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Chromium, Molybdenum and Tungsten Carbonyl Complexes with Hybrid "Tripod-like" Ligands

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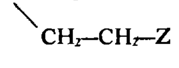
The quadridentate hybrid «tripod-like» ligands, tris-(2-diphenylphosphinoethyl)amine (NP_3), tris(2-isopropylthioethyl)amine (NS_3), bis(2-diphenylphosphinoethyl)-2-diethylaminoethylamine (N_2P_2), bis(2-diphenylphosphinoethyl)-2-methoxyethylamine (NOP_2), bis-(2-methylthioethyl)-2-diethylaminoethylamine (N_2S_2), bis(2-diethylaminoethyl)-2-diphenylphosphinoethylamine (N_3P), tris(2-diethylaminoethyl)amine (N_4), react with the Cr, Mo, and W hexacarbonyls. The ligands with a donor set N_2P_2, NOP_2, N_2S_2, and NS_3 act as terdentate ligands to yield complexes $M(CO)_3L$ which are monomeric and soluble in organic solvents. Insoluble complexes have been obtained with NP_3 as the ligand; mass spectra show that these compounds also have an empirical formula $M(CO)_3$ NP_3. The $Mo(CO)_3NP_3$ complex can be converted into $Mo(CO)_2NP_3$ in which NP_3 acts as a quadridentate ligand. No compounds have been isolated with the N_4 and N_3P ligands.

Introduction

Substituted carbonyl complexes of group VIb metals have been widely studied[1] and it is known that ligands with P and As donor atoms replace carbonyls from $M(CO)_6$ (M = Cr, Mo, W) more readily than ligands containing N, O, and S.

Recently[2,3] potentially quadridentate ligands with PS_3, PAs_3, and P_4 as the donor sets have been utilized to prepare M^0 and M^{II} carbonyl complexes of these. Only QP [QP = tris(o-diphenylphosphinophenyl)phosphine] acts as a quadridentate ligand in complexes of the type $M(QP)(CO)_2$. The first two behave as terdentate.

We proposed to extend the variety of donor sets utilizing hybrid «tripod-like» ligands of the type (1), with different combinations of peripherial donor atoms.



$X = Y = Z = PPh_2$ (NP_3)
$X = Y = PPh_2$, $Z = NEt_2$ (N_2P_2)
$X = Y = PPh_2$, $Z = OMe$ (NOP_2)
$X = Y = Z = S[CH(CH_3)_2]$, ($NS_3$)
$X = Y = SMe$, $Z = NEt_2$ (N_2S_2)
$X = Y = Z = NEt_2$ (N_4)
$X = Y = NEt_3$, $Z = PPh_2$ (N_3P)

(I)

Experimental Section

The ligands were prepared as described elsewhere.[4] All reactions were carried out under a dry nitrogen atmosphere, although the solid complexes were not affected appreciably in the air.

Preparation of $M(CO)_3L$ ($L = NP_3$). 1 mmole of metal carbonyl and the stoichiometric quantity of ligand was irradiated in di-n-butyl ether (50 ml). A fine precipitated formed, which was filtered, washed with much di-n-butyl ether and petroleum ether and then dried in a nitrogen stream.

Preparation of $M(CO)_3L$ ($L = N_2P_2$, NOP_2). 1 mmole) of metal carbonyl was treated with the stoichiometric quantity of ligand in much di-n-butyl ether (100-200 ml), since we observed that these complexes do not crystallize well from concentrated solutions. The solution was heated to boiling slowly with moderate and constant stirring. Simultaneously carbon monoxide was evolved and the solution turned yellow. When the colour was deep yellow (orange for chromium complexes), the solution slowly was cooled. The needle-shaped crystals, which formed on standing, were filtered off and washed with di-n-butyl ether and petroleum ether and dried in a nitrogen stream.

Preparation of $M(CO)_3L$ ($M = Mo$; $L = NS_3$, N_2S_2). The preparation was carried out as before, but di-n-butyl ether was substituted by n-butanol, because the ligands partially decompose at high temperature.

Preparation of $Mo(CO)_2NP_3$. The complex $Mo(CO)_3NP_3$ was placed in a sublimator and slowly heated to *ca.* 270-280°C/10^{-5} mm. The compound lost carbon monoxide, colouring more intensely, and then sublimed. The complex obtained in this way was already pure enough for analysis. The other compounds of the type $M(CO)_3NP_3$ (M = Cr, W) decomposed under these conditions and we could not obtain a sufficient quantity for analysis.

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(2) Wai See Tsang, Devon W. Meek, and Andrew Wojcicki, *Inorg. Chem.*, *7*, 1263 (1968).
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Table I.

Compound	Colour	Analyses %						CO Stretches (cm^{-1})[a]
		Calcd.			Found			
		C	H	N	C	H	N	
$Cr(CO)_3NP_3$	bright-yellow	68.44	5.36	1.77	69.00	5.44	1.83	1910s[b], 1810vs[b]
$Cr(CO)_3NOP_2$[c]	yellow orange	64.25	5.55	2.20	63.81	5.64	2.01	1915s, 1820s, 1790s
$Cr(CO)_3N_2P_2$	orange	65.67	6.25	4.13	65.55	6.70	3.82	1915s, 1830vs, 1790s
$Mo(CO)_3NP_3$[d]	yellow	64.83	5.08	1.68	65.08	4.99	1.63	1930s[b], 1825vs[b]
$Mo(CO)_3NOP_2$	yellow	60.10	5.19	2.06	60.08	5.59	1.90	1930vs, 1830s, 1800s
$Mo(CO)_3N_2P_2$[e]	yellow	61.67	5.88	3.89	61.03	6.05	3.87	1930vs, 1830s, 1808s
$Mo(CO)_3N_2S_2$	sand	40.53	6.35	6.30	40.88	6.74	6.30	1910vs, 1780vs, 1770sh
$Mo(CO)_3NS_3$[f]	sand	42.93	6.60	2.78	42.16	6.76	2.79	1920vs, 1800s, 1790s
$Mo(CO)_2NP_3$	deep yellow	65.53	5.25	1.74	65.34	5.41	1.82	1835vs, 1750vs
$W(CO)_3NP_3$	yellow	54.74	4.59	1.52	54.98	4.33	1.65	1915s[b], 1810vs[b]
$W(CO)_3NOP_2$	yellow	53.21	4.60	1.83	51.75	4.58	1.94	1915vs, 1815s, 1790s
$W(CO)_3N_2P_2$	yellow	54.96	5.23	3.46	54.58	5.56	3.35	1915vs, 1820s, 1790s

[a] in dichloroethane solution; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. [b] in nujol mulls. [c] molecular weight: Calcd.: 635.6; Found: 620. [d] Mo analysis: Calcd.: 11.51%; Found: 11.25%. [e] molecular weight: Calcd.: 720.6; Found: 709. [f] molecular weight: Calcd.: 503.6; Found: 536.

Reactions of N_4 and N_3P with $M(CO)_6$ (M=Cr, Mo, W). No complex was obtained with these ligands: the solutions rapidly became darker and soon reduced to a pitch.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Molar conductivity values were measured on a WTW model LBR/B conductance bridge. Molecular weights were determined in dichloroethane at 37°C with a Mechrolab Model 301 A vapour osmometer calibrated with benzil. The mass spectra were recorded on a single focusing Hitachi-Perkin-Elmer RMU-6H spectrometer.

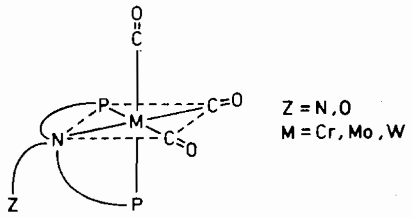
Results and Discussion

Analytical data and some physical properties of the complexes are given in Table I.

The complexes obtained with N_2P_2, NOP_2, and N_2S_2 ligands are crystalline, easily soluble in common organic solvents, monomeric and non-ionic as shown by the molecular weight and conductivity measurements performed on the typical complexes.

The i.r. spectra of the carbonyls substituted with N_2P_2 and NOP_2 have three strong and sharp bands in the carbonyl stretching frequency region and are very similar to those of PNP (PNP=N,NBis(2-diphenylphosphinoethyl)ethylamine)[5] substituted carbonyl complexes. A structural study performed on Cr-(PNP)$(CO)_3$ showed that this complex has a *cis* configuration,[6] thus we can suggest for our compounds a similar *cis* geometry with P, N, P as bonding atoms and the remaining donor atom not engaged in bonding (II).

The compound obtained with N_2S_2 shows CO stretching bands similar to the previous complexes. The displacement of the bands to lower frequencies has to be expected, since sulphur has less π-bonding ability than phosphorus. Therefore in this complex the coordinated atoms have to be considered SNS with a tripod arm free as before.



(II)

The complexes with NP_3 are quite insoluble in the common organic solvents, thus precluding molecular weight measurements in solution. The analytical data show that these compounds also have an empirical formula $M(CO)_3NP_3$. The i.r. spectra of the solids show only two bands in CO stretching region; moreover the band at lower frequency is very broad. The mass spectra of the $Mo(CO)_3NP_3$ and $W(CO)_3NP_3$ compounds are very similar. The ion with highest mass appears at m/e 807 for the Mo compound and at m/e 893 for the W compound. The isotopic peaks of these ions show the presence of only one metal atom and the difference between the masses of the most abundant isotopes of W and Mo corresponds to the difference between 893 and 807. Three ions with similar isotopic peaks at intervals of 28 m/e units are present in both spectra: these peaks should correspond to the loss of three CO's. If three CO's are still present, the molecular masses should be 28 m/e units highest, *i.e.* m/e 921 and m/e 835 respectively. This mass difference may be explained by two hypotheses:

(a) a removal of C_2H_4 owing to the transposition of a $P(C_6H_5)_2$, which joins to the metal;

(b) the compound that sublimes only contains two CO's.

It seems that the first hypothesis has to be exluded, since the ions $MoP(C_6H_5)_2^+$ and $WP(C_6H_5)_2^+$ have not been revealed. Therefore we tried to isolate and analyse the compounds having mass of 807 and 893 m/e units by sublimation under high vacuum.

Only the Mo compound was obtained with the pump

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(5) G.R. Dobson, R. Craig Taylor, and T.D. Walsh, *Inorg. Chem.*, 6, 1929 (1967).

(6) F.A. Cotton and M.D. La Prade, *J. Amer. Chem. Soc.*, 31, 7000 (1969)

that was available. This complex is soluble in organic solvents and the i.r. spectrum shows two sharp CO stretchings clearly shifted towards low frequencies, the elemental analysis too agrees the formula $Mo(CO)_2NP_3$: therefore may be supposed that all four donor atoms of the ligand are coordinated to the metal and that the complex is hexacoordinated with only two CO's. The chromium compound easily alters under the same conditions of temperature and pressure and the mass spectrum showed an analogous fragmentation pattern.

Since, in the mass spectra neither the monomeric species $M(CO)_3NP_3$ nor species having a higher mass have been identified, we cannot establish whether these compounds are monomeric or polymeric, their insolubility is not sufficient to prove a polymeric structure.

The complex obtained with NS_3 is analogous to the complexes with N_2P_2, NOP_2, and N_2S_2, since it is very soluble, monomeric and shows an ir spectrum similar to the complex with N_2S_2. We may therefore conclude that only two of the three equivalent sulphur atoms are coordinated, while the third atom is non-bonded.

Since complexes with N_3P and N_4 ligands have not been isolated, it may be deduced that the possibility of CO removal by tetradentate ligands diminishes as the replacement of the phosphorus atoms by atoms with a weak π-accepting ability proceeds, though at present the importance of the steric factor cannot be excluded.

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