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Some transition metal complexes of $Ph_2P(CH_2)_nP(O)Ph_2$ ($n = 1, 2$) and $Ph_2P(CH_2)P(S)Ph_2$

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Abstract

New complexes of $Ph_2P(CH_2)_nP(O)Ph_2$ ($n = 1$ (dppmO), $n = 2$ (dppeO)) and $Ph_2P(CH_2P(S)Ph_2$ (dppmS) have been synthesized. These include mono- and di-nuclear metal carbonyl derivatives of chromium, molybdenum and manganese. The cationic complexes, $[Rh(COD)L]X$ (L = dppmO, dppeO, X = PF_6; L = dppmS; X = Cl, ClO_4 PF_6), the dimers $[RhCl(CO)(dppmS)]_2$ and $[PdCl_2(dppmS)]_2$, and the mononuclear complexes $[IrCl(COD)L]$ (L = dppmO, dppeO and dppmS; COD, *cis*-1,5-cyclooctadiene) and $[PtCl_2(dppmS)_2]$ have also been prepared. The modes of coordination of the ligands have been established spectroscopically. All the dppmS complexes involve [P,S]-bidentate coordination of the ligand. The rhodium cations contain [PO]-chelated dppmO and dppeO. The complex $[Mo_2(CO)_2(dppeO)_2]$ is believed to involve [P]- and $[\eta^6\text{-}C_6H_5]$-coordination. All other complexes contain unidentate [P]-bound ligands.

Key words: Chromium; Molybdenum; Rhodium; Platinum; Palladium; Manganese; Phosphine

1. Introduction

The coordination chemistry of bis-phosphine monochalcogenides, $R_2P(CHR^1)_nP(X)R_2$ was first investigated in the mid-1970s by Grim and co-workers [1]. Since then there has been continued interest in complexes of these ligands [2–5], including reports of rhodium complexes of $Ph_2P(CH_2)_nP(O)Ph_2$ ($n = 1, 2$) and related ligands that show catalytic activity for alkene hydroformylation and methanol carbonylation [6,7].

The [P,O] ligands have been shown to exhibit either [P]-bonded unidentate coordination or chelation, depending on the metal. The ligands have the potential for strong bonding between the soft phosphorus atom and a soft metal atom (a low valent transition metal) and weaker bonding between the metal and the harder oxygen atom. While chelation might be expected to confer stability on the complex, introduction of a suitable reagent may lead to cleavage of the weak M–O bond and effective creation of an "active site" at the metal. Generation of such a site is often a prerequisite for catalysis. Not surprisingly, the related [P,S] ligands form much stronger chelates with such metals [1,4,5].

As part of a study of the coordination of ligands of this type, we wished to examine the relative ease of formation of chelated complexes and those containing unidentate ligands for a variety of transition metals.

2. Experimental details

All preparations were carried out by use of conventional N_2/vacuum line and Schlenk tube techniques. All solvents used were distilled and degassed before use. The ligands were prepared by published methods [7] and were recrystallized before use. The transition metal compounds were used as obtained from Strem Chemicals ($[Cr(CO)_6]$, $[Mo(CO)_6]$ and $[Mn_2(CO)_{10}]$) and Johnson Matthey ($[RhCl_3 \cdot 3H_2O]$, $[IrCl_3 \cdot 3H_2O]$, $[K_2PtCl_4]$ and $[PdCl_2]$), or were prepared by published methods ($[Rh(CO)_2Cl]_2$ [8], $[RhCl(COD)]_2$ [9], [Rh(COD)(acac)] [10] (acac, 2,4-pentanedionate anion), $[IrCl(COD)]_2$ [11], $[PdCl_2(COD)]$ [12], $[PtCl_2(COD)]$ [13]). The products exhibited varying stability in air and were stored in Schlenk tubes under nitrogen.

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Infrared spectra were recorded either as KBr discs or as solutions in a 0.1 mm path length NaCl cell, on a Perkin Elmer 782 IR Spectrometer (range 4000–400 cm^{-1}). Far infrared spectra were recorded as CsI discs on a Perkin Elmer 457 IR spectrometer (range 4000–250 cm^{-1}).

The $^{31}P\{^1H\}$ NMR spectra were either recorded as dichloromethane or $CDCl_3$ solutions at 20°C on a Jeol GSX 270 or a Bruker WP80 spectrometer and were referenced externally to 85% H_3PO_4. Mass spectra of the complexes were obtained with a VG TRIO-2 quadrupole mass spectrometer by the fast atom bombardment ionization technique, with nitrobenzyl alcohol as the matrix. Elemental microanalysis was carried out by Butterworth Laboratories Ltd, Teddington, Middlesex.

2.1. $[Cr(CO)_5(dppmO)$

A solution of $[Cr(CO)_6]$ (0.605 g, 2.75×10^{-3} mol) and dppmO (1.00 g, 2.5×10^{-3} mol) in diglyme (10 cm^3) was refluxed for 90 min during which a deep red solution was formed. The solvent was removed under reduced pressure, the residue treated with dichloromethane (50 cm^3), and the resulting suspension filtered. n-Hexane (20 cm^3) was added to the filtrate to give a light yellow precipitate, which was filtered off, washed with methanol (5 cm^3), and recrystallised from dichoromethane/methanol (yield = 0.25 g, 16.9%).

2.2. $[Cr(CO)_4(dppeO)_2]$

A solution of $[Cr(CO)_6]$ (0.29 g, 1.32×10^{-3} mol) and dppeO (0.50 g, 1.2×10^{-3} mol) in petroleum spirit (b.p. 80–100°C) (8 cm^3) was refluxed for 5 h, during which an orange solution and yellow precipitate were formed. The solvent was removed under reduced pressure, the residue treated with diethyl-ether (10 cm^3), and the resulting suspension filtered. The solvent was removed from the filtrate under reduced pressure to give a light yellow solid (yield = 0.15 g, 25.2%).

2.3. Reaction of $[Mo(CO)_6]$ with dppeO

2.3.1. Method 1

$Mo(CO)_6$ (0.26 g, 9.8×10^{-4} mol) and dppeO (0.83 g, 2×10^{-3} mol) were dissolved in diglyme and the solution was refluxed for 6 h. The solvent was removed *in vacuo* and the residue taken up in acetone/dichloromethane (1:1). The solution was reduced in volume and applied to a TLC plate. Elution with acetone/hexane (45:55) gave six spots with R_f values of 0.06, 0.21, 0.28, 0.38, 0.51 and 0.68. These were removed from the plate and subjected to fast atom bombardment-mass spectrometry (FAB-MS) and infrared spectroscopy, and the following identifications were made: R_f 0.06, $dppeO_2$; R_f 0.21, $\{Mo(CO)_4(dppeO)_2]$; R_f 0.28, $[Mo_2(CO)_2(dppeO)_2]$; R_f 0.51, $\{Mo(CO)_5(dppeO)]$. The remaining spots did not give Mo-containing ions in the mass spectra and showed no $\nu(C{\equiv}O)$ bands.

2.3.2. Method 2

The above process was repeated but with petroleum spirit (b.p. 100–120°C) as solvent. TLC revealed four spots, with R_f values of 0.06, 0.21, 0.38 and 0.51. Three of these were identified as $dppeO_2$, $[Mo(CO)_4(dppeO)_2]$ and $[Mo(CO)_5(dppeO)]$, respectively. The remaining spot gave no Mo-containing ions in the mass spectrum and no $\nu(C{\equiv}O)$ bands.

2.4. $[Cr_2(CO)_8(dppmS)_2]$

A solution of $[Cr(CO)_6]$ (0.15 g, 6.02×10^{-4} mol) and dppmS (0.25 g, 6.0×10^{-4} mol) in diglyme (4 cm^3) was refluxed for 4 h, during which a dark yellow solution was formed along with a yellow precipitate and a suspended black solid. The solution was filtered and the solvent then removed under reduced pressure, to give an off-white solid. This was stirred with dichloromethane (10 cm^3) and the resulting suspension was filtered to give a pale yellow solution, which was reduced in volume *in vacuo* until precipitation just occured. Precipitation was completed by the addition of a small amount of n-hexane (2 cm^3), and the off-white solid was filtered off and stirred with dichloromethane (5 cm^5). The resulting suspension was filtered, and the filtrate kept overnight in the freezer to yield an off-white crystalline solid (yield = 0.6 g, 17.2%).

2.5. $[Mo_2(CO)_8(dppmS)_2]$

A solution of $[Mo(CO)_6]$ (0.26 g, 9.8×10^{-3} mol) and dppmS (0.25 g, 6×10^{-4} mol) in diglyme (5 cm^3) was refluxed for 4 h during which a yellow solution was formed along with a black precipitate. The solvent was removed under reduced pressure and the residue stirred with dichloromethane (10 cm^3). The resulting suspension was filtered and n-hexane (10 cm^3) added to the filtrate giving light yellow microcrystals. The product was then recrystallized from dichoromethane (yield = 0.14 g, 37.3%).

2.6. $[Mn_2(CO)_8(dppeO)_2]$

A solution of $[Mn_2(CO)_{10}]$ (0.25 g, 0.64×10^{-3} mol) and dppeO (0.54 g, 1.3×10^{-3} mol) in toluene (50 cm^3), was refluxed for 1 h during which the colour of the solution changed from a bright golden yellow to orange. The volume was reduced to 20 cm^3 and the product was precipitated by the addition of cold n-hexane (50 cm^3), filtered off, and redissolved in the minimum quantity of warm toluene. Addition of a small amount of n-hexane instituted crystallization. The solution was then warmed gently and kept in the freezer overnight to give a yellow-orange crystalline solid (yield = 0.39 g, 52.4%).

Anal. Found: Mn, 8.8; C, 62.8; H, 4.5; P, 10.5. Calc.: Mn, 9.5; C, 62.0; H, 4.2; P, 10.7%.

2.7. *cis*-$[MnBr(CO)_4(dppeO)] \cdot 0.5CH_2Cl_2$

$[Mn_2(CO)_8(dppeO)_2]$ (0.8 g, 6.89×10^{-4} mol) was dissolved in dichloromethane (60 cm^3) to give a yellow solution. This was cooled to 0°C in an ice-water bath and a solution of bromine (0.12 g, 7.5×10^{-4} mol) in dichloromethane (75 cm^3) was added. The mixture was stirred at 0°C for 4 h in which time it turned orange. The solvent was removed *in vacuo* to yield orange crystals. The product was recrystallized from dichloromethane (yield = 0.39 g, 52.4%).

Anal. Found: Mn, 6.7; C, 53.4; H, 3.9; P, 8.6; Br, 13.0. Calc.: Mn, 8.3; C, 54.5; H, 3.7; P, 9.4; Br, 12.1%.

2.8. *trans*-$[MnBr(CO)_4(dppeO)]$

$[Mn_2(CO)_8(dppeO)_2]$ (0.8 g, 6.89×10^{-4} mol) was dissolved in dichloromethane (60 cm^3). The solution was cooled to 0°C in an ice-water bath and a solution of bromine (0.12 g, 7.5×10^{-4} mol) in dichloromethane (75 cm^3) was added. The solution was stirred at 0°C for 1 h and the solvent then removed *in vacuo*. The residue was taken up in chloroform (2 cm^3) and subjected to chromatography on a silica gel column (16 cm) with diethyl ether/chloroform (50:50 v/v) as eluent. The products gave two distinct bands: the first containing the major product, the *cis*-isomer, the second containing the minor product, the *trans*-isomer. The second band was collected and the solvent removed under reduced pressure to give orange crystals (yield = 0.10 g, 11.0%).

2.9. *cis*-$[Mn(NO_3)(CO)_4(dppeO)] \cdot 0.5CH_2Cl_2$

A solution of *cis*-$[MnBr(CO)_4(dppeO)]$ (0.30 g, 4.54×10^{-4} mol) in dichloromethane (3 cm^3) was treated with a solution of silver nitrate (0.085 g, 5.0×10^{-4} mol) in ethanol/water (10 cm^3/0.25 cm^3). The mixture was stirred for 30 min. The precipitated silver bromide was then filtered off and the filtrate evaporated to dryness. This residue was dissolved in acetone (2 cm^3) and the product precipitated by addition of diethyl ether (yield = 0.17 g, 59.0%).

Anal. Found: C, 53.7; H, 4.2, N, 2.3. Calc.: C, 54.3; H, 3.6; N, 2.0%.

2.10. *mer-trans*-$[MnBr(CO)_3(dppeO)_2] \cdot 0.5CH_2Cl_2$

2.10.1. Method 1

A mixture of $[MnBr(CO)_5]$ (0.5 g, 1.8×10^{-3} mol) with dppeO (1.55 g, 3.74×10^{-3} mol) was dissolved in acetone (100 cm^3) and the solution boiled under reflux for 30 min. The solution was cooled to room temperature, the solvent reduced in volume to 10 cm^3, and cold n-hexane added to precipitate the product as a orange-yellow crystalline solid, which was recrystallized from dichloromethane (yield = 1.36 g, 78.0%).

Anal. Found: C, 61.8; H, 4.7; P, 10.9; Br, 7.2. Calc.: C, 61.2; H, 4.6; P, 11.4; Br, 7.3%.

2.10.2. Method 2

cis-$[MnBr(CO)_4(dppeO)]$ (0.25 g, 3.8×10^{-3} mol) and dppeO (0.17 g, 4.1×10^{-4} mol) were dissolved in chloroform (40 cm^3). The solution was refluxed for 30 min and then allowed to cool to room temperature. The solvent was removed *in vacuo* to leave an orange-yellow crystalline solid, which was recrystallized from dichloromethane (yield = 0.22 g, 56.0%).

2.11. $[Rh(COD)(dppmO)][PF_6]$

A mixture of $[Rh(COD)(acac)]$ (0.1 g, 3.23×10^{-4} mol) and dppmO (0.27 g, 6.74×10^{-4} mol) was dissolved in dichoromethane (10 cm^3) to give a golden yellow solution, which was kept at room temperature for 20 min. The solvent was than removed *in vacuo* to give a light yellow crystalline solid. This solid, believed to be $[Rh(COD)(dppmO)_2](acac)$, was redissolved in dichloromethane (10 cm^3) and treated with a solution of $[NH_4PF_6]$ (0.06 g, 3.68×10^{-4} mol) in acteone/water (5:1 ratio) (10 cm^3), which yielded a light yellow precipitate. This precipitate was quickly filtered off and the filtrate passed through a phase separating filter paper to remove any water and water-soluble matter. The resulting solution was then reduced in volume under reduced pressure to give the crude product as a yellow crystalline solid, which was recrystallized from dichloromethane (5 cm^3) (yield = 0.18 g, 75.0%).

Anal. Found: C, 52.4; H, 4.9. Calc.: C, 52.4; H, 4.5%.

2.12. $[Rh(COD)(dppeO)][PF_6]$

This was prepared by a procedure analogous to that used for $[Rh(COD)(dppmO)][PF_6]$ (yield = 0.16 g, 66.7%).

Anal. Found: C, 53.3; H, 4.9. Calc.: C, 53.0; H, 4.7%.

2.13. $[Rh(COD)(dppmS)[PF_6] \cdot 0.5CH_2Cl_2$

A mixture of $[Rh(COD)(acac)]$ (0.1 g, 3.23×10^{-4} mol) and dppmS (0.15 g, 3.49×10^{-4} mol) was dissolved in dichoromethane (10 cm^3) to give a golden yellow solution. Treatment with a solution of $[NH_4PF_6]$ (0.06 g, 3.68×10^{-4} mol) in acetone/water (5:1 ratio) (5 cm^3) yielded a white precipitate. This was quickly filtered off and the filtrate passed through a phase separating filter paper to remove any water and any water-soluble matter. The resulting solution was then reduced in volume by evaporation under reduced pressure to give a yellow crystalline solid, which was recrystallized from dichloromethane (5 cm^3) (yield = 0.17 g, 68.0%).

Anal. Found: C, 49.9; H, 4.9. Calc.: C, 49.4; H, 4.3%.

2.14. *[Rh(COD)(dppmS)][ClO₄]*

A solution of [Rh(COD)(acac)] (0.2 g, 6.54×10^{-4} mol) in tetrahydrofuran (3 cm^3) was treated with a solution of [$HClO_4$] (60%, 0.2 g) in tetrahydrofuran (1 cm^3). This mixture was then added to dppmS (0.28 g, 6.73×10^{-4} mol) to give a deep orange solution, which within 10 min changed to a paler yellow-orange colour. The solvent was removed *in vacuo* to give a dark red oil which was washed with a little diethyl ether (5 cm^3) and pumped under reduced pressure for approximately 12 h. The oil was then extracted with acetone (3 × 10 cm^3) and the solvent removed from the extract slowly under reduced pressure to leave brick red crystals which were filtered off, washed with diethyl ether, and recrystallized from acetone (10 cm^3) (yield = 0.25 g, 78.1%).

2.15. *[Rh(COD)(dppmS)][Cl]*

A solution of $[RhCl(COD)]_2$ (0.12 g, 2.43×10^{-4} mol) and dppmS (0.21 g, 5.05×10^{-4} mol) in dichloromethane (20 cm^3) kept for 10 min at room temperature and the solvent was then removed *in vacuo* yield a dark yellow solid. This was recrystallized from dichloromethane to give dark yellow crystals (yield = 0.25 g, 78.1%).

2.16. *trans-[RhCl(CO)(dppmS)] · 2CH₂Cl₂*

A solution of $[RhCl(CO)_2]_2$ (0.20 g, 5.15×10^{-4} mol) and dppmS (0.43 g, 1.03×10^{-3} mol) in dichloromethane (20 cm^3) was kept for 20 min, during which the colour changed from orange to golden yellow. The solvent was removed under reduced pressure to yield a yellow crystalline solid, which was redissolved in the minimum quantity of warm dichloromethane (5 cm^3). The solution was kept in the freezer, and bright yellow crystals were obtained after 2–3 days (yield = 0.50 g, 85.0%).

Anal. Found: C, 48.7; H, 3.5. Calc.: C, 48.6; H, 3.6%.

2.17. *cis-[RhCl(CO)(dppmS)]₂*

A mixture of $[RhCl(CO)_2]_2$ (0.20 g, 5.15×10^{-4} mol) and dppmS (0.43 g, 1.03×10^{-3} mol) was treated with dichloromethane (20 cm^3). Vigorous stirring for 10 min with gentle warming yielded a brown solution. The solvent was removed under reduced pressure to leave a brown crystalline solid which was dissolved in the minimum quantity of warm acetone (5 cm^3). The solution was kept in the freezer, overnight, to give dark brown crystals (yield = 0.30 g 57.0%).

Anal. Found: C, 53.1; H, 4.5. Calc.: C, 53.6; H, 3.8%.

2.18. *[IrCl(COD)(dppmO)]*

A solution of $[IrCl(COD)]_2$ (0.1 g, 1.5×10^{-4} mol) and dppmO (0.13 g, 3.25 10^{-4} mol) was dissolved in dichloromethane (10 cm^3) to give an orange solution. The solution was stirred for 10 min at room temperature and the solvent was then reduced in volume. Hexane was then added to give an orange solid, which was filtered off, and recrystallized from dichloromethane to give small orange crystals (yield = 0.20 g, 87.0%).

Anal. Found: C, 54.3, H, 4.9. Calc.: C, 53.8; H, 4.7%.

2.19. *[IrCl(COD)(dppeO)] · 0.5CH₂Cl₂*

A mixture of $[IrCl(COD)]_2$ (0.1 g, 1.5×10^{-4} mol) with dppeO (0.13 g, 3.14×10^{-4} mol) was dissolved in dichloromethane (10 cm^3) to give an orange solution. The solution was stirred for 10 min at room temperature, after which the solvent was reduced in volume. n-Hexane was added to yield the product as an orange solid, which was filtered off and recrystallized from dichloromethane to afford small orange crystals (yield = 0.20 g, 87.0%).

Anal. Found: C, 53.2; H, 4.9. Calc.: C, 52.4; H, 4.7%.

2.20. *[IrCl(COD)(dppmS)] · CH₂Cl₂*

A mixture of $[IrCl(COD)]_2$ (0.1 g, 1.5×10^{-4} mol) and dppmS (0.13 g, 3.12×10^{-4} mol) was dissolved in dichloromethane (20 cm^3) to give an orange solution. The solution was stirred for 10 min at room temperature, and the solvent was then reduced in volume to give an orange solid, which was filtered off and recrystallized from dichloromethane to give small orange crystals (yield = 0.22 g, 95.6%).

Anal. Found: C, 53.7; H, 4.7. Calc.: C, 53.2; H, 4.9%.

2.21. *[PdCl₂(dppmS)]₂ · CH₂Cl₂*

A mixture of $[PdCl_2(COD)]$ (0.2 g, 7.0×10^{-4} mol) and dppmS (0.32 g, 7.7×10^{-4} mol) was dissolved in dichloromethane (10 cm^3) to give a light yellow solution. This was warmed gently for 1 min, during which the colour changed to orange. During a further 20 min at room temperature the solution became dark orange-red. The solvent was the removed *in vacuo* to give a yellow-orange solid, which was recrystallized from dichloromethane to yellow-orange microcrystals (yield = 0.35 g, 83.3%).

Anal. Found: C, 47.5; H, 3.6. Calc.: C, 48.1; H, 3.6%.

2.22. $[PtCl_2(dppmS)_2] \cdot 2CH_2Cl_2$

A mixture of $[PtCl_2(COD)]$ (0.5 g, 1.34×10^{-3} mol) and dppmS (0.61 g, 1.47×10^{-3} mol) was dissolved in dichloromethane (20 cm^3) to give a yellow solution. During 20 min at room temperature the solution became darker yellow. The solvent was then removed *in vacuo* to give a light yellow solid, which was recrystallized from dichloromethane to give yellow crystals (yield = 0.65 g, 87.8%).

Anal. Found: C, 49.9; H, 4.1. Calc.: C, 49.3; H, 3.8%.

3. Results and discussion

A number of the products were obtained as CH_2Cl_2 solvates. Formation of solvates with this solvent has been commonly observed [14].

3.1. Complexes of dppmO and dppeO

Previous studies have shown that dppmO and dppeO can coordinate in both [P,O]-bonded bidentate and [P]-bonded unidentate modes. The mode of bonding is most readily distinguished by infrared spectroscopy and relies on the change in frequency of the P=O stretching vibration. Such changes have long been recognized as indicative of oxygen–metal bonding in, for example, Ph_3PO complexes [15]. In the case of dppmO and dppeO, the free ligands display ν(P=O) values of 1180 and 1195 cm^{-1}, respectively. Shaw and co-workers have reported complexes containing [P]-bonded unidentate ligands, such as $[MX_2L_2]$ (M = Pd, Pt; X = a variety of anions), show ν(P=O) bands in the range 1180–1200 cm^{-1}, whereas the cations $[Ml_2]^{2+}$ (M = Pd, Pt) containing [P,O]-bonded bidentate ligands give bands between 1095 and 1130 cm^{-1} [2].

^{31}P NMR data is also useful in assigning the coordination mode. For example, the $[MX_2L_2]$ complexes show values of δ(P) in the range −2–20 ppm and those of δ(P=O) in the range 25–35 ppm, whereas the values for the $[Ml_2]^{2+}$ cations are 2–36 ppm and 50–68 ppm, respectively (the free ligand values are −30.8 (δ(P)) and 26.2 (δ(P=O)) and −12.9 (δ(P)) and 26.2 (δ(P=O)) for dppmO and dppeO, respectively). Similar changes in δ(P=O) values have been observed for other unidentate and bidentate complexes of platinum and bidentate complexes of rhodium [2,6].

3.1.1. Chromium and molybdenum carbonyl derivatives

The reactions of $[Cr(CO)_6]$ with dppmO or dppeO gave mixtures of products as revealed by tlc analysis of reaction mixtures. Moreover these mixtures could not be separated by column or preparative TLC, and so isolation of products depended on reaction conditions and recrystallization of crude product mixtures. For these reasons, yields were low and characterization relied on infrared and mass spectroscopic measurements rather than elemental analysis or NMR spectroscopy.

The only pure products isolated by these crystallization procedures were $[Cr(CO)_5dppmO]$ and *cis*-$[Cr(CO)_4(dppeO)_2]$, which were identified by spectroscopic methods (Table 1). Infrared data are consistent with [P]-bonded unidentate coordination in both complexes (ν(P=O) values of 1185 and 1190 cm^{-1}, respectively). These values contrast with a frequency of 1135 cm^{-1} in the chelate complex, $[Cr(CO)_4$-$(Ph_2PCHPrP$-

TABLE 1. Infrared and FAB mass spectral data for dppmO- and dppeO-metal carbonyl complexes

Complex	ν(P=O) (cm^{-1})	ν(C≡O) (cm^{-1})	*m/z*
$[Cr(CO)_5(dppmO)]$	1185	2060m, 1985w, 1944s	592(M$^{+\cdot}$), 564, 536, 508, 480, 452
cis-$[Cr(CO)_4(dppeO)_2]$	1190	2060w, 1980m, 1938s, 1885m	992(M$^{+\cdot}$), 954, 936, 880
$[Mo(CO)_5(dppeO)]$	1187	2035m, 1950w, 1910s	652(M$^{+\cdot}$), 624, 596, 568, 540, 512
cis-$[Mo(CO)_4(dppeO)_2]$	1180	2020w, 1919m, 1908vs, 1885s	1038M$^{+\cdot}$), 1038, 982, 954, 926, 512
$[Mo_2(CO)_4(dppeO)_2\}$	1190	1900s, 1840s	1136(M$^{+\cdot}$), 1108, 1080, 1052, 568, 540, 512
$[Mn_2(CO)_8(dppeO)$	1190	1950vs	1162(M$^{+\cdot}$), 1106, 1078, 1050, 1022, 994, 938
cis-$[MnBr(CO)_4(dppeO)]$	1175	2090m, 2010sh, 1990vs, 1960m	576(M$^{+\cdot}$− 3CO), 548, 469
trans-$[MnBr(CO)_4(dppeO)]$	1175	1955s	576 (M − 3CO)$^{+\cdot}$, 548, 469
cis-$[Mn(NO_3)(CO)_4(dppeO)]$	1170	2090m, 2025sh, 1995vs, 1960m	531(M − 4CO)$^{+\cdot}$, 469
mer-trans-$[MnBr(CO)_3(dppeO)_2]$	1170	2030w, 1960vs, 1910m	962 (M − 3CO)$^{+\cdot}$, 939, 883

(O)Ph_2)] [1a]. The pattern of C≡O stretching frequencies for both complexes prepared in this work is very similar to those observed for other [$Cr(CO)_5L$] and *cis*-[$Cr(CO)_4L_2$] complexes [16]. It is not obvious why neither [$Cr(CO)_4(dppmO)_2$] nor the chelate complex [$Cr(CO)_4(dppmO)$] were obtained under more forcing conditions.

Similar reactions of [$Mo(CO)_6$] with dppeO also gave a complex mixture of products. Once again the compounds could not be obtained in large amounts by column or preparative TLC. However, infrared and FAB mass spectrometry of microsamples obtained from normal TLC separation proved informative. Thus, FAB-MS indicated the formation of both [$Mo(CO)_5$(dppeO)] and [$Mo(CO)_4(dppeO)_2$]. Infrared spectra of the former exhibited a pattern of bands consistent with those observed for other [$Mo(CO)_5L$] complexes ([$Mo(CO)_5$(dppeO)]: 2035m, 1950w, 1910s; [$Mo(CO)_5(PPh_3)$]: 2073m, 1984w, 1952s; [$Mo(CO)_5(PMe_3)$]: 2071m, 1951w, 1943s). Similarly [$Mo(CO)_4(dppeO)_2$] (ν(C≡O): 2020w, 1919m, 1908vs, 1885s) exhibits a similar spectrum to those of other *cis*-[$Mo(CO)_4L_2$] complexes (*e.g.* *cis*-[$Mo(CO)_4(PPh_3)_2$]: 2022w, 1929sh, 1911vs, 1899s).

One further molybdenum-containing product was obtained from the reaction in refluxing diglyme. The highest mass ion in the FAB-MS of this product corresponded to [$Mo_2(CO)_4(dppeO)_2$]$^+$. This product also exhibited ν(C≡O) vibrations at 1900s and 1840s cm^{-1}. Clearly the highest ion in the FAB-MS may be a fragment ion. However, the infrared spectrum is markedly different from those of the complexes [$Mo_2(CO)_8(dppmS)_2$] (M = Cr, Mo) (*vide infra*), and is very similar to that of [$(OC)_2MoAsPh_2CH_2AsPh(C_6H_5)$] (ν(C≡O at 1897s and 1838s) in which the metal is coordinated by one arsenic atom and one η^6-phenyl ring [17]. By analogy, we propose that the dinuclear molybdenum–dppeO complex has the structure shown in Fig. 1, in which the metal atoms both achieve 18-electron configurations.

3.2. Manganese carbonyl derivatives

Treatment of [$Mn_2(CO)_{10}$] with dppeO gave [$Mn_2(CO)_8(dppeO)_2$] in moderate yield. The infrared spectrum of this compound displayed ν(P=O) band at 1190 cm^{-1}, and a single ν(C≡O) band at 1950 cm^{-1}. This is consistent with ligands exhibiting [P]-bonded unidentate coordination in a 1,2-diaxial structure.

Reaction of this dimer with bromine gave rise to both *cis*- and *trans*-isomers of [$MnBr(CO)_4$(dppeO)], which were separated by column chromatography. The frequencies of the ν(C≡O) bands exhibited by both isomers are similar to those observed for related molecules [16]. The ν(P=O) values of 1175 cm^{-1} are again consistent with unidentate coordination.

It has previously been reported that treatment of complexes of palladium(II) and platinum(II), such as [$PdBr_2(dppeO)_2$] containing unidentate ligands, with $AgNO_3$ followed by NH_4PF_6 gives rise to the chelated complexes such as [$Pd(dppeO)_2](PF_6)_2$ [2]. Similar treatment of [$MnBr(CO)_4$(dppeO)] failed to yield the chelated complex cation. However, after reaction with $AgNO_3$ alone, the complex [$Mn(NO_3)(CO)_4$(dppeO)] · $0.5CH_2Cl_2$ was isolated, in which the ligand also exhibited unidentate coordination (ν(P=O) at 1170 cm^{-1}).

Reaction of either *cis*-[$MnBr(CO)_4$(dppeO)] with one molar equivalent of dppeO or [$MnBr(CO)_5$] with two molar equivalents of the ligand yielded [$MnBr(CO)_3(dppeO)_2$]. This compound is assigned a *mer-trans* geometry on the basis of the ν(C≡O) bands (2030w, 1960vs, 1910m cm^{-1}) which are very similar to those of *mer-trans*-[$MnBr(CO)_3(PPh_3)_2$] (2046w, 1955vs, 1916m cm^{-1}). Again, the dppeO ligands exhibit [P]-bonded unidentate coordination (ν(P=O) at 1170 cm^{-1}).

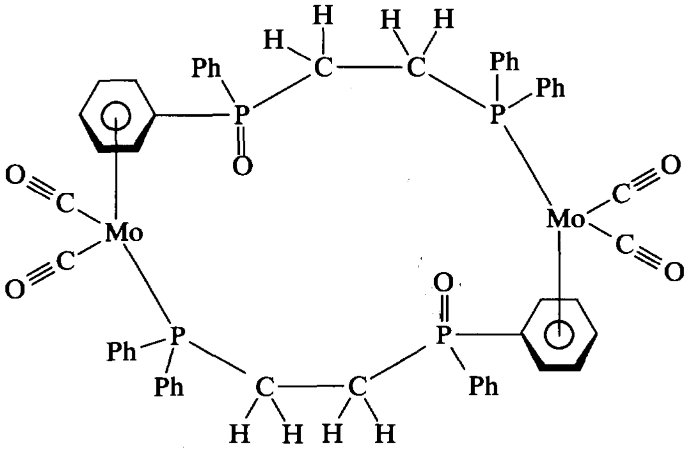

Fig. 1.

Reaction of dppmO with $[Mn_2(CO)_{10}]$ gave a complex mixture of products, as revealed by TLC and by infrared spectroscopy in the carbonyl region. This mixture could not be separated cleanly by TLC, and was not investigated further.

3.1.3. *Rhodium and iridium complexes*

The salt $[Rh(COD)L][PF_6$ (L = dppmO, dppeO) were prepared by a two stage process. Treatment of [Rh(COD)(acac)] with two molar equivalents of ligand yielded intermediate complexes tentatively formulated as $[Rh(COD)L_2](acac)$ on the basis of FAB-MS. When these intermediates were treated with NH_4PF_6 the complexes $[Rh(COD)L]PF_6$ were obtained in good yield. The complexes showed ν(P=O) values of 1130 (dppmO) and 1150 (dppeO)cm^{-1} consistent with [P,O]-bidentate coordination in both cases. This was confirmed by the ^{31}P NMR data (Table 2).

Reaction of $[IrCl(COD)]_2$ with the ligands gave [IrCl(COD)(dppmO)] and [IrCl(COD)dppeO)] · CH_2Cl_2. Both complexes involve [P]-bound unidentate coordination, as indicated by the infrared and ^{31}P NMR data (Table 2).

3.2. *Complexes of dppmS*

[P,S]-chelation may also be distinguished from [P]- or [S]-bonded unidentate coordination by ^{31}P NMR and infrared spectroscopy [1c,1e,4,5]. This can be illustrated by data for dppmS (ν(P=S) at 605 cm^{-1}; δ(P) at −29.1, δ(P(S)) at 39.2 ppm; J(P–P(S)) = 74.0 Hz) and *fac*-$[MnBr(CO)_3(dppmS)]$ which shows ν(P=S) at 575 cm^{-1}; δ(P(S)) at 59.3 ppm; δ(P) at 33.4 ppm; J(P–P(S) = 66.0 Hz.

3.2.1. *Chromium and molybdenum carbonyl complexes*

The chelate complexes, $[M(CO)_4(dppmS)]$ (M = Cr, Mo) have been reported previously by Grim and coworkers [1c]. In the present work, we found that these complexes could be obtained in good yield under the conditions previously reported (refluxing diglyme) but in shorter reaction times (1–2 h). The infrared spectra also agree exactly with those previously reported. However, the FAB-MS of the chromium complex showed the presence of the weak dinuclear ion $[Cr_2(dppmS)_2]^{+\cdot}$ as well as the expected sequence of ions, $[Cr(CO)_n$-$(dppmS)]^+$ (n = 4–0). After several recrystallizations of the product, the dinuclear ion was no longer present in the FAB mass spectrum.

In a separate experiment, after 4 h reaction between $[Cr(CO)_6]$ and dppmS in refluxing diglyme, we were able to isolate in a low yield a complex formulated as $[Cr_2(CO)_8(dppmS)_2]$. This had a distinctly different colour and infrared spectrum from those of $[Cr(CO)_4$-(dppmS)] (ν(C≡O) at 2012m, 1921sh, 1897vs, 1861s cm^{-1}). Its FAB-MS also displayed a series of dinuclear ions, $[Cr_2(CO)_n(dppmS)_2]^+$ (n = 8, 6, 3, 2, 1, 0). We were unable to obtain a ^{31}P NMR spectrum, since insufficient sample was available.

The molybdenum complex $[Mo_2(CO)_8(dppmS)_2]$ was obtained in a similar manner. This complex also gave a distinctly different infrared spectrum from that of $[Mo(CO)_4(dppmS)]$ (ν(C≡O) at 2022m, 1927sh, 1907vs, 1867s cm^{-1}). The highest mass ion observed in the FAB-MS of this molecule corresponded to $[Mo_2(CO)_3$-$(dppmS)_2]^+$. The ^{31}P NMR spectrum is similar to that of $[Mo(CO)_4(dppmS)$ (δ(P) at 37.9, δ(P(S)) at 55.5 ppm. J(P–P(S)) = 78.0 Hz). The dimer also gave a ν(P=S) band at 585 cm^{-1} compared to that at 580 cm^{-1} for $[Mo(CO)_4dppmS)]$. We propose the structure shown in Fig. 2 for these dinuclear species, in which the metal atoms achieve 18-electron configurations. These are believed to be the first reported examples of μ-dppmS-bonding.

3.2.2. *Complexes of rhodium and iridium*

Treatment of $[RhCl(COD)]_2$ or [Rh(COD)(acac)] with dppmS gives the cation $[Rh(COD)(dppmS)]^+$, iso-

TABLE 2. Infrared, ^{31}P NMR and FAB mass spectra of rhodium and iridium complexes of dppmO and dppeO

Complex	ν(P = O) (cm^{-1})	δ(PPh_2)	δ$P(O)Ph_2$ (ppm)	$m/z^{+\ a}$
$[Rh(COD)(dppmO)]Pf_6$	1130	26.9 (J(Rh–P) = 162.4 Hz, J(P–P(O)) = 29.0 Hz)	65.3	611 ($C^{+\cdot}$) 502
$[Rh(CO)(dppeO)]PF_6$	1150	21.1 (J(Rh–P) = 166.2 Hz, J(P–P(O)) = 29.0 Hz)	47.8	625 ($C^{+\cdot}$) 516
[IrCl(COD)(dppmO)]	1190 (ν(Ir–Cl) 298)	7.7	22.6	736 ($C^{+\cdot}$) 701 593
[Ir(Cl(COD)(dppeO)]	1170 (ν(Ir–Cl) 295)	9.6	26.4	750 ($C^{+\cdot}$) 715 607

[a] $C^{+\cdot}$ refers to the m/z value of the cation.

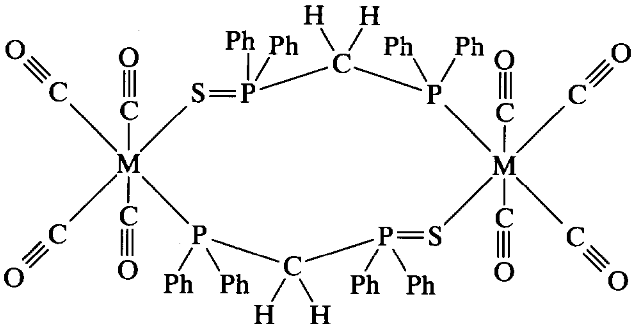

Fig. 2. M = Cr, Mo.

lated as its Cl^-, ClO_4^- and PF_6^- salts. All give identical FAB-MS, IR and ^{31}P NMR data (Table 3) consistent with the presence of chelated dppmS. However, reaction of $[RhCl(CO)_2]_2$ with dppmS gives either of two products depending on the conditions. Analytical data for both are consistent with $[RhCl(CO)(dppmS)]_2$, although the yellow form is obtained as a CH_2Cl_2 solvate. The highest mass ion in the FAB-MS of the brown form corresponds to $[Rh_2Cl_2(CO)_2(dppmS)_2]^{+\cdot}$ and related dinuclear and mononuclear fragment ions are observed. The spectrum of the yellow form is broadly similar, but shows $[Rh_2Cl_2(CO)(dppmS)_2]^{+\cdot}$ as its highest mass ion. The two forms show similar ν(P=S) values indicative of [P,S] bonding. The yellow form shows one ν(C≡O) band, whereas the brown form exhibits two. The ^{31}P NMR spectra of the two forms are virtually identical. On the basis of these properties, the two compounds are assigned as *cis* (brown), and *trans* (yellow) forms of $[RhCl(CO)(\mu\text{-dppmS})_2RhCl(CO)]$ (Figs. 3 and 4). Surprisingly, both form showed two bands which could be assigned to Rh–Cl stretching frequencies. However, it is noteworthy that *trans*-$[RhCl(CO)(dppm)]_2$, the structure of which has been confirmed by crystallography, also shows two Rh–Cl bands (303, 290 cm^{-1}) [18,19].

Reaction of $[IrCl(COD)]_2$ with dppmS gives rise to the mononuclear five coordinate complex, $[IrCl(COD)(dppmS)] \cdot CH_2Cl_2$ Spectroscopic data (Table 3) are consistent with this structure.

3.2.3. Complexes of palladium and platinum

Reaction of $[PdCl_2(COD)]$ with dppmS gives $[PdCl_2(dppmS)]_2 \cdot CH_2Cl_2$. The dinuclear nature of this product was confirmed by FAB-MS, although the highest mass ion observed corresponded to $[Pd_2Cl_3(dppmS)_2]^{+\cdot}$. The compound shows ν(Pd–Cl) vibrations at 349, 292 and 280 cm^{-1}. These values are similar to those observed for $[PdCl_2(P^tBu_2Ph)]_2$ (356, 307, 250 cm^{-1}) [20] and suggests an analogous structure (Fig. 5) containing bridging and terminal chloride ligands. However, the ν(P=S) value of 572 cm^{-1} and the ^{31}P NMR data (Table 3) suggest that the dppmS ligands

TABLE 3. Infrared and ^{31}P NMR and FAB mass spectral data for dppmS complexes

Complex	ν(C=O) (cm^{-1})	ν(P=S) (cm^{-1})	δ(pph$_2$) (ppm)	δ(P(s)Ph$_2$) (ppm)	m/z
$Cr_2(CO)_8(dppmS)_2$	2010m 1925vs 1905m	590	–	–	1160 ($M^{+\cdot}$), 1104, 1020, 992, 964, 936, 884, 580, 552, 524, 496, 468
$Mo_2(CO)_8(dppmS)_2$	2015m 1915vs 1845m	585	37.7 J(P–P(S)) = 77.7 Hz	54.5	1112 $(M - 5CO)^{+\cdot}$, 1084, 1056, 1028, 626, 598, 570, 542, 514
trans-$[RhCl(CO)(dppmS)]_2$ -$[RhCl(CO)(dppmS)]_2$	1980vs	580 (ν(Rh–Cl) 292, 273)	48.3 J(Rh–P) = 207.1 Hz J(P–P(S)) = 46.0 Hz	52.4	1136 $(M - CO)^{+\cdot}$, 1108, 1101, 1073, 1038, 554, 437, 519
cis-$[RhCl(CO)(dppmS)]_2$	2055w 1955vs	590 (ν(Rh–Cl) 292, 268)	48.4 J(Rh–P) = 207.1 Hz J(P–P(S)) = 45.0 Hz	52.2	1164 ($M^{+\cdot}$), 1136, 1108, 1101, 1073, 1038, 554, 547, 519
$[Rh(COD)(dppmS)]X$ ($X = Cl, PF_6, ClO_4$)		570 (X=Cl) 575 ($X=PF_6$) 572 ($X=ClO_4$)	40.0 J(Rh–P) = 198.8 Hz J(P–P(S)) = 51.8 Hz ($X = PF_6, ClO_4$)	57.5	627 ($C^{+\cdot}$), 519
$[IrCl(COD)(dppmS)]$		570 (ν(Ir–Cl) 292)	29.5 J(P–P(S)) = 46.3 Hz	61.6	717 $(M - Cl)^{+\cdot}$, 646, 609
$[PdCl_2(dppmS)]_2$		572 (ν(Pd–Cl) 349, 292, 280)	30.4 J(P–P(S)) = 34.1 Hz	55.8	1149 $(M - Cl)^{+\cdot}$, 1114, 1079, 1044, 973, 938
cis-$[PtCl_2(dppmS)_2]$		569 (ν(Pt–Cl) 338, 319)	7.9, 20.6 J(Pt–P) = 3265 3680 Hz J(P–P(S)) = 20.2, 29.2 Hz	50.3, 56.5	1062 $(M - Cl)^{+\cdot}$, 1027, 611

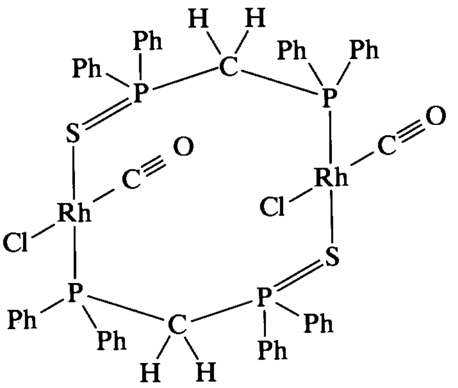

Fig. 3.

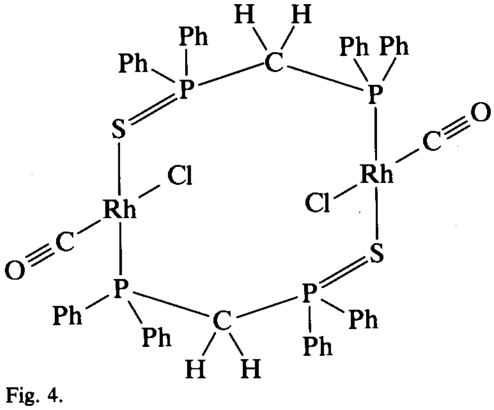

Fig. 4.

are chelated, thus conferring an 18-electron configuration on the metal atom.

The analogous reaction with [$PtCl_2$(COD)] follows a different course, yielding [$PtCl_2(dppmS)_2$]·$2CH_2Cl_2$. Two ν(Pt–Cl) bands were observed at 338 and 319 cm^{-1}, indicative of a *cis* configuration, and the single P=S stretching frequency suggests that both ligands are chelated. However, the ^{31}P NMR spectrum shows four resonances. The chemical shifts of the Ph_2P groups are also much smaller than are usually observed, and are well separated from each other, and the *J*(Pt–P) values also differ. This may be a consequence of weak coordination of at least one phosphorus atom (Fig. 6). Attempts to produce crystals suitable for an X-ray diffraction study have not been successful.

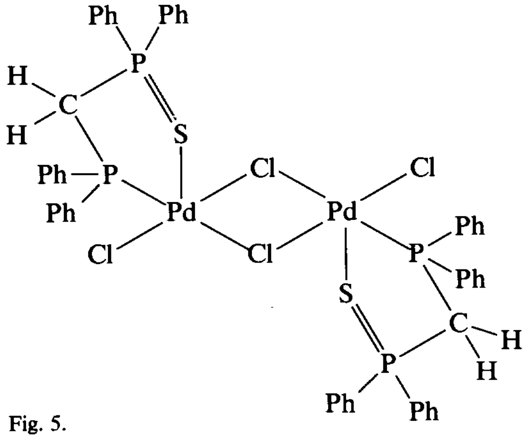

Fig. 5.

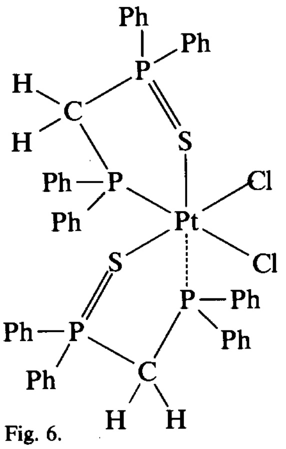

Fig. 6.

4. General conclusions

All dppmS complexes reported here involve both [P]- and [S]-coordination in either chelating or bridging modes. This accords with previous findings and with the similar coordinating abilities of phosphorus and sulphur [21,22].

The coordination behaviour of [P,O] donor ligands of the type reported in this study is much more complex and subject to subtle changes in ligand structures and between metals and ligand arrays. Thus, none of the metal carbonyl complexes reported here contain [P,O] chelation. However, the chelated complexes [$M(CO)_4(Ph_2PCHPrP(O)Ph_2)$] (M = Cr, Mo, W) have been reported [1a]. It is also noteworthy that it is possible to achieve coordination of dppeO to a molybdenum carbonyl unit via the [P] donor atom and an η^6-aromatic ring rather than by [P,O] chelation. Similarly, it is interesting to compare the coordination behaviour of rhodium(I) and iridium(I) towards the ligands used in this study. It appears that use of simple concepts such as absolute hardness values [14,15] of metals and ligand donor atoms (O = 6.08; P = 4.88; S = 4.14; $Rh^I = 5.31$; $Ir^I = 3.9$ eV) do not provide a satisfactory explanation of the observed behaviour.

We are currently engaged in further studies of ligands of this type in an attempt to systematize their coordinating abilities.

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