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Reactions of "Mixed" Bidentate Ligands with Group VIB Metal Carbonyls

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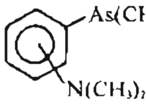
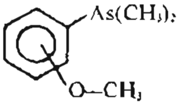
Reactions of o-N,N-dimethylamino-phenyl-diethyl-phosphine (P–N) and o-methoxy-phenyl-diethylphosphine (P–O) with metal carbonyls M(CO)$_6$ (M = Cr, Mo, W) yield substituted penta- and tetracarbonyls of the type M(CO)$_5$(P–O), M(CO)$_5$(P–N), M(CO)$_4$(P–O)$_2$, M(CO)$_4$(P–N)$_2$ and M(CO)$_4$(P–N) depending on the reaction conditions and the ligand used. Infrared spectra for these complexes are reported and discussed.

Introduction

In previous papers[1,2] we have described the reactions of group VIB metal carbonyls with bidentate « mixed » ligands (As–N) and (As–O) having the functional groups in the *ortho* and/or *para* position:



ortho and *para*, (As–N)



ortho and *para*, (As–O)

Depending on the experimental conditions and the reaction products were the pentacarbonyls M(CO)$_5$(As–N) and M(CO)$_5$(As–O), and the *cis*-tetracarbonyls M(CO)$_4$(As–N)$_2$ and M(CO)$_4$(As–O)$_2$ in which the « mixed » ligand is coordinated only through the As atom, with the exception of Mo(CO)$_4$(As–N) in which the *ortho* bidentate ligand acts as a chelating group. We have suggested that the non-occurrence of the complexes M(CO)$_4$(As–N) or M(CO)$_4$(As–O) is probably due to the small coordinating ability of the N and O atoms, even when the functional groups are in favorable chelating positions.

In the present paper we report the reactions of M(CO)$_6$ (C = Cr, Mo and W) metal carbonyls with the following « mixed » ligands: *o*-N,N-dimethylamino-phenyl-diethylphosphine (P–N) and *o*-methoxyphenyl-diethylphosphine (P–O).

Experimental Section

Materials. The ligands (P–N)[3] and (P–O)[4] and the complexes Mo(CO)$_4$ (1,5-cyclooctadiene),[5] Cr(CO)$_4$ (norbornadiene)[6] and W(CO)$_4$ (norbornadiene)[7] have been synthesized following the procedures reported in the literature.

Instrumentation. Infrared spectra in the CO stretching region were recorded on a Perkin-Elmer Mod. 621 spectrophotometer and calibrated against the known bands of polystyrene (Table II). Molecular weights were determined using a Mecrolab Mod. 302 osmometer.

Complexes. All reactions were carried out in a nitrogen atmosphere. Analytical data and physical properties of the complexes reported are collected in Table I.

a. M(CO)$_5$(P–O) and M(CO)$_5$(P–N). Equimolar amounts of M(CO)$_6$ and (P–O) or (P–N) were refluxed for a convenient time (Mo, 10 h; Cr, 15 h; W, 18 h) in a mixtuxre of hexane-heptane (b.p. ~ 85°C). Removal of the solvent under water aspirator vacuum, followed by sublimation of the unreacted hexacarbonyl, gave the crude products which were crystallized from methanol. Chromatography on alumina was carried out where necessary. Upon heating the complexes M(CO)$_5$(P–N) at ~160°C, derivatives the M(CO)$_4$(P–N) were obtained in almost quantitative yield

b. M(CO)$_4$(P–N). M(CO)$_6$ (~2 mmoles) and an equimolar amount of ligand (P–N) dissolved in anhydrous *n*-buthylether (10÷20 ml) were heated overnight in an evacuated tube (internal vol. ~250 ml) at appropriate temperatures (Mo, 140°; Cr, 150°; W, 155°C). Removal of the solvent under reduced pressure, followed by sublimation of the unreacted hexacarbonyl gave a yellow residue which was dissolved in benzene and chromatographed on alumina. By elution with hexane three compounds were separated. The isomer *trans*–M(CO)$_4$(P–N)$_2$ (0÷10%), which moved with the solvent front, was followed closely by the pentacarbonyl compound M(CO)$_5$(P–N), which was often present in small quantities. Since the isomer *cis*–M(CO)$_4$(P–N) (50÷70%) moved rather slowly, it was best removed from the column by elution with CH$_2$Cl$_2$. These compounds can also

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(1) G. Rizzardi, R. Ros, and L. Sindellari, *Gazz. Chim. Ital.*, *98*, 1231 (1968).
(2) M. Vidali, R. Ros, and G. Rizzardi, *Gazz. Chim. Ital.*, *98*, 1240 (1968).
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Table I. Physical Properties and Analytical Data for « mixed » Ligand Derivatives

Compound	Colour	M.P. (°C)	Molecular weight Calculated (Found)	Analysis Calculated (Found) C	H	N
$Cr(CO)_5(P-O)$	pale-yellow	54-55	—	49.5 (49.2)	4.4 (4.2)	
$Cr(CO)_5(P-N)$	white	50-51	411 (363)	49.6 (51.1)	4.9 (5.01)	3.4 (3.5)
$Mo(CO)_5(P-O)$	white	52-55	432 (415)	44.4 (44.8)	4.0 (4.2)	
$Mo(CO)_5(P-N)$	white	48-49	—	44.8 (45.6)	4.4 (4.5)	3.1 (3.08)
$W(CO)_5(P-O)$	pale-yellow	61-62	—	36.9 (36.8)	3.3 (3.3)	
$W(CO)_5(P-N)$	pale-yellow	57-58	—	37.6 (37.9)	3.7 (3.8)	2.6 (2.5)
cis–$Cr(CO)_4(P-O)_2$	yellow	153-154	546 (535)	57.1 (56.8)	6.27 (6.30)	
cis–$Mo(CO)_4(P-O)_2$	white	167	—	52.9 (52.8)	5.8 (5.8)	
cis–$W(CO)_4(P-O)_2$	yellow	185	678 (665)	46.0 (45.8)	5.0 (5.0)	
cis–$Cr(CO)_4(P-N)$	yellow	54-55	373 (379)	51.5 (50.7)	5.40 (5.37)	3.75 (3.8)
cis–$Mo(CO)_4(P-N)$	yellow	92-93	417 (388)	46.1 (46.2)	4.8 (5.1)	3.36 (3.34)
cis–$W(CO)_4(P-N)$	pale-yellow	111-112	505 (483)	38.0 (37.6)	3.99 (4.04)	2.77 (2.57)
trans–$Mo(CO)_4(P-O)_2$	yellow	90-91	—	52.89 (53.05)	5.80 (5.85)	
trans–$Mo(CO)_4(P-N)_2$	pale-yellow	101-102	—	52.8 (52.6)	6.33 (6.31)	4.40 (4.4)
trans–$W(CO)_4(P-O)_2$	yellow	108-109	678 (642)	46.0 (45.7)	5.05 (4.95)	
trans–$W(CO)_4(P-N)_2$	yellow	126-127	—	46.4 (46.8)	5.56 (5.72)	3.9 (3.9)

Table II. Infrared Spectra of « mixed » Ligand Derivatives in the Carbonyl Strctching Rcgion [a]

Compound	$\nu(CO)$, cm^{-1} [b]			
	a_1	b_1	$e+a_1$ accidentally degenerate	
$Cr(CO)_5(P-O)$	2060 m	1976 m	1936 s	
$Cr(CO)_5)(P-N)$	2061 m	1975 m	1937 s	
$Cr(CO)_5(As-N)$ [c]	2057 w	1973 m	1935 s	
$Mo(CO)_5(P-O)$	2070 m	1982 m	1940 s	
$Mo(CO)_5(P-N)$	2071 m	1980 m	1941 s	
$W(CO)_5(P-O)$	2064 m	1977 m	1938 s	
$W(CO)_5(P-N)$	2066 m	1975 m	1940 s	
$W(CO)_5(As-N)$ [c]	2068 w	1974 m	1940 s	
	a_1		$a_1+b_1+b_2$	
cis–$Cr(CO)_4(P-O)_2$	2006 m	1907 s	1888 vs	1875 s
cis–$Cr(CO)_4(As-O)_2$	2003 m	1907 s	1889 vs	1873 s
cis–$Mo(CO)_4(P-O)_2$	2015 m	1913 s	1898 vs	1883 s
cis–$Mo(CO)_4(As-O)_2$ [c]	2016 m	1913 s	1900 vs	1881 s
cis–$W(CO)_4(P-O)_2$	2012 m	1908 s	1890 vs	1877 s
cis–$W(CO)_4(As-O)_2$ [c]	2012 m	1905 s	1891 vs	1876 s
cis–$W(CO)_4(As-N)_2$ [c]	2011 m	1906 s	1890 vs	1878 vs
cis–$Cr(CO)_4(P-N)$	2008 m	1904 s	1886 vs	1867 s
cis–$Mo(CO)_4(P-N)$	2018 m	1911 s	1898 vs	1873 s
cis–$Mo(CO)_4(As-N)$ [c]	2016 m	1913 s	1899 vs	1880 vs
cis–$W(CO)_4(P-N)$	2014 m	1902 s	1887 vs	1871 s
			e_u	
trans–$Cr(CO)_4(P-O)_2$			1879 s	
trans–$Cr(CO)_4(P-N)_2$			1881 s	
trans–$Mo(CO)_4(P-O)_2$			1887 s	
trans–$Mo(CO)_4(P-N)_2$			1886 s	
trans–$W(CO)_4(P-O)_2$		1940 vw	1881 s	
trans–$W(CO)_4(P-N)_2$			1882 s	

[a] Cyclohexane solution. [b] Relative intensities: s, strong; m, medium; v, very; w, weak. [c] G. Rizzardi, R. Ros, and L. Sindellari, *Gazz. Chim. Ital.*, 98, 1231 (1968).

be prepared by reacting diene derivatives of the type $M(CO)_4(diene)$ [diene = 1,5-cyclooctadiene, M = Mo; norbornadiene, M = Cr and W] with stoichiometric amounts of the ligand (P–N) in boiling heptane.

c. $M(CO)_4(P-O)_2$. Following the same preparative route described above a mixture of *cis*– $(50\div 70\%)$ and *trans*–$M(CO)_4(P-O)_2$ $(3\div 20\%)$ was obtained, together with small amounts of the pentacarbonyls $M(CO)_5(P-O)$. These complexexs were separated by chromatography on alumina in the order *trans*–$M(CO)_4(P-O)_2$, $M(CO)_5(P-O)$, and *cis*–$M(CO)_4(P-O)_2$ using hexane/CH_2Cl_2 as solvents.

Results and Discussion

It is known that the replacement of CO groups in metal carbonyls by tervalent phosphorus or arsenic compounds proceeds stepwise with increasing difficulty, and that electronegative substituents on the phosphorus or arsenic donor atoms favor this replacement.[8-10] Bidentate ligands such as diphosphines[11] or diarsines[12] (L–L) replace four CO groups in the hexacarbonyls of group VIB metals to give complexes of the type $M(CO)_2(L-L)_2$ (M = Cr, Mo and W). The use of

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(9) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962)

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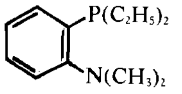
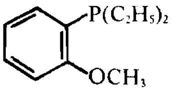
(12) H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1803 (1960).

such bidentate ligands is of special interest because of the expected stabilization of the products caused by entropy effects, and also because they necessarily replace CO groups in *cis*-position.

As a continuation of our studies on the reactions of bidentate ligands with the group VIB hexacarbonyls we have used as « mixed » ligands *o*-N,N-dimethylamino-phenyl-diethyl-phosphine (P–N) and *o*-methoxy-phenyl-diethylphosphine (P–O).



(P–N)



(P–O)

The reaction products were of three types depending on the experimental conditions and on the ligand:

i) *$M(CO)_5(P–O)$ and $M(CO)_5(P–N)$*. These complexes have been obtained by reacting $M(CO)_6$ (M = Cr, Mo, W) in a refluxing mixture of hexane-heptane and have been characterized by elemental analysis, molecular weight measurements (Table I), and ir spectra (Table II). The mode of ligand attachment in the complexes has been inferred from comparison of their carbonyl stretching frequencies with those of known complexes containing substituents bonded through P or N.[13,14]

ii) *$M(CO)_4(P–N)$*. These complexes were obtained at higher temperatures (140÷155°C) than were used in the preparation of the pentacarbonyl derivatives. They were purified by chrmatography on alumina to separate the small amounts of *trans*–$M(CO)_4(P–N)_2$ and $M(CO)_5(P–N)$ that were present in the reaction mixture. Analytical data for the complexes $M(CO)_4(P–N)$ are reported in Table I; their ir spectra (Table II) are in agreement with a *cis* structure in which the « mixed » ligand (P–N) acts as a bidentate. These complexexs were also prepared by reacting diene derivatives of the types (diene)$M(CO)_4$ [diene = 1.5-cyclooctadiene, M = Mo; norbornadiene, M = Cr and W] with the stoichiometric amount of the ligand (P–N). The ir spectra of these samples were identical with those of the compounds prepared by the procedure described above.

iii) cis–*$M(CO)_4(P–O)_2$*. These complexes were synthesized as descrxibed above. The main product of the reaction was the *cis* isomer which was separated from the *trans* isomer by chromatography on alumina.

It is worth noting that the derivatives *trans*–$M(CO)_4(P–O)_2$ isomerize to the *cis*-derivatives either on heating the solid at the melting point of the *trans*-isomer, or in solution of chlorinated solvents (CH_2Cl_2,, $CHCl_3$). Rapid dissolution of a sample of the *trans*-compound in these solvents, followed by immediate inspection of the infrared spectrum in the carbonyl stretching region, has shown that the amount of *cis*-isomer increases slightly during the time of measurement. In the case of the derivative $W(CO)_4(P–O)_2$, the almost complete conversion of the *trans*-isomer to the *cis* take place in about 20 hr. The band at 1881 cm^{-1} (*trans*-isomer) disappears as the carbonyl stretching bands at 1877, 1890, 1908 and 2012 cm^{-1} (*cis*-isomer) increase in intensity

If the reactions are carried out at higher temperatures and for longer times there is no further replacement of CO groups by the mixed ligands *o*-N,N-dimethylamino-phenyl-diethyl-posphine (P–N) and *o*-methoxy-phenyl-diethylphosphine (P–O).

This reluctance of the phosphines (P–O) and (P–N) and the analogous arsines (As–O) and (As–N)[1] to replace more than two CO groups may be due to the steric crowding around the donor atoms.

Table II descrives some further comments. A tentative assignment of the CO stretching bands is there reported, based upon literature data on carbonyl derivatives of the same symmetry.[14] The monosubstituted derivatives are characterised by a medium intensity band in the range 1974-1982 cm^{-1}, attributed to the formally infrared inactive b_1 mode. The appearance of such band is not surprising owing to the assymmetry of the organic ligand, which may cause the selection rules for the C_{4v} point group to break down. Furthermore, the strong band in the region 1935-1941 cm^{-1} is evidently formed by the accidental degeneracy of the e and the lower energy a_1 modes. For the *cis*-disubstituted derivatives only the highest energy band can be unambigously assigned to the a_1 mode. The other three bands at lower energy cannot be assigned with certainty to the remaining a_1, b_1, and b_2 modes required by the C_{2v} symmetry, since no force constant calculations have been carried out. The *trans*-disubstituted derivatives show the expected strong e_u band (D_{4h} symmetry) in the range 1879-1887 cm^{-1}. The very weak band at 1940 cm^{-1} of *trans*–$W(CO)_4(P–O)_2$ may be due to one of the two formally infrared inactive a_{1g} and b_{1g} modes.

Acknowledgment. We gratefully acknowledge the Italian Council of Research (C. N. R. Rome) for financial support of this work.

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