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REACTIONS OF METAL CARBONYL CLUSTER COMPLEXES WITH MULTIDENTATE PHOSPHINE LIGANDS; REACTIONS WITH BIS(DIPHENYLPHOSPHINO)METHANE

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Summary

Reactions of $Rh_6(CO)_{16}$ with bis(diphenylphosphino)methane (dppm) gave $Rh_6(CO)_{14}$(dppm), $Rh_6(CO)_{12}(dppm)_2$, or $Rh_6(CO)_{10}(dppm)_3$, depending upon the reaction conditions. $Rh_4(CO)_{10}$(dppm) may be obtained from the reaction of $Rh_4(CO)_{12}$ with dppm, but this derivative rapidly decomposes in solution to give $Rh_4(CO)_8(dppm)_2$, $Rh_6(CO)_{14}$(dppm), and $Rh_6(CO)_{12}(dppm)_2$. $Ir_4(CO)_{10}$(dppm) and $Ir_4(CO)_8(dppm)_2$ have also been prepared, and their structures are discussed on the basis of infrared and ^{31}P NMR spectroscopic data.

Introduction

Transition metal clusters are attracting a great deal of interest, particularly with respect to their potential as catalysts, where adjacent metal centres offer the possibility for cooperative reactivity leading to new, more active, or more selective, catalysts [1]. However, only a few examples are known for which such clusters have been shown to be the catalytically active species. This is partly because it is difficult to maintain the metal cluster framework under catalytic reaction conditions due to the ease of oxidation, fragmentation, and/or aggregation of the cluster complexes. We [2], and others [3—7], have shown that the presence of bridging or capping ligands increases the stability of the metal framework. We have therefore undertaken an investigation of the reactions of multidentate phosphine ligands with transition metal carbonyl cluster complexes. This paper reports the results of our studies of the reactions of bis(diphenylphosphino)methane (dppm), a bidentate ligand which can coordinate to metal complexes in a bridging or chelating mode. Furthermore, our interest in transition metal clusters supported on silica via bidentate and tridentate phosphine ligands [8], required the characterisation of soluble analogues in order to aid the characterisation of the supported clusters.

Substitution reactions between transition metal carbonyl cluster complexes and monodentate phosphine or phosphite ligands have been fairly extensively

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studied, but there are few reports of substitution reactions with bidentate phosphine ligands. During the course of this work the preparation and structural analysis of $Rh_6(CO)_{10}(dppm)_3$ was reported [9]. $Ru_3(CO)_{10}(dppm)$ [10] and $Ru_3(CO)_8(dppm)_2$ [11] have been prepared from $Ru_3(CO)_{12}$, and isomeric bis(diphenylphosphino)ethane (dppe) derivatives of $H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{10}$(dppe) [12] and $H_4Ru_4(CO)_{10}(\mu$-dppe) [13] have been structurally characterised. $Rh_4(CO)_8(dppm)_2$ [14], $Co_4(CO)_8(dppm)_2$ [15], $Rh_6(CO)_{10}(dppe)_3$ [16], $Rh_6(CO)_{15}(dppe)$ [17], $Rh_6(CO)_{13}(dppe)_3$ [17] and $Rh_6(CO)_{12}(dppb)_2$ [17] (dppb = bis(diphenylphosphino)butane) have also been reported.

Experimental

IR spectra were recorded in 0.5 mm NaCl cells on a Perkin—Elmer 681 spectrophotometer. NMR spectra were recorded on a Bruker WM 250 or a Jeol FX-90Q instrument. All reactions were carried out under nitrogen or argon atmospheres using dry, degassed solvents. $Rh_4(CO)_{12}$ [18], $Rh_6(CO)_{16}$ [19], $Ir_4(CO)_{12}$ [20], and dppm [21], were prepared by previously published methods.

Microanalyses were carried out by Elemental Micro-Analysis Ltd. (Devon). The mass spectrum of $Ir_4(CO)_8(dppm)_2$ was measured on a VG Analytical ZAB HF spectrometer using the Fast Atom Bombardment (FAB) technique.

Reactions of $Rh_6(CO)_{16}$ with dppm

(a) Dppm (72 mg, 0.19 mmol) in dichloromethane (20 cm^3) was added dropwise to a stirred suspension of $Rh_6(CO)_{16}$ (200 mg, 0.19 mmol) in dichloromethane (10 cm^3) at room temperature. After 20 h, 60/80° petroleum ether (15 cm^3) was added. Slow evaporation of solvent under a N_2 stream gave dark red crystals of $Rh_6(CO)_{14}(dppm)$ (196 mg, 75%). (Found: C, 33.59; H, 1.54; P, 5.2; Cl, 0.43. $C_{39}H_{22}O_{14}P_2Rh_6 \cdot 0.09CH_2Cl_2$ calcd.: C, 33.50; H, 1.60; P, 4.42; Cl, 0.46%).

(b) Dppm (367 mg, 0.96 mmol) and $Rh_6(CO)_{16}$ (500 mg, 0.47 mmol) were reacted as in (a). After stirring for 40 h at room temperature, florisil (3 g, 100—200 mesh) was added to the dark red solution and stirring was continued under a stream of N_2 until all the product was absorbed onto the florisil. This florisil with the reaction product was then placed on top of a 15 cm florisil column and the products eluted with petroleum ether/dichloromethane. Two bands were eluted, the first band was $Rh_6(CO)_{14}(dppm)$ (95 mg, 15%), followed by $Rh_6(CO)_{12}(dppm)_2$ which was obtained as dark red crystals by slow evaporation of the solvent (388 mg, 48%). (Found: C, 43.25; H, 2.60; P, 7.57; Cl, 1.85. $C_{62}H_{44}O_{12}P_4Rh_6 \cdot 0.43CH_2Cl_2$ calcd.: C, 42.63; H, 2.57; P, 7.04; Cl, 1.73%).

(c) Dppm (290 mg, 0.75 mmol) and $Rh_6(CO)_{16}$ (200 mg, 0.19 mmol) were reacted as in (a) above. After stirring at room temperature for 40 h, addition of petroleum ether followed by slow evaporation of the solvent gave large dark red crystals of $Rh_6(CO)_{10}(dppm)_3$ (334 mg, 87%). (Found: C, 48.72; H, 3.30; P, 9.09; Cl, 2.15. $C_{85}H_{66}O_{10}P_6Rh_6 \cdot 0.67CH_2Cl_2$ calcd.: C, 48.83; H, 3.22; P, 8.82; Cl, 2.24%).

Reactions of $Rh_4(CO)_{12}$ with dppm

(a) Dppm (83.5 mg, 0.22 mmol) in toluene (10 cm^3) was added dropwise over 30 min with vigorous stirring to $Rh_4(CO)_{12}$ (167.8 mg, 0.22 mmol) in hexane (40 cm^3). The resulting suspension was stirred for a further 1 h, and then the solvent was removed by evaporation under reduced pressure. The crude red solid was washed with hexane, and recrystallised from CH_2Cl_2/heptane by rapid evaporation, to give maroon crystals of $Rh_4(CO)_{10}$(dppm). (Found: C, 39.73; H, 2.36. $C_{35}H_{22}O_{10}P_2Rh_4$ calcd.: C, 39.06; H, 2.06%). An analytically pure sample could not be obtained because of the ready decomposition in solution.

(b) $Rh_4(CO)_8(dppm)_2$ was prepared by the method of Carré et al. [14].

Reactions of $Ir_4(CO)_{12}$ with dppm

(a) $Ir(CO)_2Cl$(*p*-toluidine) (1.063 g, 2.72 mmol), dppm (0.262 g, 0.68 mmol), acid-washed mossy zinc (9.0 g), 2-methoxyethanol (150 cm^3), and water (6 cm^3) were placed in a 500 cm^3 heavy-walled glass pressure vessel. The mixture was saturated with CO, and then pressurised to 4 atm with CO. The reaction vessel was heated to 90°C for 45 min, with stirring, and then cooled, vented, and the solution filtered under nitrogen (the yellow solution rapidly darkens to deep red on exposure to air). The filtrate was reduced in volume and chromatographed on Florisil using a 5/1 petroleum ether/dichloromethane eluant. Two bands were collected, a yellow band of $Ir_4(CO)_{10}$(dppm) followed by an orange band of $Ir_4(CO)_8(dppm)_2$. The yellow product was recrystallised from CH_2Cl_2/hexane to give yellow crystals of $Ir_4(CO)_{10}$(dppm) (57 mg, 6%). (Found: C, 29.32; H, 1.45. $C_{35}H_{22}O_{10}P_2Ir_4$ calcd.: C, 29.33; H, 1.55%).

(b) $Ir_4(CO)_{12}$ (234 mg, 0.21 mmol) and dppm (162 mg, 0.42 mmol) in toluene (30 cm^3) were heated under reflux for 3 h. The resulting orange-red solution was filtered and evaporated to dryness under reduced pressure to give an orange-red solid. Recrystallisation from benzene/heptane gave orange-red crystals of $Ir_4(CO)_8(dppm)_2$ (260 mg, 71%). (Found: C, 40.90; H, 2.70. $C_{58}H_{44}O_8P_4Ir_4 \cdot 0.5C_6H_6$ calcd.: C, 40.68; H, 2.64%). M (mass spectrometry), 1760, as required for $C_{58}H_{44}O_8P_4Ir_4$ (based on ^{192}Ir).

Results and discussion

Treatment at room temperature of a dichloromethane solution of $Rh_6(CO)_{16}$ with dppm leads to ready substitution of carbonyl ligands, the degree of substitution depending upon the stoichiometry of the reactants. Thus, a 1/1 molar ratio of dppm and $Rh_6(CO)_{16}$ gives $Rh_6(CO)_{14}$(dppm), a 2/1 ratio yields a mixture of $Rh_6(CO)_{14}$(dppm) (15%) and $Rh_6(CO)_{12}(dppm)_2$ (48%) while a 4/1 ratio yields only $Rh_6(CO)_{10}(dppm)_3$. The infrared and NMR spectroscopic data for these derivatives are given in Table 1. During the course of this work, the synthesis and crystal structure of $Rh_6(CO)_{10}(dppm)_3$ was reported [9]. The dppm ligands in this derivative are coordinated in a bridging mode such that one phosphorus atom is coordinated to each Rh atom, and there are 6 terminal CO ligands and 4 face-bridging CO ligands. A comparison of the ^{31}P NMR spectra of $Rh_6(CO)_{14}$(dppm), $Rh_6(CO)_{12}(dppm)_2$ and $Rh_6(CO)_{10}(dppm)_3$ indicates that the dppm ligands are coordinated in the same (bridging) mode in all three

TABLE 1

INFRARED AND ^{31}P NMR DATA

Complex	ν(CO) (cm^{-1}) [a]	δ ^{31}P $\{^1$H$\}$ [b]
$Rh_6(CO)_{14}(dppm)$	2086m, 2055vs, 2024m, 1998w, 1780m, 1760(sh), 1725w	11,5 (apparent doublet of triplets) (^1J(P—Rh) 144) [c]
$Rh_6(CO)_{12}(dppm)_2$	2058s, 2028s, 2009s, 1974m, 1785(sh), 1747s, 1719(sh)	11,75 (doublet of multiplets) (^1J(P—Rh) 130)
$Rh_6(CO)_{10}(dppm)_3$	2008s, 1988(sh), 1978s, 1955s, 1760(sh), 1718(sh), 1704s, 1698(sh)	11,9 (doublet of multiplets) (^1J(P—Rh) 128)
$Rh_4(CO)_{10}(dppm)$	2069s, 2039m, 2018s, 1996m(sh), 1879w, 1847m, 1811m	−6,9 (apparent doublet of triplets) (^1J(P—Rh) 128)
$Rh_4(CO)_8(dppm)_2$	2066(sh), 2060m, 2015s, 1982vs(br), 1848w, 1806m, 1785m	−5,1 to −7,3 (very broad multiplet at 25°C)
$Ir_4(CO)_{10}(dppm)$	2071s, 2041m, 2012s, 1985m(sh), 1860w, 1826m, 1790m	−52,3(*s*) (*at* 25°*C* and −95°C)
$Ir_4(CO)_8(dppm)_2$	2007s, 1974s(br), 1957s, 1832vw, 1783m, 1762m	−49,4(broad *s*) (at 25°C); −23,5(P_1)(d, $J(P_1—P_4)$ 42), −44,85 (P_2) (dd, $J(P_2—P_3)$ 48, $J(P_2—P_4)$ 101) −49,8 (P_3) (d, $J(P_3—P_2)$ 48), −61,5 (P_4) (dd, $J(P_4—P_1)$ 42, $J(P_4—P_2)$ 101) (*at* −95°*C*).

[a] CH_2Cl_2 solvent. [b] Chemical shifts with respect to H_3PO_4 *as external reference*; CH_2Cl_2 used as solvent; *s* = singlet, *d* = doublet, dd = doublet of doublets. [c] Coupling constants in *Hz*.

complexes. A chelating mode of coordination would give a 4-membered ring which would lead to a marked difference in the chemical shift of the phosphorus [22]. The infrared spectra show the presence of terminal and face-bridging carbonyl ligands in all three complexes, with the stretching frequencies shifting to lower values with increasing degree of substitution, as expected.

The tetranuclear rhodium cluster, $Rh_4(CO)_{12}$, also reacts readily with dppm to give either $Rh_4(CO)_8(dppm)_2$ or $Rh_4(CO)_{10}(dppm)$, depending upon the reaction conditions.

The preparation and structure of $Rh_4(CO)_8(dppm)_2$ has been previously reported [14]. As in the case of the $Rh_6(CO)_{16}$ derivatives, the dppm ligand adopts a bridging coordination mode in $Rh_4(CO)_8(dppm)_2$. To obtain the deri-

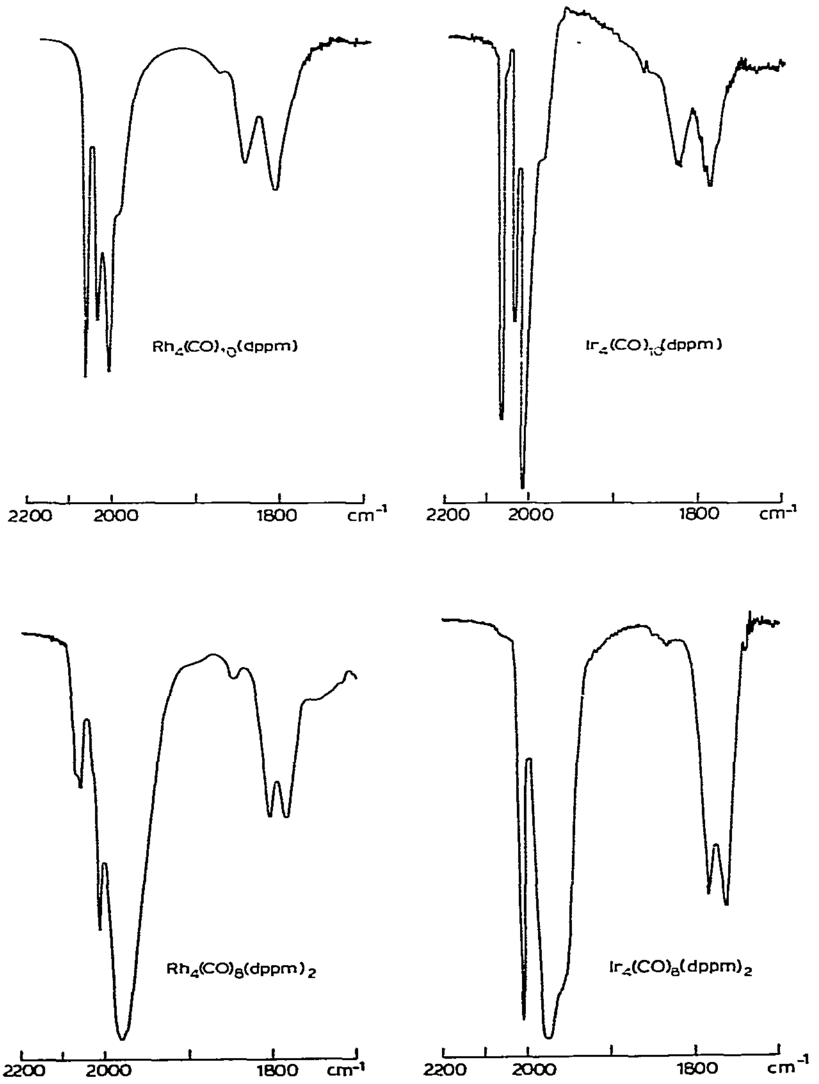

Fig. 1. Infrared spectra of $M_4(CO)_{10}(dppm)$ and $M_4(CO)_8(dppm)_2$ (M = Rh or Ir).

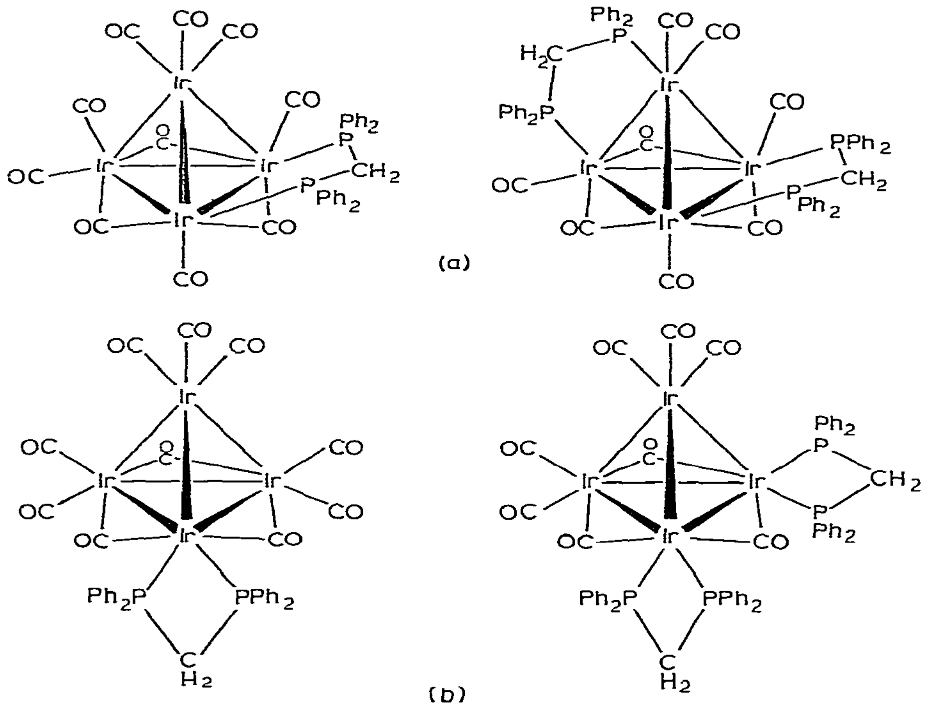

Fig. 2. Possible structures for $Ir_4(CO)_{10}(dppm)$ and $Ir_4(CO)_8(dppm)_2$ with (a) bridging dppm, and (b) chelating dppm ligands.

vative $Rh_4(CO)_{10}(dppm)$, the reaction between $Rh_4(CO)_{12}$ and dppm is carried out in a solvent mixture (hexane/toluene) in which the product is insoluble since, in contrast to the stable $Rh_4(CO)_8(dppm)_2$, solutions of $Rh_4(CO)_{10}(dppm)$ decompose rapidly to give a mixture of $Rh_4(CO)_8(dppm)_2$, $Rh_6(CO)_{14}(dppm)$ and $Rh_6(CO)_{12}(dppm)_2$. The infrared and NMR spectroscopic data for these Rh_4 derivatives are given in Table 1. Once again, the similarity in the ^{31}P NMR chemical shifts of $Rh_4(CO)_{10}(dppm)$ and the known $Rh_4(CO)_8(dppm)_2$ indicates that the dppm ligand also adopts a bridging rather than chelating coordination mode in $Rh_4(CO)_{10}(dppm)$.

$Ir_4(CO)_{12}$ reacts with dppm to give $Ir_4(CO)_8(dppm)_2$ in good yield. Since the substitution of more than two carbonyl ligands is kinetically favoured in this reaction [23], the derivative $Ir_4(CO)_{10}(dppm)$ cannot be prepared by this route. Instead, we used the method of Stuntz and Shapley [24], which leads to $Ir_4(CO)_{11}L$ and $Ir_4(CO)_{10}L_2$ (L = monodentate tertiary phosphine) derivatives. Thus, the reaction of $Ir(CO)_2Cl$(*p*-toluidine) with dppm in the presence of zinc metal and under CO pressure gives a mixture of $Ir_4(CO)_{10}(dppm)$ and $Ir_4(CO)_8(dppm)_2$ which can be separated by column chromatography. The infrared spectra of these iridium derivatives are very similar to the analogous rhodium complexes (Fig. 1 and Table 1), except that in the bis(dppm) derivatives, the bands at 2066 and 2060 cm^{-1} present in the rhodium complex are absent in the iridium complex. This suggests that the rhodium and iridium complexes are structurally similar, and therefore that the dppm ligands in the iridium com-

TABLE 2

SOME ^{31}P NMR DATA

Sample	δ(P) [a]	δ(F) [b]	Δ [c]	ΔR [d]
PPh_2Me		—28.1		
$Ir_4(CO)_{10}(PPh_2Me)_2$ [e]	—5.7		+22.4	
	—28.2		—0.1	
dppm		—21.8		
$Ir_4(CO)_{10}(dppm)$	—52.3		—30.5	—52.9
				—30.4

[a] δ(P) is the observed chemical shift of the phosphorus atom. [b] δ(F) is the chemical shift of the uncoordinated phosphine ligand. [c] Δ is the coordination chemical shift, i.e. Δ = δ(P) — δ(F). [d] ΔR is the coordination shift of a chelated phosphine complex minus the coordination shift of an equivalent phosphorus in a nonchelated analogue. [e] Ref. [26].

plexes also adopt a bridging coordination mode (i.e. the structure shown in Fig. 2a). Further support for this conclusion is provided by the fact that the infrared spectrum of $Ir_4(CO)_{10}$(diars) (diars = 1,2-bis(dimethylarsino)benzene) (ν(CO): 2071m, 2038s, 2026w, 2001m, 1996w, 1847vw, br, 1805w, br) [25], in which the diars ligand is coordinated in a chelating mode to one iridium atom, is quite different from the dppm derivatives reported here. However, the chemical shifts observed in the ^{31}P NMR spectra of $Ir_4(CO)_{10}(dppm)$ and $Ir_4(CO)_8(dppm)_2$ (Table 1) suggest that in both complexes the phosphorus atoms are involved in four-membered rings and therefore that the dppm ligands are coordinated in a chelating mode to one iridium atom (i.e. the structure shown in Fig. 2b). Thus, for example, using the method developed by Garrou [22], we can calculate ring contributions ΔR for $Ir_4(CO)_{10}(dppm)$ based on the Δ values of $Ir_4(CO)_{10}(PPh_2Me)_2$, using the data given in Table 2. The large negative ΔR values obtained (—52.9 and —30.4) are typical of those obtained when the phosphorus atoms are part of a 4-membered ring [22]. A 5-membered ring typically gives large positive ΔR values. On the basis of the infrared and ^{31}P NMR spectroscopic data it is therefore not possible to characterise the bonding mode of the dppm ligand in these iridium complexes. We are therefore currently undertaking X-ray crystal structure determinations of $Ir_4(CO)_8(dppm)_2$ and some related complexes.

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