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(η^3-ALLYL)DICARBONYLMOLYBDENUM(II) COMPLEXES OF THE UNSYMMETRICAL DITERTIARY PHOSPHINES $Ph_2PCH_2CH_2P(C_6H_4X)_2$ ($X = m$-F, p-F or m-CF_3)

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Summary

Complexes of the type $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{–}P')]$ ($X = Cl$ or Br; $P\text{–}P' = R_2PCH_2CH_2PPh_2$; $R = m\text{-}FC_6H_4$ (**1a**), $p\text{-}FC_6H_4$ (**1b**), $m\text{-}CF_3C_6H_4$ (**1c**)) have been prepared from the reaction of $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$ with the relevant ditertiary phosphines in acetone. From their ^1H NMR and IR data these complexes have been assigned essentially octahedral structures in which the allyl moiety is *trans* to the unidentate anion, and the two *cis*-carbonyl groups and two phosphorus donor atoms of the bidentate ligand are approximately coplanar. CO force constants have been calculated.

Introduction

Allylmolybdenum(II) complexes of the type $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$ ($X = Cl$, or Br) undergo interesting reactions with tertiary monophosphines PR_3 or the corresponding ditertiary phosphines. Monotertiary phosphines PR_3 ($R = Ph$, $n\text{-}C_4H_9$) are reported to undergo allyl elimination reactions with $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$ to form zerovalent carbonyl complex $[Mo(CO)_2(PR_3)_2(MeCN)_2]$ [1,2], whereas diphosphines (P–P) are reported to replace acetonitrile groups to form molybdenum(II) complexes, $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{–}P')$ [3–8]. The unusual dynamic properties of these complexes are well documented [9]. A survey of the literature reveals that numerous complexes of this type with symmetrical diphosphines have been reported [5,6,9], but little is known of those involves unsymmetrical diphosphines, (**1**). It was thus considered of interest to prepare a few complexes containing unsymmetrical diphosphines. The main advantage of such a ligand over a symmetrical analogue is that with the former the ^{31}P NMR spectrum provides direct measurement of phosphorus–phosphorus couplings. In this paper we report a

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few complexes of molybdenum(II) with three new unsymmetrical fluorine-substituted tetraaryldiphosphines (**1**) $Ph_2PCH_2CH_2P(C_6H_4X)_2$ (**1a**, X = *m*-F; **1b**, X = *p*-F; **1c**, X = *m*-CF_3).

Experimental

All preparations were carried out under dry nitrogen using solvents and reactants freed from moisture and oxygen by standard procedures. Physical measurements and experimental techniques were as described elsewhere [10–12].

The ^1H NMR spectra were recorded on a JEOL FX-200 spectrophotometer in $CDCl_3$, and IR spectra on a Perkin–Elmer 620 spectrophotometer with $CHCl_3$ as solvent.

Ligands were synthesised by standard methods [12]. Complexes $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$ (X = Cl or Br) were prepared from $[Mo(CO)_3(MeCN)_3]$ by a published method [13].

Synthesis of complexes

1-Diphenylphosphino-2-bis(m-fluorophenyl)phosphinoethanechloro(η^3-allyl)dicarbonylmolybdenum(II), $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1a})]$. To a clear yellow solution of $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$ (0.34 g, 1.09 mmol) in 15 ml of acetone a solution of ligand **1a** (0.47 g, 1.08 mmol) in 10 ml of acetone was added dropwise with stirring to give a deep red solution. The mixture was refluxed for 2 h then allowed to cool to room temperature. Solvent was removed under reduced pressure to leave an orange solid, which on recrystallization at 0°C from chloroform and petroleum ether (40–60°C) yielded orange crystals (yield 0.40 g, 70%).

1-Diphenylphosphino-2-bis(m-fluorophenyl)phosphinobromo(η^3-allyl)dicarbonylmolybdenum(II), $[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1a})]$. This was prepared by the procedure described but starting from $[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$. It was obtained as brown crystals (yield 60%).

The analogous complexes involving ligands **1b** and **1c** were prepared by the same method.

Results and discussion

Analytical and physical data are given in Table 1. Solution infrared data in the carbonyl absorption region, force constants (calculated by Cotton–Kraihanzel's method [14]), and ^1H NMR data are listed in Table 2.

(η^3-Allyl)dicarbonylmolybdenum(II) complexes were prepared by replacement of two acetonitrile groups by the relevant diphosphine as shown in eq. 1.

$$[XMo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2] + P\text{–}P' \xrightarrow[\text{reflux}]{\text{acetone}} [XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{–}P')] + 2MeCN \quad (1)$$

(X = Cl, Br; P–P′ = **1a**, **1b** or **1c**)

All these complexes are orange to brown crystalline solids, very soluble in common organic solvents such as benzene, chloroform and dichloromethane, but insoluble in n-hexane and petroleum ether.

TABLE 1

ANALYTICAL AND PHYSICAL PROPERTIES OF THE COMPLEXES $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P')]$ (X = Cl, Br, P–P′ = **1a**, **1b** or **1c**)

Complex	M.p. (°C)	Colour	Analysis; (Found (calcd.) (%))	
			C	H
$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1a})]$	140–141	Orange	55.8 (56.2)	4.0 (4.1)
$[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1a})]$	145–146	Brown	52.1 (52.7)	3.5 (3.8)
$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1b})]$	155–156	Orange	56.0 (56.2)	3.9 (4.1)
$[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1b})]$	165–167	Brown	52.5 (52.7)	3.7 (3.8)
$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1c})]$	108–110	Orange	51.7 (52.0)	3.3 (3.6)
$[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1c})]$	123–125	Deep orange	48.9 (49.0)	3.1 (3.4)

The solution infrared spectra of complexes $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P')]$ exhibit two bands of equal intensity in the carbonyl absorption region (Table 2). These bands were assigned to A_1 and B_1 modes of carbonyl stretching, consistent with the C_{2v} symmetry of the complexes. These two frequencies are indicative of the presence

TABLE 2

IR AND ^1H NMR DATA FOR COMPLEXES $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P')]$ (X = Cl, Br, and P–P′ = **1a**, **1b**, **1c**)

Complex	$\nu(CO)$ (cm^{-1})		Force constants (mdynes $Å^{-1}$)		^1H NMR data (δ, ppm) [a]		
	A_1	B_1	K_1	K_i	Aromatic protons	Methylene protons	Allyl protons
$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1a})]$	1948(s)	1851(s)	14.57	0.75	7.20–7.60 (m)	2.30(m) 2.95(m)	1.90(d), H(a) 3.55(qt), H(s) 3.75(m), H(c)
$[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1a})]$	1952(s)	1854(s)	14.63	0.74	7.15–7.60 (m)	2.25(m) 2.95(m)	1.85(d), H(a) 3.65(qt), H(s) 3.80(m), H(c)
$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1b})]$	1945(s)	1850(s)	14.54	0.72	7.25–7.65 (m)	2.35(m) 3.00(m)	1.85(d), H(a) 3.65(qt), H(s) 3.90(m), H(c)
$[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1b})]$	1950(s)	1860(s)	14.66	0.69	7.20–7.70 (m)	2.30(m) 3.05(m)	1.80(d), H(a) 3.60(qt), H(s) 3.70(m), H(c)
$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1c})]$	1938(s)	1845(s)	14.46	0.71	7.25–7.70 (m)	2.50(m) 2.85(m)	2.00(d), H(a) 3.50(qt), (Hs) 3.80(m), H(c)
$[BrMo(CO)_2(\eta^3\text{-}C_3H_5)(\mathbf{1c})]$	1945(s)	1854(s)	14.58	0.70	7.30–7.60 (m)	2.45(m) 2.90(m)	1.90(d), H(a) 3.55(qt), H(s) 3.85(m), H(c)

[a] s = sharp, m = multiplet, d = doublet, qt = quartet; a = *anti*, s = *syn*, c = *meso*.

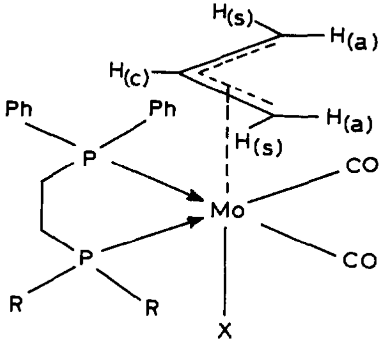

Fig. 1. Structure of complexes $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P')]$ ($R = m\text{-}FC_6H_4$, $p\text{-}FC_6H_4$, $m\text{-}CF_3C_6H_4$; $X = Cl$, Br).

of two *cis*-carbonyl groups in the complex. A comparison of CO force constants (Table 1) with those of corresponding complexes containing bidentate N-donor ligands [4] reveals a slight increase in CO stretching force constants which reflects the higher bond order expected for a CO group *trans* to π-bonding ligands (phosphorus donor atoms). Further, all the CO stretch–stretch interaction constants (K_i) are positive, i.e. $K_i > 0$.

The infrared spectra of all the complexes as KBr discs show two major changes. First, the P-aryl frequency observed at ~ 1085 cm^{-1} in the free ligands is shifted to 1100–1110 cm^{-1} in the complex, which can be taken as an evidence for the coordination of phosphorus to the metal [15]. Second, all these molybdenum complexes show a sharp band at ~ 885 cm^{-1}, which confirms the chelating behaviour of the ligands [16].

Under normal scanning procedures only broad featureless bands were observed in the ^1H NMR spectrum owing to strong $^1H\text{-}^{31}P$ coupling, and so ^{31}P decoupled spectra were obtained. The room temperature $^1H\{^{31}P\}$ NMR spectra of the complex $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P')]$ exhibit three sets of resonances with intensity ratio 2/2/1 for the allyl moiety (Table 2), characteristic of the AA′BB′X spin system of symmetrical trihapto allylmetal complexes. The assignments of the chemical shifts to *anti*, *syn*, and *meso* protons were made as described in the literature [4].

The methylene protons of the ligands in these complexes give two complex multiplets centered at δ ~ 2.3 and δ ~ 3.0 ppm (Table 2), indicating differentially shielded axial and equatorial protons, and this is interpreted in terms of an AA′BB′ spin system. The phenyl protons gave a complex multiplet at δ 7.20–7.70 ppm.

On the basis the data obtained, the complexes $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P')]$ are assigned octahedral structures in which an allyl group is *trans* to X, and the two carbonyl groups are in a *cis*-disposition. The donor atoms of the bidentate ligands are assumed to be approximately coplanar with the carbonyl ligand as shown in Fig. 1.

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