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1,1,1-TRIS(HYDROXYMETHYL)PROPANEPHOSPHITE DERIVATIVES OF GROUP VI METAL CARBONYLS

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Summary

1,1,1-Tris(hydroxymethyl)propanephosphite (TMPP) reacts with Group VI metal carbonyls to give mono- and di-substituted derivatives. IR spectra indicate a *trans* configuration for the di-substituted derivatives. A number of mixed ligand carbonyls (L—L)(TMPP)M$(CO)_3$ (M = Cr, Mo, W; L—L = *o*-phen or 2,2'-bipy) and (L—L)$(TMPP)_2$M$(CO)_2$ (M = Mo, W) have also been synthesized.

Introduction

The behaviour of several phosphorus donor ligands such as organic phosphines and phosphites has been extensively investigated in the ligand exchange reactions of metal carbonyls, but bicyclic phosphites have received little attention. A few reactions of such a ligand, 1,1,1-tris(hydroxymethyl)propanephosphite (TMPP), with some alkyl-, aryl- and allyl-cobalt carbonyls have been studied [1,2], but reactions with binary metal carbonyls have not been previously investigated.

We describe here the preparation and charcterisation of some TMPP substituted derivatives of Group VI metal carbonyls, viz., (TMPP)M$(CO)_5$, *trans*-$(TMPP)_2$M$(CO)_4$, (M = Cr, Mo, W; L—L = *o*-phen or 2,2'-bipy) and (L—L)-$(TMPP)_2$M$(CO)_2$ (M = Mo, W).

Results and discussion

TMPP reacted with chromium, molybdenum and tungsten hexacarbonyls in refluxing xylene (6—10 h) to give a mixture of mono- and *trans*-di-substitution products. The reactivity was in the order Mo > Cr > W. Monosubstitution products were obtained in very poor yield, whereas the yield of disubstituted derivatives was good. The yield of the mono-substituted derivatives could not be improved even by varying reaction conditions. The mono- and di-substituted

TABLE 1

CHARACTERISTICS AND ANALYSES FOR THE TMPP COMPLEXES

Complex	Reflux solvent, h	Colour, m.p. (°C)	Yield (%)	ν(CO) (cm^{-1})	Found (calcd.) (%)			
					C	H	N	P
(TMPP)Mo(CO)$_5$	Xylene, 6	Yellow, 105	16.6	2080s, 1972w, 1940s, 1910(sh)	32.2 (33.2)	2.6 (2.8)		7.3 (7.8)
(TMPP)W(CO)$_5$	Xylene, 10	Pale Yellow, 120	23.5	2082s, 1976w, 1938s, 1908(sh)	26.1 (27.2)	2.2 (2.3)		6.9 (6.4)
trans-(TMPP)$_2$Mo(CO)$_4$	Xylene, 6	Cream, 198	27.2	2010vw, 1944vw, 1886vs	35.6 (36.1)	3.9 (4.1)		11.8 (11.7)
trans-(TMPP)$_2$W(CO)$_4$	Xylene, 10	White, 218	43.1	2010vw, 1940vw, 1890s(br)	28.5 (31.0)	3.4 (3.6)		9.7 (10.0)
(*o*-phen)(TMPP)Mo(CO)$_3$	Toluene, 8	Deep blue	70.0	1904s, 1810s, 1778s				5.8 (5.9)
(*o*-phen)(TMPP)W(CO)$_3$	Toluene, 10	Violet	62.5	1900s, 1802s, 1770s			4.1 (4.6)	5.0 (5.1)
(2,2′-bipy)(TMPP)Cr(CO)$_3$	Toluene, 10	Deep blue	67.4	1900s, 1802s, 1770s				6.5 (6.8)
(2,2′-bipy)(TMPP)Mo(CO)$_3$	Toluene, 8	Deep blue	68.0	1902s, 1810s, 1778s	46.1 (45.8)	3.5 (3.8)	5.4 (5.6)	6.1 (6.2)
(2,2′-bipy)(TMPP)W(CO)$_3$	Toluene, 10	Violet	63.0	1900s, 1804s, 1770s				5.1 (5.3)
(*o*-phen)(TMPP)$_2$W(CO)$_2$	Xylene, 20	Purple	32.3	1926vw, 1852s, 1764s				8.2 (8.3)
(2,2′-bipy)(TMPP)$_2$Mo(CO)$_2$	Xylene, 16	Purple	38.6	1928vw, 1854s, 1766s				9.6 (9.8)
(2,2′-bipy)(TMPP)$_2$W(CO)$_2$	Xylene, 20	Purple	40.5	1926vw, 1854s, 1764s	39.0 (40.0)	3.8 (4.2)	3.8 (3.9)	8.3 (8.6)

derivatives were separated by column chromatography. In spite of several attempts no more than two CO groups could be displaced. The monosubstituted derivatives are yellow and disubstituted derivatives white to cream coloured. Both types of derivatives are air-stable.

$(TMPP)M(CO)_5$ derivatives dissolve in polar and nonpolar solvents, while the $(TMPP)_2M(CO)_4$ complexes have a very low solubility in nonpolar solvents. They dissolve fairly readily in polar solvents such as chloroform, dichloromethane, acetone, diethyl ether and ethanol.

(*o*-Phen)$M(CO)_4$ and (2,2'-bipy)$M(CO)_4$ derivatives gave *cis*-(L—L)(TMPP)$M(CO)_3$ in good yields when refluxed with TMPP in toluene for 10 h. These derivatives are deep blue to violet in colour and air-stable. They decompose without melting when heated in sealed capillary. They are readily soluble in chloroform, dichloromethane, acetone and ethanol.

(L—L)$(TMPP)_2M(CO)_2$ (M = Mo, W) derivatives were obtained from *trans*-$(TMPP)_2M(CO)_4$ and *o*-phenanthroline or 2,2,-bipyridine after prolonged refluxing (16—20 h) in xylene.

The spectra of TMPP substituted molybdenum and tungsten pentacarbonyls show four CO bands. Since these derivatives possess C_{4v} symmetry only three CO stretching bands due to $2a_1 + e$ modes are expected. The appearance of an additional band (~1910 cm^{-1}) in each case (Table 1) clearly indicates the distortion from perfect C_{4v} symmetry due to the ligand interference, resulting in the appearance of the Raman active CO band of the b_1 mode. The spectra of the analogous chromium derivative is somewhat puzzling. The appearance of five bands in CO region indicates that the symmetry is even lower than C_{4v}. The splitting of an e mode into a' and a'' is not unexpected, and has been observed for several P and S donor substituted metal carbonyls [3,4].

The infrared spectra of disubstituted derivatives is consistent with the *trans* configuration. Only one very strong CO band at ~1885 cm^{-1}, attributable to the e_u mode, is observed. In addition two much weaker high frequency satellites also appear, possibly because of the distortion from perfect D_{4h} symmetry, as has been previously suggested [5,6]. Of the three CO stretching modes bands due to the a_{1g} and b_{1g} modes which are only Raman active gain some intensity in the infrared, and appear at ~2010 and 1940 cm^{-1}, respectively.

The spectra of mixed tricarbonyls of the type (L—L)(TMPP)$M(CO)_3$ resemble closely the spectra of analogous derivatives [7—9]. Three CO stretching bands at ~1900, 1800 and 1770 cm^{-1}, all of strong intensity, are present, which is in agreement with the C_s symmetry of the molecules.

The spectra of the mixed tetrasubstituted derivatives, (L—L)$(TMPP)_2M(CO)_2$, show only two stretching CO bands consistent with the $a_1 + b_2$ modes of C_{2v} symmetry. An additional very weak band (~1926 cm^{-1}) is problably due to the formation of trace quantity of (L—L)$(TMPP)_2M(CO)_3$ in which the bidentate (L—L) ligands act as monodentate.

Experimental

All experiments were performed under dry nitrogen or in vacuo. Infrared spectra were measured on a Perkin—Elmer Spectrophotometer model 577 in KBr discs. Phosphorus was estimated as ammonium phosphomolybdate.

Preparation of [1,1,1-tris(hydroxymethyl)propanephosphite]pentacarbonylchromium(0) and bis[1,1,1-tris(hydroxymethyl)propanephosphite]tetracarbonylchromium(0)

A mixture of hexacarbonylchromium (0.2 g) and TMPP (0.15 g) was refluxed for 8 h in xylene (10 ml) under nitrogen. After cooling the solvent was removed in vacuo. Unchanged $Cr(CO)_6$ was sublimed out to leave a yellowish white residue, which was chromatographed on an alumina column to give two products. Elution with a 1/1 mixture of hexane and benzene (30 ml) gave a yellow solution which on removal of solvent in vacuo yielded yellow crystals of [1,1,1-tris(hydroxymethyl)propanephosphite]pentacarbonylchromium(0) (19.1%), m.p. 97°C. (Found: C, 35.2; H, 2.9; P, 8.3. $C_{11}H_{11}CrO_8P$ Calcd.: C, 37.3; H, 3.1; P, 8.6%.) ν(CO): 2076vs, 1990m, 1945(sh), 1920s, 1890(sh) cm^{-1}.

When the coloured material had been removed from the column chloroform (25 ml) was used for further elution, and evaporation gave bis[1,1,1-tris(hydroxymethyl)propanephosphite]tetracarbonylchromium(0) (27.7%), m.p. 172°C. (Found: C, 42.1; H, 4.2; P, 12.2. $C_{16}H_{22}CrO_{10}P_2$ Calcd.: C, 39.3; H, 4.5; P, 12.7%.) υ(CO): 2008vw, 1942 vw, 1882vs cm^{-1}. It is very sparingly soluble in non-polar solvents but dissolves fairly readily in polar solvents such as chloroform, dichloromethane, acetone and diethyl ether.

Molybdenum and tungsten complexes. Similar procedures yielded the analogous molybdenum and tungsten derivatives. The pentacarbonyls had solubilities similar to those described for the analogous chromium complexes but the di-substituted derivatives are completely insoluble in non-polar solvents. Reaction conditions and analytical data are summarised in Table 1.

Preparation of o-phenanthroline [1,1,1-tris(hydroxymethyl)propanephosphite]-tricarbonylchromium(0)

(*o*-Phenanthroline)tetracarbonylchromium(0) (0.2 g) and TMPP (0.1 g) were refluxed in toluene for 12 h under nitrogen, during which the mixture turned violet and dark crystals separated. After cooling the solvent was removed by vacuum evaporation. Uncharged reactants were removed by washing with diethyl ether and the residual blue solid was dried in vacuo. It was shown to be *o*-phenanthroline [1,1,1-tris(hydroxymethyl)propanephosphite] tricarbonylchromium(0) (yield 66.5%). (Found: C, 52.3; H, 4.2; N, 5.8; P, 6.3. $C_{21}H_{19}CrN_2O_6P$ Calcd.: C, 52.7; H, 4.0; N, 5.9; P, 6.5%.) ν(CO): 1900s, 1808s, 1770s cm^{-1}. On heating in a sealed capillary it decomposed without melting. It was air-stable in solid state but decomposed slowly in polar solvents.

Preparation of o-phenanthrolinebis[1,1,1-tris(hydroxymethyl)propanephosphite]dicarbonylmolybdenum (0)

On refluxing a mixture of *trans*-$(TMPP)_2Mo(CO)_4$ (0.2 g) and *o*-phenanthroline (0.07 g) in xylene (10 ml) under nitrogen, a purple solid separated out. It was filtered off, and after washing several times with diethyl ether and drying in vacuo it analysed correctly for *o*-phenanthrolinebis[1,1,1-tris(hydroxymethyl)propanephosphite]dicarbonylmolybdenum(0) (yield 40.5%). (Found: C, 47.8; H, 4.9; N, 4.4; P, 8.9. $C_{26}H_{30}MoN_2O_8P_2$ Calcd.: C, 47.6; H, 4.2; N, 4.3; P, 9.5%.) ν(CO): 1926vw, 1852s, 1766s cm^{-1}. It had a low solubility as compared to (*o*-phen)(TMPP)$M(CO)_3$ derivatives.

Details of other derivatives are given in Table 1.

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