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Reactions of "Mixed" Ligands with Group VIb Metal Carbonyls[1]

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In the course of investigations of "mixed" derivatives of the Group VIb metal carbonyls,[3] it became desirable to prepare complexes of the type $M(CO)_3X_2Y$ (M = Cr, Mo, W) containing two amine groups (X) and another Lewis base ligand (Y). However, although $M(CO)_4(dipy)$[4] and $M(CO)_4(phen)$[4] yield $M(CO)_3X_2Y$ complexes with both phosphines and phosphites, the initial attempt to prepare an analogous complex of a diamine through the reaction of $Mo(CO)_4(tmen)$[4] with triphenylphosphine resulted in the exclusive replacement of the bidentate ligand.[5] An effort was therefore

$$Mo(CO)_4(tmen) + 2P(C_6H_5)_3 \longrightarrow trans\text{-}Mo(CO)_4[(PC_6H_5)_3]_2$$

made to prepare complexes of the desired type through synthesis and use of "mixed" polydentate ligands containing both phosphine and amine functional groups.[6] Herein are reported the reactions of three such ligands—1-(diphenylphosphino)-2-(diethylamino)ethane (NP), bis(diethylaminoethyl)phenylphosphine (NPN), and bis(diphenylphosphinoethyl)ethylamine (PNP)—with group VIb metal carbonyls and with $Mo(CO)_4(phen)$.

Experimental Section

Ligands.—The ligands were prepared in a manner *wholly* analogous to that employed by Mann and Millar[7] in the synthesis of $(C_6H_5)P(C_2H_4)_2N(C_6H_5)$. The following reaction scheme for the preparation of NP typifies those for the other two ligands as well

$$(C_6H_5)_2PH + C_2H_5MgBr \xrightarrow[\text{benzene}]{\text{dry ether}} (C_6H_5)_2PMgBr + C_2H_6$$

$$(C_6H_5)_2PMgBr + BrC_2H_4N(C_2H_5)_2 \xrightarrow{\text{benzene}} NP + MgBr_2$$

The amine was obtained as the hydrobromide salt through reaction of concentrated HBr and $(C_2H_5)_2NC_2H_4OH$,[8] was extracted into ether from solution in aqueous ammonia, and was dried and distilled at reduced pressure under a nitrogen atmosphere. NP, after hydrolysis of the reaction mixture, drying, and removal of the solvent *in vacuo* was vacuum distilled to give a colorless oil (bp 140–143° (0.05 mm)). This ligand has also been prepared by another method.[9] *Anal.* Calcd for $C_{18}H_{24}NP$: C, 75.81; H; 8.42; N, 4.91; P, 10.86. Found: C, 75.04; H, 8.48; N, 4.81, P, 10.80.

Reaction of $(C_6H_5)P(MgBr)_2$ with 2 equiv of $BrC_2H_4N(C_2H_5)_2$, followed by an identical work-up, gave NPN as a colorless oil (bp 135–137° (0.03 mm)). *Anal.* Calcd for $C_{18}H_{33}N_2P$: C, 70.09; H, 10.78; N, 10.04; P, 9.08. Found: C, 69.85; H, 10.58; N, 9.90; P, 9.05.

PNP was prepared through reaction of $(C_6H_5)_2PMgBr$ and $C_2H_5N(C_2H_4Cl)_2$. The amine hydrochloride was obtained through reaction of the corresponding alcohol and $SOCl_2$,[10] and the amine was freed and distilled immediately before use. After hydrolysis of the reaction mixture and removal of the solvent *in vacuo* the crude PNP was vacuum distilled (115° (0.01 mm)) to remove unreacted $(C_6H_5)_2PH$. The residue was then dissolved in hexane and filtered, and the solvent was removed. The solid thus obtained was recrystallized twice from hot ethanol to give white needles of the product (mp 50–51°). *Anal.* Calcd for $C_{30}H_{33}NP_2$: C, 76.78; H, 7.08; N, 2.98; P, 13.20. Found: C, 76.69; H, 6.93; N, 3.25; P, 13.45.

Derivatives.—All reactions were carried out under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer Model 421 or 621 spectrophotometer and were calibrated against the known bands of polystyrene (see Table I).

a. **$M(CO)_4(NP)$ and $M(CO)_3(PNP)$.**—Equimolar amounts of $M(CO)_6$ and NP or PNP were refluxed overnight in an appropriate solvent. (NP: Cr, 2,2,5-trimethylpentane; Mo, *n*-heptane; W, mesitylene. PNP: Cr, xylene; Mo, toluene; W, mesitylene.) The products, which precipitated from the solutions as yellow crystals, were then washed with petroleum ether (bp 60–90°) and dried *in vacuo*. Recrystallization from acetone–water was carried out where necessary. In other experiments, the carbonyl stretching region of the infrared spectrum was monitored during the progress of the reactions. Bands attributable to $M(CO)_5(NP)$ and $Mo(CO)_4(PNP)$ were observed and are reported in the table. $Mo(CO)_3(PNP)$ was also prepared by mixing equimolar amounts of (cycloheptatriene)-$Mo(CO)_3$[11] and PNP in *n*-heptane, from which it precipitated at room temperature. *Anal.* Calcd for $Cr(CO)_4(NP)$ ($C_{22}H_{24}CrNO_4P$): C, 58.79; H, 5.38. Found: C, 59.27; H, 5.78. Calcd for $Mo(CO)_4(NP)$ ($C_{22}H_{24}MoNO_4P$): C, 53.56; H, 4.90; N, 2.83; P, 6.27. Found: C, 53.09; H, 5.37; N, 2.99; P, 6.70. Calcd for $W(CO)_4(NP)$ ($C_{22}H_{24}NO_4PW$): C, 45.46; H, 4.16. Found: C, 45.87; H, 4.06. Calcd for $Cr(CO)_3(PNP)$ ($C_{33}H_{33}CrNO_3P_2$): C, 66.55; H, 5.46. Found: C, 66.51; H, 5.60. Calcd for $Mo(CO)_3(PNP)$ ($C_{33}H_{33}MoNO_3P_2$): C, 61.03; H, 5.12; N, 2.16; P, 9.54. Found: C, 61.62; H, 5.38; N, 2.11; P, 9.53. Calcd for $W(CO)_3(PNP)$ ($C_{33}H_{33}NO_3P_2W$): C, 53.76; H, 4.48; P, 6.41. Found: C, 52.15; H, 4.45; P, 6.68.

b. **$Mo(CO)_4(NPN)$.**—Reaction of equimolar amounts of $Mo(CO)_6$ and NPN in *n*-heptane gave a bright yellow solution. Monitoring the carbonyl stretching region of the infrared spectrum showed the reaction not to proceed beyond the formation of $Mo(CO)_4(NPN)$, which was obtained as a yellow *oil* after evaporation of the solvent *in vacuo* and chromatography on silica. *Anal.* Calcd for $C_{22}H_{33}MoN_2O_4P$: C, 51.16; H, 6.44; N, 5.43; P, 6.00. Found: C, 52.20; H, 7.09; N, 5.21; P, 5.55. Reaction of equimolar amounts of NPN and (cycloheptatriene)$Mo(CO)_3$[11] also failed to yield $Mo(CO)_3(NPN)$ (see discussion).

c. **$Mo(CO)_3(phen)(NP)$, $Mo(CO)_3(phen)(NPN)$, and $[Mo(CO)_3(phen)]_2(PNP)$.**—Equimolar amounts of $Mo(CO)_4(phen)$ and NP or NPN were refluxed in xylene for 1 hr; for PNP a 2:1 ratio of $Mo(CO)_4(phen)$ to ligand was employed under the same reaction conditions. The deep blue solutions were cooled, and the purple-black products were collected by suction filtration. They were then washed with petroleum ether and dried *in vacuo*. *Anal.* Calcd for $Mo(CO)_3(phen)(NP)$ ($C_{33}H_{32}MoN_3O_3P$): C,

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[3] (a) L. W. Houk and G. R. Dobson, *J. Chem. Soc., Sect. A*, 317 (1966); (b) L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966).

[4] dipy = 2,2′-dipyridyl; phen = *o*-phenanthroline; en = ethylenediamine; tmen = N,N,N′,N′-tetramethylethylenediamine; teen = N,N,-N′,N′-tetraethylethylenediamine; diphos = 1,2-bis(diphenylphosphino)-ethane.

[5] Subsequent evidence for the formation of $Mo(CO)_3$(diamine)Y complexes with Y ligands less sterically demanding than triphenylphosphine has been obtained by J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 992 (1967), and in this laboratory (G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, in press).

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Table I

Carbonyl Stretching Frequencies for Group VIb Metal Carbonyl Derivatives of "Mixed" Ligands

Complex	ν_{CO}, cm^{-1} [a]	Medium
$Cr(CO)_5(NP)$[b]	2067 w, 1946 s, 1940 s	Hydrocarbon
$Mo(CO)_5(NP)$[b]	2078 w, 1954 s, 1948 s	Hydrocarbon
$W(CO)_5(NP)$[b]	2076 w, 1950 s, 1939 s	Hydrocarbon
$Mo(CO)_5[P(C_6H_5)_3]$[c]	2073, 1951, 1951	Hydrocarbon
$Mo(CO)_5[N(C_2H_5)_3]$[d]	2070, 1936, 1918	Hydrocarbon
$Cr(CO)_4(NP)$	2011 m, 1901 s, 1886 s, 1845 s	Chloroform
$Mo(CO)_4(NP)$	2019 m, 1905 s, 1893 s, 1849 s	Chloroform
$W(CO)_4(NP)$	2013 m, 1898 s, 1884 s, 1844 s	Chloroform
$Mo(CO)_4(NPN)$	2017 m, 1905 s, 1890 s, 1862 s	Ethyl ether
$Mo(CO)_4(PNP)$[b]	2025 m, 1929 s, 1907 s, 1900 s	Hydrocarbon
$Mo(CO)_4$(diphos)[e,f]	2020 m, 1919 s, 1907 s, 1881 s	1,2-Dichloroethane
$Mo(CO)_4$(diphos)	2028 m, 1932 s, 1919 s, 1906 s	Hydrocarbon
$Mo(CO)_4$(teen)[e]	2015 m, 1894 s, 1874 s, 1830 s	Chloroform
$Cr(CO)_3(PNP)$	1923 s, 1824 s, 1791 s	Chloroform
$Mo(CO)_3(PNP)$	1932 s, 1834 s, 1804 s	Chloroform
$W(CO)_3(PNP)$	1928 s, 1828 s, 1791 s	Mull
$Mo(CO)_3(NPN)_2$ (?)	1938 s, 1839 s, 1818 s	Hydrocarbon
$Mo(CO)_3$(diphos)$(C_6H_{11}NH_2)$[g]	1929 s, 1836 s, 1802 s	Chloroform
$Mo(CO)_3$(phen)(NP)[e]	1918 s, 1824 s, 1789 s	Chloroform
$Mo(CO)_3$(phen)(NPN)	1913 s, 1819 s, 1787 s	Chloroform
$[Mo(CO)_3(phen)]_2(PNP)$	1916 s, 1821 s, 1788 s	Chloroform
$Mo(CO)_3(phen)[P(C_6H_5)_3]$[h]	1919 s, 1820 s, 1788 s	Chloroform
$Mo(CO)_2(phen)(NP)_2$[b]	1811 s, 1736 s	Chloroform
$Mo(CO)_2(phen)(NPN)_2$	1807 s, 1733 s	Chloroform
$Mo(CO)_2(phen)[P(C_6H_5)_3]_2$[h]	1815 s, 1836 s	Chloroform

[a] Relative intensities: s, strong; m, medium; w, weak. [b] Observed in solution only. [c] R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962). [d] R. Poilblanc, *Compt. Rend.*, **256,** 4910 (1963). [e] See ref 4. [f] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961). [g] G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, in press. [h] See ref 3a.

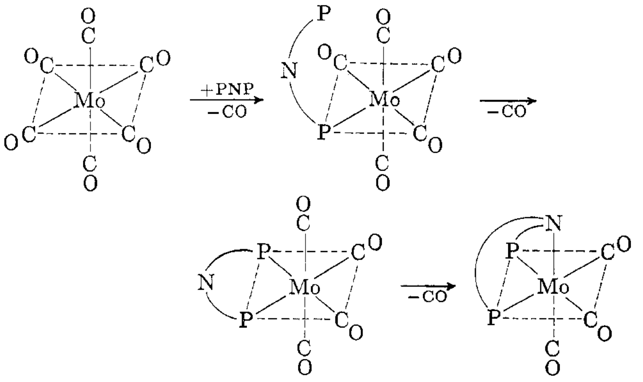
61.40; H, 5.00; N, 6.51. Found: C, 61.93; H, 5.34; N, 5.90. Calcd for $Mo(CO)_3$(phen)(NPN) ($C_{33}H_{41}MoN_4O_3P$): C, 59.29; H, 6.14; N, 8.38. Found: C, 59.11; H, 6.11; N, 8.70. Calcd for $Mo(CO)_3(phen)_2(PNP)$ ($C_{60}H_{49}Mo_2N_5O_6P_2$): C, 60.61; H, 4.15; N, 5.89; P, 5.21. Found: C, 60.37; H, 4.14; N, 5.94; P, 5.02.

d. **$Mo(CO)_2$(phen)$(NP)_2$ and $Mo(CO)_2$(phen)$(NPN)_2$.**—$Mo(CO)_4$(phen) and a fourfold excess of the appropriate ligand were refluxed under nitrogen in xylene. With time, the solution color changed from red-orange to blue to green. The reaction mixtures were monitored in the carbonyl stretching region of the infrared spectrum until no more trisubstituted complex was present (about 12 hr). Upon cooling, $Mo(CO)_2(phen)(NPN)_2$ precipitated out as blue-black crystals, which were washed with petroleum ether and dried *in vacuo*. *Anal.* Calcd for $C_{50}H_{74}MoN_6O_2P_2$: C, 63.30; H, 7.81; N, 8.86. Found: C, 62.88; H, 7.73; N, 9.14. The isolation of pure $Mo(CO)_2(phen)(NP)_2$ could not be effected although the infrared spectrum of the reaction mixture or of a crude precipitate obtained indicated its presence.

e. **$Mo(CO)_4$(teen).**—One gram of $Mo(CO)_6$, 1 ml of teen, and 9 ml of toluene were refluxed for 1 hr, after which time the yellow product was collected by suction filtration, washed with petroleum ether, and dried *in vacuo*. The complex decomposes slowly even *in vacuo*. *Anal.* Calcd for $C_{14}H_{24}MoN_2O_4$: C, 44.21; H, 6.36; N, 7.37. Found: C, 42.54; H, 5.99; N, 7.58.

Results and Discussion

The order of attachment of the coordinating atoms for these ligands as successive carbonyl groups are replaced and the mode of ligand attachment in the resulting complexes may be inferred through comparison of carbonyl stretching spectra of the derivatives obtained to those of known or easily synthesized "model" complexes containing substituents bonded through P or N. Carbonyl stretching frequencies are sensitive to metal–ligand π bonding, and thus coordination through phosphorus or nitrogen may be distinguished, since the requisite d orbitals are not energetically accessible in nitrogen, as they are in phosphorus. The results of such comparisons (Table I), when due allowance is made for lowered carbonyl stretching frequencies in more polar solvents, and the slight differences between the reported complexes and the "models" indicate that carbonyl groups in $M(CO)_6$ are successively replaced first by *each* ligand phosphorus and then by a single ligand nitrogen. For example, the formation of $Mo(CO)_3(PNP)$ proceeds through the steps



I

Thus the final products $M(CO)_4(NP)$, $Mo(CO)_4(NPN)$, and $M(CO)_3(PNP)$ are obtained.

The inability of NPN to replace a third carbonyl from $Mo(CO)_6$ merits further comment. An attempt to prepare $Mo(CO)_3(NPN)$ through replacement of cycloheptatriene from $(C_7H_8)Mo(CO)_3$ through the slow addition of an equimolar amount of the ligand was also unsuccessful, the product obtained being an ill-defined air-sensitive yellow solid the infrared spectrum of which (Table I) indicated the presence of two phosphorus atoms and one nitrogen atom in the coordination sphere of Mo. Thus the product might be formulated as $Mo(CO)_3(NPN)_2$, in which one NPN is bonded to Mo through a nitrogen and a phosphorus, while the other NPN is bonded only through phosphorus. This behavior is not inconsistent with the following observations.

(1) Though $M(CO)_3(amine)_3$ complexes are well known, they have been reported only for primary and cyclic amines.

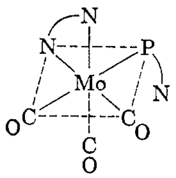
(2) $Mo(CO)_4(en)$[4] and $Mo(CO)_4(tmen)$[4] are air stable, but the corresponding complex of the bulky teen[4] decomposes *in vacuo* despite the order of electron-releasing ability of substituent groups in the ligands, $H < CH_3 < C_2H_5$.

(3) While triphenylphosphine replaces tmen from $Mo(CO)_4(tmen)$ to give, finally, *trans*-$Mo(CO)_4[P(C_6H_5)_3]_2$ as the only product, less sterically demanding ligands, *e.g.*, trimethyl phosphite, give spectroscopic evidence for the formation of the "mixed" trisubstituted complexes, $Mo(CO)_3(tmen)(phosphite)$.[5]

(4) Amine basicities vary in the order: diethylamine > triethylamine > cyclohexylamine. $Mo(CO)_3(phen)(amine)$ complexes have been reported[3b] for diethylamine and cyclohexylamine, but the bulkier triethylamine does not form an analogous complex.

These results should indicate that the relatively weaker bonding of amines than phosphines in such complexes renders amine–metal bond formation quite sensitive to steric factors; attempted correlations of ligand bonding properties to ligand basicity in such systems should be made with extreme caution.

Reactions of $Mo(CO)_4(phen)$ with the ligands give complexes in which one or two carbonyls are replaced only by phosphorus atoms of the ligands (Table I), the remaining carbonyls being mutually *cis*, again as demonstrated by comparison of the infrared spectra of the derivatives and "model" complexes. The failure of the amines to coordinate is not surprising, since such coordination would involve the replacement of a carbonyl *trans* to the phen ligand(II) rather than *trans* to the more strongly π-accepting phosphorus, as is possible with the coordination of two independent ligands (III). The similarity of the carbonyl stretching spectra for the derivatives reported here and the "model" complexes, in which the two phosphorus atoms are believed to be *trans* to one another,[3a] supports similar stereochemistry. Somewhat higher carbonyl stretching frequencies would be expected were the phosphorus atoms *cis* since, for the *trans* isomer, each carbonyl is also *trans* to a phen nitrogen (III) while, for the *cis* isomer, one carbonyl is *trans* to a nitrogen and the other is *trans* to a phosphorus (IV).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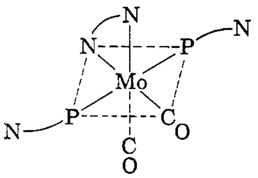
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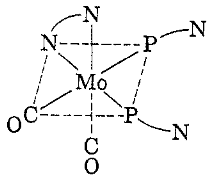
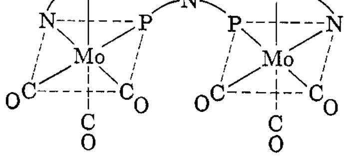

IV

The ligand PNP functions as a bridging group to give the first example of a "mixed" binuclear derivative of the group VIb metal carbonyls. Bridging occurs through the two phosphorus atoms, the amine being uncoordinated (V), as determined by chemical analysis and infrared spectral data (Table I).


V

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Basic Zinc Dialkylphosphinothioates

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Interest in the structure and properties of coordination polymers, involving bridging phosphinate groups,[1] prompted us to examine the ability of the thio derivatives of phosphinic acid to act as bridging groups between tetrahedral metal ions. During the course of an investigation of the polymeric nature of Zn(II) and Co(II) dialkylphosphinothioates of stoichiometry $M(R_2PSO)_2$ (where M = Zn(II), Co(II) and R = C_2H_5, n-C_4H_9), we obtained under certain conditions zinc salts which display basic properties.

Running different preparations, using the metal acetates and the dialkylphosphinothioic acids in ethanol, we obtained the normal salts, which are polymers in noncoordinating solvents and in the solid state.[2] The normal salts $Co(R_2PSO)_2$ could also be obtained using cobalt carbonate, whereas the reaction with zinc car-

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