bond to a single metal atom may be due to the nature of the phosphorus atom in this ligand. The proximity of the three lone electron pairs on the three nitrogen atoms may cause the phosphorus atom to be relatively strongly basic but weakly electron-accepting. Thus, although the lone pair on the phosphorus is readily donated to the metal atom forming a strong σ-bond, the negative charge accumulating on the metal atom from such bonding cannot be efficiently removed by back donation to an empty d-orbital of the phosphorus atom since the lone electron pairs from the nitrogen atoms already partially occupy the d-orbitals on the phosphorus atom. The tendency for the phosphorus atom in tris-(dimethylamino)-phosphine to participate in partial double bonding with the transition metal atom is therefore relatively small in comparison with other ligands containing trivalent phosphorus or in comparison with carbon monoxide, nitric oxide, or isocyanides.[22]

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(20) D. J. Bertelli, Ph.D. Dissertation, University of Washington, 1961, p. 63.

(21) R. A. Plowman and F. G. A. Stone, *Z. Naturforsch.*, **17b**, 575 (1962).

(22) It might appear that the reluctance for more than two tris-(dimethylamino)-phosphine residues to bond to a single metal atom could also arise from steric rather than electronic factors. In this connection it is of interest that cycloheptatrienemolybdenum tricarbonyl reacts with triphenylphosphine to form the complex $[(C_6H_5)_3P]_3Mo(CO)_3$, indicating that three triphenylphosphine residues can be bonded to a single metal atom. This result coupled with the observation in this work that tris-(dimethylamino)-phosphine reacts with cycloheptatrienemolybdenum tricarbonyl to form the complex $(Tdp)_2Mo(CO)_4$ makes an explanation based on steric factors relatively unlikely since tris-(dimethylamino)-phosphine would appear to be less demanding sterically than the bulky triphenylphosphine. Nevertheless, despite extensive work by various research groups on tricovalent phosphorus derivatives of metal carbonyls, insufficient data are available to permit definite conclusions.

The relative positions of the metal carbonyl bands in the infrared spectra of the metal carbonyl derivatives of tris-(dimethylamino)-phosphine (Table I) support this small tendency of this ligand for partial double bonding with transition metal atoms. The metal carbonyl bands are shifted to lower frequencies than the corresponding bands in the pure metal carbonyl derivatives to an extent at least as large as in other trivalent phosphorus complexes. This shift arises from increased partial double bonding between the metal and the carbon atom of the carbonyl group in order to remove the negative charge accumulating from the tris-(dimethylamino)-phosphine–transition metal bonds. Such an effect has been observed previously in other classes of compounds where the transition metal acquires a negative charge either due to a weakly electron-accepting (*i.e.*, weakly "back-bonding") ligand as in the complexes (diethylenetriamine)M(CO)$_3$ ($M =$ Cr and Mo)[3] or due to the formation of a negatively charged ion as in numerous metal carbonyl anions such as $[Co(CO)_4]^-$.[23]

A characteristic feature of the infrared spectra of metal complexes of tris-(dimethylamino)-phosphine is the presence of one or two strong bands in the range 975–945 cm.$^{-1}$, possibly due to the phosphorus–nitrogen bonds of the ligand. The presence of bands in this region of intensity comparable to the metal carbonyl or other strong bands is a useful indication of the presence of tris-(dimethylamino)-phosphine in a complex. Weaker absorptions in the infrared spectra of the tris-(dimethylamino)-phosphine complexes also attributed to this ligand occur in the regions 1475–1435, 1275–1255, 1185–1140, and 1060–1055 cm.$^{-1}$.

B. Proton N.m.r. Spectra of the Complexes (Table II).—The proton n.m.r. spectra of tris-(dimethylamino)-phosphine and the complexes containing *one* tris-(dimethylamino)-phosphine bonded to a metal atom exhibit a doublet due to the methyl protons. This may be attributed to the eighteen equivalent protons of the six methyl groups being split by the phosphorus nucleus ($I = {}^1/_2$). The separations of the two peaks of the doublet range from 8.4 c.p.s. in $C_5H_5V(CO)_3$(Tdp) to 10.2 c.p.s. in (Tdp)Mo(CO)$_5$. In addition, the π-cyclopentadienyl rings in $C_5H_5V(CO)_3$(Tdp), $[C_5H_5Fe(CO)_2$(Tdp)]I, and the two isomers of C_5H_5Mo(CO)$_2$(Tdp)I and the π-cycloheptatrienyl ring in C_7H_7MoCO(Tdp)I exhibit resonances due to the five or seven equivalent protons of the ring which in some cases are split up to 2.5 c.p.s. by the phosphorus atom bonded to the same metal atom.

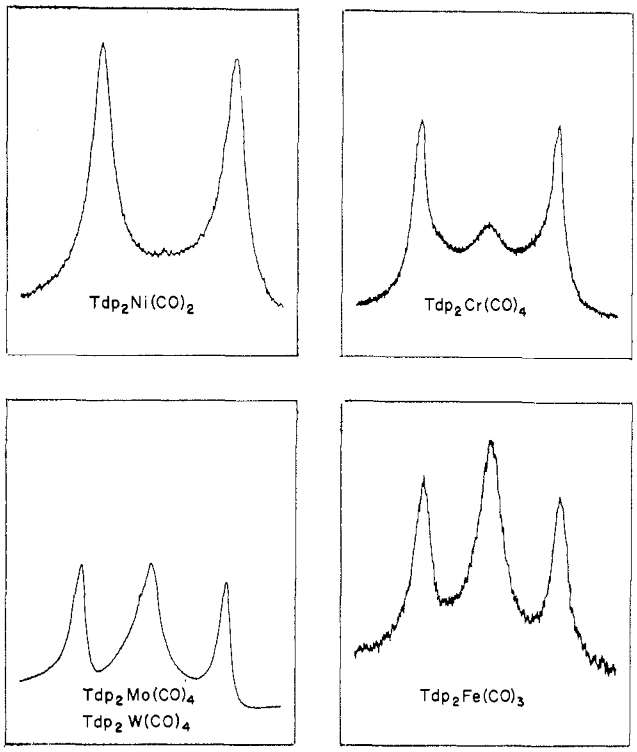

Fig. 1.—Shapes of methyl resonances in complexes with two tris-(dimethylamino)-phosphines bonded to a single metal atom.

The proton n.m.r. spectra of the complexes containing *two* tris-(dimethylamino)-phosphines bonded to a metal atom (Fig. 1) are of considerable interest since they yield information concerning the coupling between the two phosphorus atoms. If the coupling between the two phosphorus atoms is zero or very small in comparison with the phosphorus–hydrogen coupling of 8 to 10 c.p.s., a doublet would be expected analogous to the doublet observed in complexes with only one tris-(dimethylamino)-phosphine bonded to a metal atom. The complex (Tdp)$_2$Ni(CO)$_2$ (Fig. 1) exhibits this type of spectrum. If the coupling between the two phosphorus atoms is very large in comparison with the phosphorus–hydrogen coupling of 8 to 10 c.p.s., a 1:2:1 triplet would be expected entirely analogous to the pattern expected from two equivalent phosphorus atoms coupled to the methyl protons.[24,25] This type of spectrum is approximated by that of the complexes (Tdp)$_2$Fe(CO)$_3$ and [(Tdp)$_2$Co(CO)$_3$][Co(CO)$_4$] (Fig. 1).

Interpolation between these two limiting cases permits predictions of patterns for compounds where the phosphorus–phosphorus coupling is appreciable but not very large in comparison with the phosphorus–hydrogen coupling. The spectrum of (Tdp)$_2$Cr(CO)$_4$ (Fig. 1) illustrates a case where the phosphorus–phosphorus coupling is barely significant; in this spectrum the center peak of the triplet is much lower and broader than the outer peaks. As the phosphorus–phosphorus coupling increases relative to the phosphorus–hydrogen coupling, the center peak of the triplet would be expected to become narrower and higher. The spectra of (Tdp)$_2$M(CO)$_4$ ($M =$ Mo and W) illustrate another intermediate situation where the center peak is approximately the same height as the outer peaks.

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[23] See the discussion of infrared spectra of metal carbonyl derivatives in J. Chatt, P. L. Pauson, and L. M. Venanzi, "Organometallic Chemistry," H. H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 477–480.

[24] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, New York, N. Y., 1961, pp. 71–77.

[25] For a more detailed analysis of related spectra see R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961). It is not possible to calculate an exact value for the phosphorus–phosphorus coupling using only the splittings in the proton n.m.r. spectra.

Thus, by the shapes of the triplets of the methyl resonances it is possible to estimate qualitatively from readily obtainable proton n.m.r. spectra phosphorus–phosphorus coupling constants in various complexes containing two tris-(dimethylamino)-phosphines. By this method the phosphorus–phosphorus coupling constants are found to increase in the series: $(Tdp)_2Ni(CO)_2 << (Tdp)_2Cr(CO)_4 < (Tdp)_2Mo(CO)_4 \cong (Tdp)_2W(CO)_4 < (Tdp)_2Fe(CO)_3 < [(Tdp)_2Co(CO)_3]^+$.

The complex $(Tdp)_2Ni(CO)_2$ in the above series by analogy with the tetrahedral $Ni(CO)_4$[26] and other tetrahedral nickel(0) complexes would also be expected to be tetrahedral. The complexes $(Tdp)_2M(CO)_4$ (M = Cr, Mo, and W) on the basis of a single strong band in the carbonyl region of the infrared spectrum (Table I) appear to have the two tris-(dimethylamino)-phosphines in the *trans* positions of an octahedron; similarly the complexes $(Tdp)_2Fe(CO)_3$ and probably $[(Tdp)_2Co(CO)_3]^+$ [27] have the two tris-(dimethylamino)-phosphines in the *trans* positions of a trigonal bipyramid. The n.m.r. data thus suggest that the coupling between phosphorus atoms bonded to a metal with the tetrahedral configuration is negligible whereas coupling between phosphorus atoms bonded in *trans* positions to a metal atom with an octahedral or trigonal bipyramidal configuration is appreciable. The coupling between phosphorus atoms in the *trans* positions of the trigonal bipyramidal systems appears to be somewhat greater than similar coupling in octahedral systems. The large coupling between phosphorus atoms in *trans* positions may be related to the well known "*trans* effect" in substitution reactions in square-planar and octahedral systems.[28]

C. Reactions of Tris-(dimethylamino)-phosphine with Metal Carbonyls and Hydrocarbon Complexes of Metal Carbonyls.—As discussed above nickel tetracarbonyl reacts with excess tris-(dimethylamino)-phosphine at temperatures only slightly above room temperature to give the complex $(Tdp)_2Ni(CO)_2$ and not the complex $(Tdp)_4Ni$ analogous to $(PCl_3)_4Ni$.[2] Reaction of the cyclopentadienyl nickel carbonyl derivative $[C_5H_5NiCO]_2$[17] with tris-(dimethylamino)-phosphine at room temperature yields this same complex $(Tdp)_2Ni(CO)_2$ together with bis-(cyclopentadienyl)-nickel, apparently according to the equation

$$[C_5H_5NiCO]_2 + 2Tdp \rightleftarrows (Tdp)_2Ni(CO)_2 + (C_5H_5)_2Ni$$

It is to be noted that this reaction is the reverse reaction of the preparation of $[C_5H_5NiCO]_2$ from $Ni(CO)_4$ and $(C_5H_5)_2Ni$[17] with $(Tdp)_2Ni(CO)_2$ replacing the nickel tetracarbonyl. This substitution of two carbonyl groups with tris-(dimethylamino)-phosphine residues appears to alter significantly the position of the equilibrium, possibly because carbon monoxide due to its high volatility can escape from the system driving the equilibrium in the direction favoring $[C_5H_5NiCO]_2$ and carbon monoxide, whereas tris-(dimethylamino)-phosphine due to its much lower volatility cannot escape from the system.

Dicobalt octacarbonyl was found to react exothermically with tris-(dimethylamino)-phosphine, evolving gas and producing a yellowish solution from which yellow crystals of the composition $(Tdp)_2Co_2(CO)_7$ could be isolated. The high conductivity in acetone solution supports the ionic formulation $[(Tdp)_2Co(CO)_3]^+[Co(CO)_4]^-$, analogous to previously reported compounds $[(R_3P)_2Co(CO)_3][Co(CO)_4]$.[4] The carbonyl region of the infrared spectrum is also consistent with this formulation. The band at 1877 $cm.^{-1}$ may be assigned to the $Co(CO)_4^-$ ion and the bands at 1970 and 1982 $cm.^{-1}$ to the $(Tdp)_2Co(CO)_3^+$ ion. The shift to higher frequencies by $\sim$100 $cm.^{-1}$ of the carbonyl bands in $(Tdp)_2Co(CO)_3^+$ as compared with the band in the isoelectronic $(Tdp)_2Fe(CO)_3$ (1871 $cm.^{-1}$) is exactly the change that would be expected in going from a neutral species to positively charged species due to a lowering of the metal–carbon bond order and concomitant raising of the carbon–oxygen bond order due to a reduced negative charge on the metal atom.

In addition to the formation of yellow pentane-insoluble $[(Tdp)_2Co(CO)_3][Co(CO)_4]$ in good yield in the reaction between dicobalt octacarbonyl and tris-(dimethylamino)-phosphine, a red pentane-soluble compound was produced in low yield but not obtained in the pure state. Analytical data, although relatively poor, and the infrared spectrum suggested the possible formulation of this red species as $[(Tdp)Co(CO)_3]_2$ analogous to other compounds of a similar type,[4] but the characterization of this compound was very unsatisfactory.

The reaction between iron pentacarbonyl or triiron dodecacarbonyl and tris-(dimethylamino)-phosphine was found to yield a mixture of the compounds $(Tdp)Fe(CO)_4$ and $(Tdp)_2Fe(CO)_3$.[5] The composition of mixtures obtained from such reactions could be analyzed readily by proton n.m.r. since the sharp methyl doublet due to $(Tdp)Fe(CO)_4$ and the sharp methyl triplet due to $(Tdp)_2Fe(CO)_3$ both showed up clearly in spectra of mixtures. Fractional vacuum sublimation proved to be an excellent method for separating pure $(Tdp)Fe(CO)_4$ and pure $(Tdp)_2Fe(CO)_3$ from the mixtures due to the great differences in the volatilities of these two complexes.

The infrared spectrum due to the carbonyl groups in $(Tdp)_2Fe(CO)_3$ exhibits only a single strong band, indicating that the carbonyl groups are located at the *trans* positions of the trigonal bipyramid.[6] In an attempt to prepare *cis*-$(Tdp)_2Fe(CO)_3$ the reaction between cyclooctatetraeneiron tricarbonyl and tris-(dimethylamino)-phosphine was investigated. However, the *trans* isomer identical with the product obtained from $Fe_3(CO)_{12}$ and tris-(dimethylamino)-phosphine was obtained. The tris-(dimethylamino)-

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[26] L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935).

[27] Although carbonyl bands at 1970 and 1982 $cm.^{-1}$ are observed in $[(Tdp)_2Co(CO)_3]^+$, the separation of only 12 $cm.^{-1}$ in the frequencies of these bands suggests that the symmetry of this cation must be very nearly that of the neutral molecule $(Tdp)_2Fe(CO)_3$ and that it is reasonable to assume that the two tris-(dimethylamino)-phosphines are bonded in the *trans* positions of a trigonal bipyramid in both of these species.

[28] See, for example, J. V. Quagliano and L. Schubert, *Chem. Rev.*, **50**, 201 (1952); F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

phosphine residues are probably too bulky to occupy *cis* positions in a trigonal bipyramid.

Reactions of tris-(dimethylamino)-phosphine with chromium and molybdenum hexacarbonyls yielded the substitution products (Tdp)M$(CO)_5$ (M = Cr and Mo) but the reaction of tris-(dimethylamino)-phosphine with tungsten hexacarbonyl yielded the substitution product $(Tdp)_2W(CO)_4$. In order to prepare the chromium and molybdenum complexes of the type $(Tdp)_2M(CO)_4$ the reactions between the bicyclo-[2.2.1]heptadiene–metal tetracarbonyl derivatives[11,13] and tris-(dimethylamino)-phosphine were used. Displacement of the hydrocarbon residues occurred in the expected manner, the reaction being somewhat more rapid with the molybdenum complex.

The complexes $(Tdp)_2M(CO)_4$ (M = Cr, Mo, and W) all exhibit asingle strong band in the metal carbonyl region, indicat ing that the two tris-(dimethylamino)-phosphine groups are located at the *trans* positions of the octahedron. As in the case of the trigonal bipyramidal $(Tdp)_2Fe(CO)_3$ system, the tris-(dimethylamino)-phosphine residues appear to be too bulky to occupy *cis* positions in an octahedron. *trans*-Complexes are even obtained from the reactions involving the displacement of the bicyclo[2.2.1]heptadiene system, which because of its chelating nature is forced to occupy the *cis* positions of the octahedron. A rearrangement thus must occur in the reaction between tris-(dimethylamino)-phosphine and the bicyclo[2.2.1]heptadiene–metal tetracarbonyl derivatives involving conversion of an unfavorable *cis* isomer to a favorable *trans* isomer.

In an attempt to prepare $(Tdp)_3M(CO)_3$[3] complexes (M = Cr and Mo) the reactions between the cycloheptatriene–metal tricarbonyl derivatives and tris-(dimethylamino)-phosphine were investigated. Instead of the expected products, the compounds *trans*-$(Tdp)_2M(CO)_4$ identical with those described above were obtained in an unusual reaction. Again the reluctance for two tris-(dimethylamino)-phosphine residues to occupy *cis* positions is demonstrated.

The reaction between cyclopentadienylvanadium tetracarbonyl[16] and tris-(dimethylamino)-phosphine was investigated and found to yield the compound $C_5H_5V(CO)_3(Tdp)$, the first tertiary phosphine substitution product of cyclopentadienylvanadium tetracarbonyl to be reported. The presence of a cyclopentadienyl resonance at $\tau = 5.39$ and a methyl resonance at $\tau = 7.78$ (doublet, $J = 8.4$ c.p.s.) confirms the proposed formulation.

The reaction between the mercury derivative Hg-$[Co(CO)_4]_2$[15] and tris-(dimethylamino)-phosphine was also investigated and found to yield the expected substitution product $Hg[Co(CO)_3(Tdp)]_2$, analogous to previously reported complexes of the type Hg[Co-$(CO)_3PR_3]_2$.[7]

D. Reactions of Tris-(dimethylamino)-phosphine with Metal Carbonyl Halide Derivatives.—Several hydrocarbon metal carbonyl halides were available and it seemed of interest to investigate reactions of these with tris-(dimethylamino)-phosphine in order to establish whether displacement of carbonyl groups, the halogen atom, or the hydrocarbon residue would occur.

Reaction between cyclopentadienyliron dicarbonyl iodide and tris-(dimethylamino)-phosphine yielded a product of the composition $[C_5H_5Fe(CO)_2(Tdp)]I$ as yellow benzene-insoluble crystals. The high conductivity of acetone solutions demonstrates the ionic character of this compound, indicating that in this reaction the tris-(dimethylamino)-phosphine replaced the iodine. This complex may thus be regarded as a salt of the $[C_5H_5Fe(CO)_2(Tdp)]^+$ ion analogous to the $[C_5H_5Fe(CO)_2P(C_6H_5)_3]^+$ ion.[8] The analogous reaction between cyclopentadienyliron dicarbonyl chloride and tris-(dimethylamino)-phosphine yielded a similar yellow solid, demonstrated by infrared spectra and analyses to be a mixture of iron(II) chloride and $[C_5H_5Fe(CO)_2(Tdp)]Cl$.

Reaction between cyclopentadienylmolybdenum tricarbonyl iodide and tris-(dimethylamino)-phosphine yielded a product of the composition $C_5H_5Mo(CO)_2$-(Tdp)I as red benzene-soluble crystals. In contrast to $[C_5H_5Fe(CO)_2(Tdp)]I$ this molybdenum complex possesses a low conductivity in acetone solution, indicating it to be covalent. Thus in the reaction with tris-(dimethylamino)-phosphine a carbonyl group rather than an iodine atom in $C_5H_5Mo(CO)_3I$ is replaced. The similar reaction between cycloheptatrienylmolybdenum dicarbonyl iodide and tris-(dimethylamino)-phosphine yielded a product of the composition $C_7H_7MoCO(Tdp)I$ as brown benzene-soluble crystals. Again the carbonyl group rather than the iodine atom is replaced by the ligand to form a covalent derivative. This compound could not be obtained pure, possibly due to a tendency to lose tris-(dimethylamino)-phosphine on drying.

The proton n.m.r. spectrum of $C_5H_5Mo(CO)_2(Tdp)I$ was unexpectedly complex (Fig. 2). A singlet and a doublet were observed in the cyclopentadienyl region and two overlapping doublets in the methyl region. This indicated $C_5H_5Mo(CO)_2(Tdp)I$ to be a mixture of two isomers. This was confirmed by preparing samples which exhibited these resonances in different relative intensities but which had the same composition. Unfortunately, $C_5H_5Mo(CO)_2(Tdp)I$ could not be separated into the pure isomers by chromatography on alumina. Nevertheless, observations of the relative intensities of the resonances in different samples (Fig. 2) has permitted the assignment of the doublet ($J = 1.6$ c.p.s.) cyclopentadienyl resonance at $\tau = 4.74$ and the doublet ($J = 9.0$ c.p.s.) methyl resonance at $\tau = 7.35$ to one of the isomers (isomer A) and the singlet cyclopentadienyl resonance at $\tau = 4.67$ and the doublet ($J = 8.7$ c.p.s.) methyl resonance at $\tau = 7.41$ to the other isomer (isomer B).

It is of interest that the n.m.r. spectrum of C_7H_7-MoCO(Tdp)I indicates it to be a single pure isomer in contrast to $C_5H_5Mo(CO)_2(Tdp)I$. The two isomers of $C_5H_5Mo(CO)_2(Tdp)I$ might have the structures I and II, differing as to whether the tris-(dimethylamino)-phosphine and iodine occupy *cis* or *trans* positions.

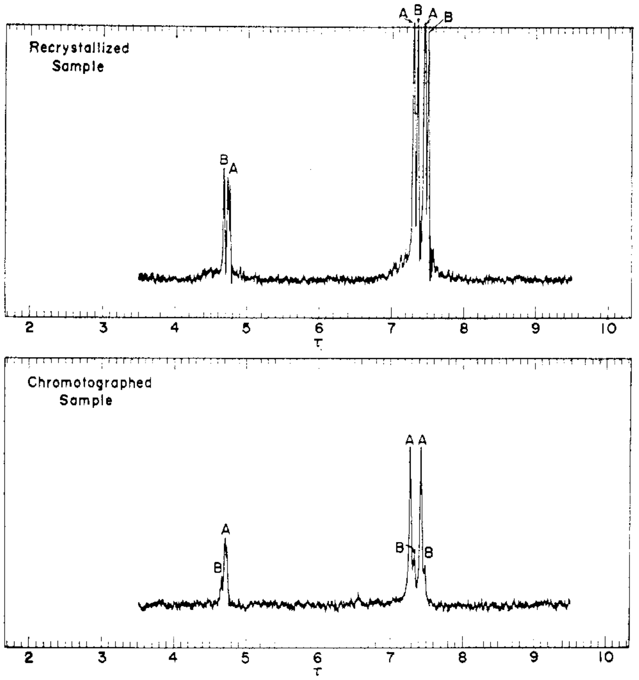
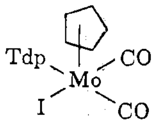
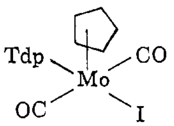


Fig. 2.—Proton n.m.r. spectra of different samples of $C_5H_5Mo(CO)_2(Tdp)I$.

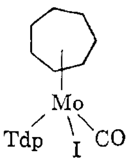
Such isomerism cannot occur in $C_7H_7MoCO(Tdp)I$ (III), which has only three groups besides the seven-membered ring bonded to the metal atom.



I



II



III

The reaction of the halide derivative $C_3H_5Fe(CO)_3I$[21] with tris-(dimethylamino)-phosphine was entirely different from the reactions described above. In this case the ligand displaced both the allyl group and the iodine atom to form the complex $(Tdp)_2Fe(CO)_3$, which was identical with the product obtained from the reaction of $Fe_3(CO)_{12}$ or $C_8H_8Fe(CO)_3$ with tris-(dimethylamino)-phosphine.

Reactions of tris-(dimethylamino)-phosphine with manganese pentacarbonyl bromide and heptafluoropropyliron tetracarbonyl iodide were investigated. In the former case the yellow-orange crystalline product was not obtained pure; in the latter case a brown viscous liquid was obtained which defied attempts at crystallization. Reaction of tris-(dimethylamino)-phosphine with germanium(II) iodide gave a yellow liquid which could not be crystallized. This product, which was not obtained in the pure state, is presumably the compound $(Tdp)GeI_2$, analogous to other compounds of the type $R_3P{\cdot}GeI_2$.[1]

Acknowledgment.—The author is indebted to Mr. M. Bisnette for experimental assistance; to Dr. F. B. Brown of Union Carbide Olefins Company, South Charleston, West Virginia, for supplying dicobalt octacarbonyl; and to Dr. P. C. Lauterbur for helpful discussions on n.m.r. spectra.

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Transition Metal Complexes of a Constrained Phosphite Ester. II. Compounds of Cobalt(I), Cobalt(III), and Nickel(II) with 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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The preparation and characterization of some cobalt and nickel complexes of 4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane, $P(OCH_2)_3CCH_3$, are described. Maximum coordination numbers are observed for the yellow diamagnetic $[Co(P(OCH_2)_3CCH_3)_5]ClO_4$ and the colorless diamagnetic $[Co(P(OCH_2)_3CCH_3)_6](ClO_4)_3$ which arise from a disproportionation reaction of $Co(ClO_4)_2{\cdot}6H_2O$ with the ligand. The colorless octahedral complex exhibits bands at 325 mμ (ϵ 340) and 280 mμ (ϵ 2000) which are assigned to d → d transitions. The ligand field strength provided by this phosphite is shown to be about the same as that of the cyanide ion. The yellow diamagnetic $[Ni(P(OCH_2)_3CCH_3)_5H_2O](ClO_4)_2$ is also described.

Introduction

Attempts to synthesize isolable complexes of cobalt and nickel with trialkyl phosphites such as triethyl and trimethyl phosphite have been unsuccessful[2] although some reaction is indicated by color changes. We have been investigating the coordinating properties of the phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane, $P(OCH_2)_3CCH_3$. This polycyclic ligand, hereafter referred to as L, in contrast to trialkyl phosphites has associated with it very low ligand–ligand repulsion due to steric effects and hence can function as a strong coordinating agent. In the first paper of

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[2] A. E. Arbuzov and V. Zoroastrova, *Dokl. Akad. Nauk SSSR*, **84**, 503 (1952); *Chem. Abstr.*, **46**, 10038*f* (1952).