Journal of Organometallic Chemistry, 339 (1988) 97–101
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

1,2-Bis(di-*p*-tolylphosphino)ethane complexes of Group VI metal carbonyls

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(Received July 8th, 1987)

Abstract

New complexes of the type [$M(CO)_4$(dptpe)] (M = Cr, Mo, W) have been isolated from the reaction of the ligand, 1,2-bis(di-*p*-tolylphosphino)ethane (dptpe) with Group VI metal hexacarbonyls in a suitable solvent such as methylcyclohexane. The resulting [$M(CO)_4$(dptpe)] complexes on treatment with an excess of pyridine produces the mixed ligand complexes [$M(CO)_3$(py)(dptpe)], whereas the reaction of [$XMo(CO)_2(\eta^3$-allyl)$(MeCN)_2$] (X = Cl, Br) with dptpe gives [$XMo(CO)_2(\eta^3$-allyl)(dptpe)]. The formulation of the structures of these complexes follows from elemental analyses and ^1H NMR, $^{31}P\{^1H\}$ NMR and IR spectral studies. Carbonyl force constants have been calculated from the $\nu(CO)$ stretching frequencies by the Cotton and Kraihanzel method.

Introduction

The chemistry of Group VI metal carbonyl ditertiary phosphine complexes is extensive, see for examples ref. 1–8. The introduction of a *p*-CH_3 group in the phenyl ring of these ditertiary phosphines would be expected to enhance the solubility of their complexes and make them more amenable to physical studies, especially NMR spectroscopy [9]. As part of an investigation of the chemistry of ditertiary phosphine complexes of Group VI metals, a series of similar complexes have been prepared involving the symmetrical ditertiary phosphine ligand, dptpe. The effects of the phosphorus donor atoms and the chelate ring size on the spectral properties of these compounds are discussed.

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Experimental

The dptpe was purchased from Strem Chemicals and used as received. Procedures described previously [5,6] were used for the preparation of the chromium(0), molybdenum(0), tungsten(0) and molybdenum(II) complexes.

Results and discussion

The syntheses of metal carbonyl complexes of the type, *cis*-$[M(CO)_4(dptpe)]$, *cis*-$[M(CO)_3(Py)(dptpe)]$ (M = Cr, Mo, W) and $[XMo(CO)_2(\eta^3\text{-allyl})(dptpe)]$ (X = Cl or Br) are described in the experimental section. Some of their physical and analytical data are given in Table 1.

The ease of replacement of carbonyl by dptpe was found to fall in the order Mo > Cr > W. It has been shown [4] that phosphines can reduce electron density more effectively on Mo than on Cr. This is consistent with the greater extension of the 4*d* orbitals of the second-row metals than of the 3*d* orbitals of the first-row metals, which results in greater overlap of the metal orbitals with the phosphorus 3*d* orbital.

Four ν(CO) vibrations were observed in the solution infrared spectra of the complexes $[M(CO)_4(dptpe)]$ (M = Cr, Mo, W), as expected for an octahedral *cis*-$[M(CO)_4(P\text{-}P)]$ complex with C_{2v} symmetry (Table 2). The four vibrations are assigned to A_1, B_1, A_1^2 and B_2 modes of carbonyl stretching in the order of decreasing frequency [10–12], which confirm the C_{2v} symmetry of the complexes and the bidentate chelating behaviour of the ligand, dptpe. These complexes have octahedral coordination at the metal, and thus contain two types of CO groups, axial and equatorial, as shown below:

Table 1

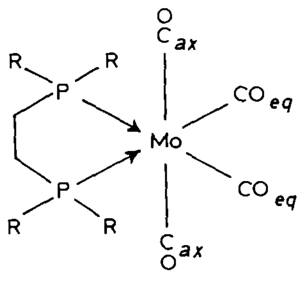
Elemental analyses and some physical properties

Compound	Colour	Melting point (Decomp.) (°C)	Analysis (Found (calcd.)(%))	
			C	H
$[Cr(CO)_4(dptpe)]$	Light yellow	123–124	65.90 (66.02)	5.05 (5.21)
$[Mo(CO)_4(dptpe)]$	Light yellow	158	61.70 (61.64)	4.95 (4.87)
$[W(CO)_4(dptpe)]$	White	121–122	54.25 (54.42)	4.10 (4.30)
$[Cr(CO)_3(Py)(dptpe)]$	Yellow	144	68.25 (68.16)	5.65 (5.57)
$[Mo(CO)_3(Py)(dptpe)]$	Yellowish red	168–170	63.85 (63.96)	5.10 (5.23)
$[W(CO)_3(Py)(dptpe)]$	Yellow	134–136	56.80 (56.94)	4.50 (4.65)
$[ClMo(CO)_2(\eta^3\text{-allyl})(dptpe)]$	Orange	118–119	61.60 (61.55)	5.35 (5.46)
$[BrMo(CO)_2(\eta^3\text{-allyl})(dptpe)]$	Orange	126–127	57.85 (57.79)	5.25 (5.13)

Table 2

IR $\nu(CO)$ frequencies and force constants of Group VI metal hexacarbonyl complexes of dptpe

Compound	$\nu(CO)$ (cm^{-1})				Force constants (mdynes/Å)		
	A_1^1	A_1^2	B_1	B_2	K_1	K_2	K_i
$[Cr(CO)_4(dptpe)]$	2000	1945	1895	1875	14.49	15.08	0.29
$[Mo(CO)_4(dptpe)]$	2005	1940	1905	1880	14.55	15.22	0.28
$[W(CO)_4(dptpe)]$	2016	1976	1898	1873	14.50	15.21	0.33
	A'	A''	A'		K_1	K_i	
$[Cr(CO)_3(Py)(dptpe)]$	1950	1842	1820		14.12	0.42	
$[Mo(CO)_3(Py)(dptpe)]$	1942	1836	1815		14.02	0.40	
$[W(CO)_3(Py)(dptpe)]$	1938	1830	1810		13.94	0.41	
	A_1	B_1					
$[ClMo(CO)_2(\eta^3\text{-allyl})(dptpe)]$	1925	1840			14.32	0.65	
$[BrMo(CO)_2(\eta^3\text{-allyl})(dptpe)]$	1935	1845			14.43	0.69	



(R = p-$CH_3C_6H_4$)

The $[M(CO)_3(Py)(dptpe)]$ ($M = Cr$, Mo, W; $Py = C_5H_5N$) complexes exhibit three IR active $\nu(CO)$ bands in the carbonyl absorption region corresponding to $2A'$ and A'' modes (Table 2), as expected for similarly substituted octahedral *cis*-$[M(CO)_3Y(P\text{–}P)]$ complexes having C_s symmetry. The disappearance of the $\nu(CO)$ band at ~ 2000 cm^{-1} in these complexes indicates that one of the CO groups in the parent complex $[M(CO)_4dptpe]$ has been replaced by the pyridine group. Moreover, the appearance of three bands at ~ 1595, ~ 1580 and ~ 400 cm^{-1} confirms the presence of the pyridine group.

The η^3-allyl complexes of the type $[XMo(CO)_2(\eta^3\text{-allyl})(dptpe)]$ were prepared by treatment of $[XMo(CO)_2(\eta^3\text{-allyl})(MeCN)_2]$ with dptpe in acetone. In the carbonyl absorption region they exhibit two strong IR active bands of approximately equal intensity which can be assigned to the A_1 and B_1 carbonyl stretching modes in a complex with C_{2v} symmetry having *cis*-coordinated carbonyl groups.

Force constant calculations (Table 2) were made by the Cotton–Kraihanzel method [10,11] as described elsewhere [5,6]. It has been shown [10,13] that the CO stretching frequencies or force constants provide a scale of relative inherent π-acidities, but it has been effectively argued that these quantities also reflect σ-effects

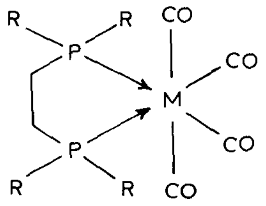
Table 3

$^{31}P\{^{1}H\}$ NMR parameters for $[M(CO)_4(dptpe)]$ complexes (M = Cr, Mo or W)

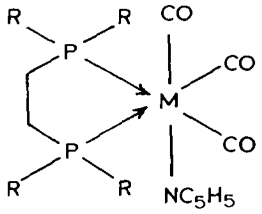
Compound	Chemical shift (ppm) $\delta P(p\text{-}CH_3C_6H_4)_2$	Coordination chemical shift (ppm) $\Delta P(p\text{-}CH_3C_6H_4)_2$	Ring contribution [a] ΔR (ppm)	$J(^{183}W-^{31}P)$ (Hz)
$[Cr(CO)_4(dptpe)]$	+78.45	+91.90	+31.00	–
$[Mo(CO)_4(dptpe)]$	+55.46	+68.91	+26.00	–
$[W(CO)_4(dptpe)]$	+39.51	+52.96	+27.66	228.82

[a] ΔR = coordination chemical shift of the chelated phosphine complex – coordination chemical shift of an equivalent phosphorus in a non-chelated analogue [17].

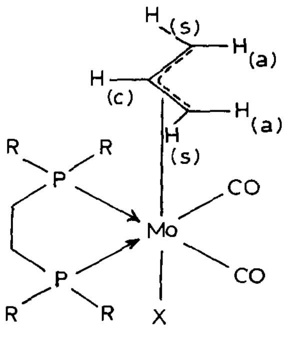
[14,15], perhaps to a lesser extent. The carbonyl stretch may most nearly reflect the effective net charge of the metal centre. In the systems studied here and earlier [5], ν(CO) values or the CO stretching force constants increase with the apparent electronegativities of the phosphorus substituents from p-$CH_3C_6H_4$ group to m-



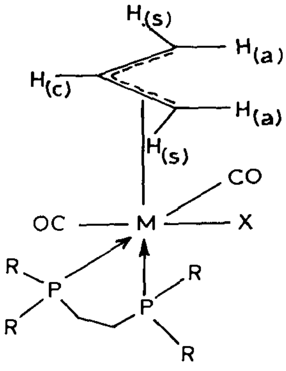
(I)



(II)



(III)



(IV)

(R = p-$CH_3C_6H_4$; X = Cl or Br ;
a = anti , s = syn and c = meso)

$CF_3C_6H_4$ group, which shows that the phosphine carrying the *m*-$CF_3C_6H_4$ substituents on phosphorus is a better π-acceptor than that containing the *p*-$CH_3C_6H_4$ substituents.

The ^{1}H NMR spectra of the carbonyl complexes show a slight downfield shift of the aromatic as well as the aliphatic proton signals relative to those from the free ligand. The pyridine protons in [M(CO)$_3$(Py)(dptpe)] appear as a multiplet at ~ 8.95 ppm, whereas the complexes [XMo(CO)$_2$(η^3-allyl)(dptpe)] exhibit three allyl signals in the intensity ratio 1/2/2 on ^{31}P decoupling, characteristic of an $AA'BB'X$ spin system. The ^{31}P NMR spectra of the complexes [M(CO)$_4$(dptpe)] (Table 3) showed the expected A_2 spin system consisting of a single sharp line. The spectrum of the tungsten complex contained satellites arising from coupling to ^{183}W ($I = \frac{1}{2}$, natural abundance 14%). The coordination chemical shifts (Δ) [16], ring contribution (ΔR) and tungsten–phosphorus coupling, $J(^{183}\text{W}-^{31}\text{P})$ [17] have also been determined.

As assumed on the basis of the spectral data, the carbonyl complexes [M(CO)$_4$(dptpe)] and [M(CO)$_3$(Py)(dptpe)] (M = Cr, Mo, W; X = Cl or Br), have been assigned *cis*-octahedral structures, I and II, respectively, in which the metal atom is hexacoordinate. The [XMo(CO)$_2$(η^3-allyl)diphos] complexes have been described previously [6,7] as octahedral, (III), with the allyl group *trans* to the unidentate anion and the two phosphorus atoms and the *cis*-carbonyl groups approximately coplanar. But, it has been shown [8] by X-ray crystallography that the structure of [XMo(CO)$_2$(η^3-allyl)(diphos)] can be conveniently described as pseudooctahedral on the assumption that the allyl moiety occupies one coordination site. The Mo atom is surrounded by six ligands, including an allyl group, two terminally coordinated carbonyl groups, the bidentate diphos ligand and a chlorine atom. The η^3-allyl group and one of the phosphorus atoms of the chelate lie *trans* to one another, occupying the so-called apical positions in the pseudooctahedral coordination geometry. Since the complexes [XMo(CO)$_2$(η^3-allyl)(dptpe)] (X = Cl, Br) have similar NMR and IR spectra, we assume that they have structures analogous to that of [ClMo(CO)$_2$(η^3-allyl)diphos] (IV).

References

1 J. Chatt and H.R. Watson, J. Chem. Soc., (1961) 4980.
2 C.A. McAuliffe and W. Levason, Phosphine, Arsine and Stibine Complexes of Transition Elements, Elsevier, New York, 1979.
3 G.T. Andrews, I.J. Colguhoun and W. McFarlane, Polyhedron, 2 (1983) 783.
4 R.L. Cook and J.G. Morse, Inorg. Chem., 23 (1984) 2332.
5 P.N. Kapoor, D.D. Pathak, G. Gaur and P.C. Mercykutty, J. Organomet. Chem., 311 (1986) 103.
6 P.N. Kapoor, D.D. Pathak, G. Gaur and P.C. Mercykutty, J. Organomet. Chem., 322 (1987) 71.
7 B.J. Bridson, J. Organomet. Chem., 125 (1977) 225.
8 J.W. Faller, D.A. Haitko, R.D. Adams and D.F. Chodosh, J. Am. Chem. Soc., 101 (1979) 865.
9 C.A. Tolman, J. Am. Chem. Soc., 94 (1972) 8.
10 F.A. Cotton, C.S. Kraihanzel, J. Am. Chem. Soc., 84 (1962) 4432.
11 C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 553.
12 B.J. Bridson and G.F. Griffin, J. Mol. Struct., 41 (1977) 99.
13 C.A. Tolman, Chem. Rev., 77, 313 (1977).
14 R.J. Angelici and C.M. Igemanson, Inorg. Chem., 8 (1969) 83.
15 G.R. Dobson, Acc. Chem. Res., 9 (1976) 300.
16 S.O. Grim, W.L. Briggs, R.C. Barth, C.A. Tolman and J.P. Jesson, Inorg. Chem., 13 (1974) 1095.
17 P.E. Garrou, Chem. Rev., 81 (1981) 229.