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Mixed-metal cluster chemistry 15: some bidentate phosphine chemistry of tungsten–iridium clusters ☆

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Abstract

Reactions of $[Cp_2W_2Ir_2(CO)_{10}]$ (**4**) with equimolar amounts of the bidentate phosphines bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) afford the substitution products $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-}L)(CO)_5]$ [L = dppm (**5**), dppe (**6**)] in excellent yields (76% and 80%, respectively). The clusters **5** and **6** are fluxional in solution, with the interconverting isomers of **6** resolvable at low temperatures. Variable-temperature ^{31}P- and ^{13}C-NMR for **5** and **6** enable structural assignment of the isomers. ^{13}C-NMR exchange spectroscopy (EXSY) spectra reveal that the fluxional process observed with **5**, and which interconverts the isomers of **6**, involves a 'waggling' of the $CpW(CO)_2$ group over the W_2Ir faces or complete tripodal rotation at the apical $CpW(CO)_2$. Reaction of $[CpWIr_3(CO)_{11}]$ (**1**) with an equimolar amount of the bidentate phosphine 1,2-bis-(diphenylphosphino)benzene (pdpp) affords the substitution product $[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-}pdpp)(CO)_6]$ (**7**) in reasonable yield (62%). Spectroscopic data suggest **7** adopts one configuration in solution, in contrast to the two configurations observed with $[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-}L)(CO)_6]$ [L = dppe (**2**), dppm (**3**)], a result ascribed to the inflexible diphosphine backbone. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; Iridium; Carbonyl; Cyclopentadienyl; Cluster; Fluxionality; Phosphine

1. Introduction

There has been considerable interest in the chemistry of mixed-metal clusters [1,2], with ligand substitution a particular focus. Our studies have involved replacing carbonyl by phosphine in mixed molybdenum/tungsten–iridium clusters [3–11], which proceeds in a stepwise fashion under mild conditions, and results in the carbonyl ligand geometry in the ground state shifting from all-terminal to one in which the three edges of one face of the tetrahedral core are spanned by bridging carbonyls; this gives three different ligation sites with respect to the $M_3(\mu\text{-}CO)_3$ plane, namely radial, axial and apical (Fig. 1). As part of these investigations, we reported the syntheses and X-ray structural characterization of $[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-}L)(CO)_6]$ [L = dppe (**2**), dppm (**3**)] [4], obtained from reaction of $[CpWIr_3(CO)_{11}]$ (**1**) with 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm), respectively. More recently, we have reported the variable-temperature ^{13}C- and ^{31}P-NMR spectra of **2** and **3**,

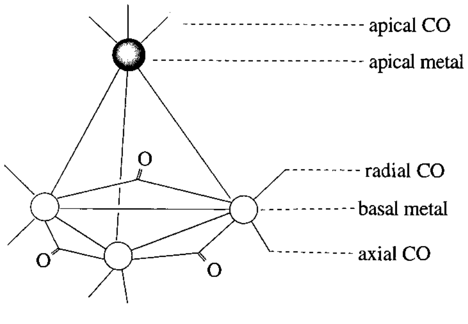

Fig. 1.

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as well as ^{13}C-NMR exchange spectroscopy (EXSY) studies which have enabled elucidation of the pathways for ligand fluxionality [9]. We have now extended these studies to explore the reactivity of **1** towards the more rigid bidentate phosphine 1,2-bis(diphenylphosphino)benzene (pdpp), and the redox-active phosphine [Fe(η^5-C$_5$H$_5$)(η^5-P$_3$C$_2$Bu$^t_2$)], and report the results herein.

[Cp$_2$W$_2$Ir$_2$(CO)$_{10}$] (**4**) is conceptually derived from **1** by replacement of an Ir(CO)$_3$ vertex with a CpW(CO)$_2$ unit. A comparison of the reactivity of **1** with **4** is also of interest. The previously reported syntheses and characterization of **2** and **3** have now been complemented by analogous studies of **4**. We report herein the reactivity of **4** towards dppe and dppm and the identification of the resulting products, together with ^{13}C-NMR EXSY studies to explore ligand scrambling.

2. Results and discussion

2.1. Syntheses and characterization of [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppm)(CO)$_5$] (5) and [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppe)(CO)$_5$] (6)

The reactions of [Cp$_2$W$_2$Ir$_2$(CO)$_{10}$] (**4**) with dppm or dppe proceed rapidly in dichloromethane at room temperature to afford the clusters [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppm)(CO)$_5$] (**5**) and [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppe)(CO)$_5$] (**6**), respectively, as the major reaction products in excellent yields (76 and 80%, respectively). The products were characterized by a combination of IR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopies, mass spectrometry and satisfactory microanalyses. Infrared spectra suggest the presence of edge-bridging carbonyl ligands in both complexes, which contrasts with the all-terminal geometry of the precursor **4**. The ^{1}H-NMR spectra contain signals assigned to cyclopentadienyl, phenyl and methylene groups for **5** and **6** in the appropriate ratios. The mass spectra of the complexes contain molecular ions and fragment ions corresponding to stepwise loss of carbonyls; isotope patterns are consistent with the presence of two iridium atoms and two tungsten atoms.

2.2. NMR studies of [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppm)(CO)$_5$] (5) and [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppe)(CO)$_5$] (6)

While the spectroscopic and analytical data above establish the molecular composition of **5** and **6**, detailed NMR studies are required to ascertain the configuration(s) adopted in solution. The ^{31}P-NMR spectrum of **5** in CD$_2$Cl$_2$ measured at 273 K shows two broad signals at -22.1 and -45.9 ppm, which coalesce at 303 K (CDCl$_3$) (Fig. 2). On cooling to 213 K (in CD$_2$Cl$_2$), the signals are resolved into two doublets (-21.9 and -45.8 ppm, $J_{\mathrm{PP}} = 48$ Hz). Similarly, the ^{13}C-NMR spectrum of **5** measured at 318 K contains a broad signal (Fig. 3), but at 213 K the fluxional processes are sufficiently slow to distinguish eight resonances of equal intensity, corresponding to one configuration in solution. We have collected extensive chemical shift data for carbonyl ligands in mixed tungsten–iridium cluster complexes [3,9–11]. The NMR chemical shift positional sequence in these mixed-metal clusters follows the trend W–Ir bridging CO (221–257 ppm) > Ir–Ir bridging CO (205–231 ppm) ≈ W terminal CO (206–228 ppm) > Ir radial CO (175–187 ppm) > Ir axial CO (158–166 ppm) ≈ Ir apical CO (159–173 ppm) [11]; it is possible to distinguish Ir–Ir bridging COs from W terminal COs due to the 15% abundant ^{183}W-coupled satellites of the latter. The presence of carbonyl resonances in the bridging carbonyl region (254.4, 245.5 ppm) excludes the possibility of an all-terminal carbonyl geometry. We have previously noted that W-bound terminal carbonyls have much larger J(CW) coupling (160–190 Hz) than W-bound bridging carbonyls (70–100 Hz). The presence of three resonances in the W-bound terminal carbonyl region with large coupling (224.0 ppm, J(CW) 191 Hz; 214.0 ppm, J(CW) 156 Hz; 211.9 ppm, J(CW) 158 Hz) excludes a carbonyl-bridged W$_2$Ir basal plane (for which only two W-bound terminal carbonyls would be observed). This configuration must therefore possess a

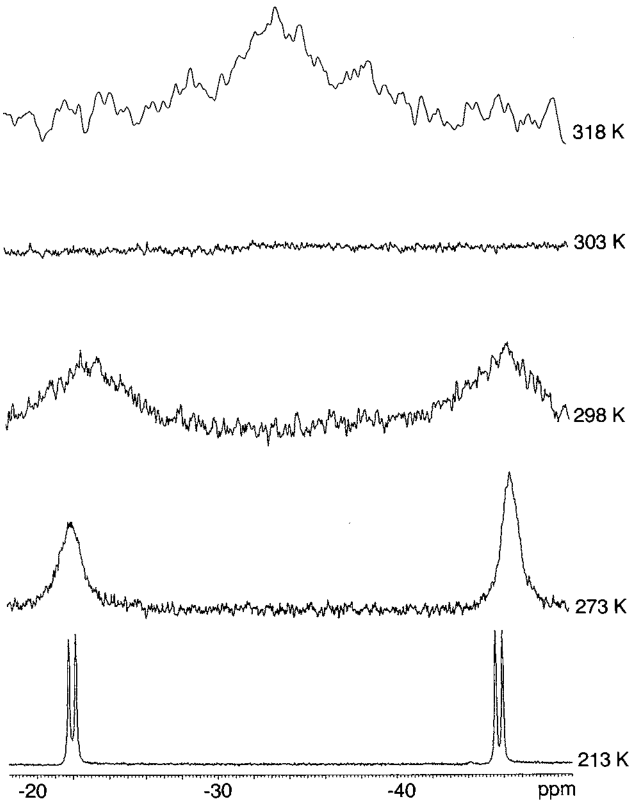

Fig. 2. Variable-temperature ^{31}P-NMR study of [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppm)(CO)$_5$] (**5**).

WIr_2 basal plane, with the diphosphine coordinated to the iridium atoms. The lack of carbonyl resonances in the Ir axial/apical CO region is consistent with the diphosphine bridging the Ir–Ir linkage and diaxially coordinated. The remaining ambiguity concerns the location of the W-bound cyclopentadienyl ligands. The apical cyclopentadienyl ligand cannot be located inclined to the $W_{ap}Ir_2$ face as this renders the phosphorus atoms equivalent, in conflict with the ^{31}P-NMR spectrum at 213 K. The apical Cp must therefore be inclined to either of the equivalent W_2Ir faces. The basal Cp can in principle be radially or axially ligated. A radial Cp would result in sterically unfavourable Cp–Cp interactions which in this case would result in the apical Cp being located over the $W_{ap}Ir_2$ face, a possibility already discounted. An axial site for this Cp ligand is therefore more likely. The configuration of **5** as assigned from NMR and steric arguments is shown in Fig. 4(a). A structural study of **5** could not be concluded satisfactorily, but confirmed the atomic connectivity and configuration assigned as above [12] . With the geometry established, it is possible to assign the ^{13}C-NMR spectrum of **5**. At 213 K, resonances are observed at 254.4 (c or d), 245.5 (d or c), 226.2 (e), 224.0 (h), 214.0 (a or b), 211.9 (b or a), 188.5 (f or g) and 187.9 (g or f) ppm, all of relative intensity 1, with the signals at 254.4, 245.5, 224.0, 214.0 and 211.9 ppm showing the expected satellite coupling to ^{183}W. In the Figures, an arbitrary assignment has been adopted for the carbonyl resonances that cannot be unambiguously assigned, to enhance clarity of presentation; a definitive assignment of the ambiguous resonances is unnecessary, as it does not affect ligand fluxionality discussion.

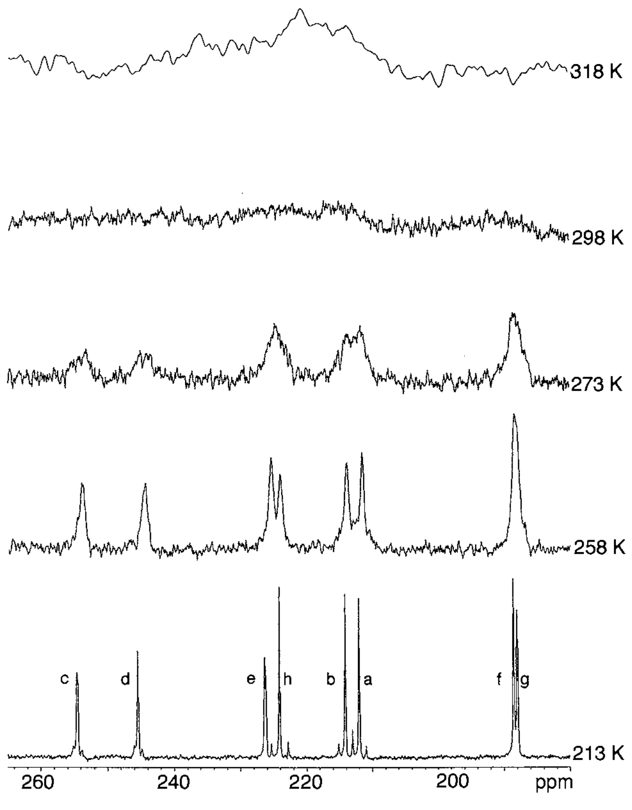

Fig. 3. Variable-temperature ^{13}C-NMR study of $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-}dppm)(CO)_5]$ (**5**).

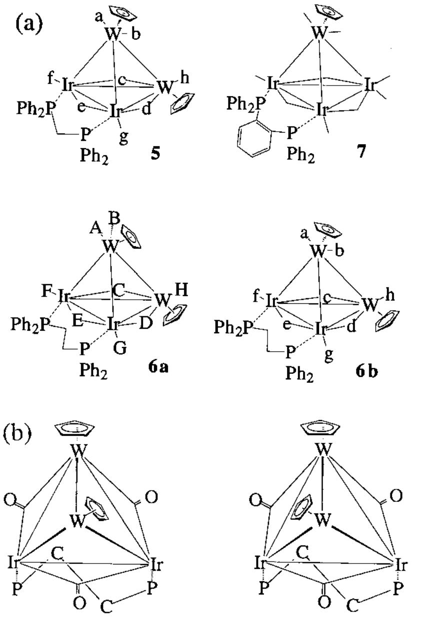

Fig. 4. Possible configurations for $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-}dppm)(CO)_5]$ (**5**), $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-}dppe)(CO)_5]$ (**6**) and $[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-}pdpp)(CO)_6]$ (**7**).

In solution, raising the temperature results in equivalence of the phosphorus atoms (Fig. 2). In principle, this could arise from either (i) a 'waggling' of the apical $CpW(CO)_2$ group, so as to place the apical cyclopentadienyl ligand over both W_2Ir faces, or (ii) complete tripodal rotation. The latter involves inclining the apical Cp towards the WIr_2 face, which configures the two Cp ligands *trans* to each other; this configuration has not thus far been observed in solution across a range of ditungsten–diiridium complexes as it is unfavourable on electronic grounds (we have previously noted the preference of Cp ligands to avoid a mutually *trans* arrangement in $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(CO)_6(L)]$ derivatives [3,11]). The existing data do not permit discrimination between these two possibilities.

It is of interest to determine whether ^{183}W chemical shifts could help distinguish between radially and axially ligated cyclopentadienyl, as this is the major uncertainty in configuration assignments of tungsten–iridium clusters. Cluster **5** provides a well-defined example of tungsten atoms occupying apical and axial Cp-ligated basal sites. A ^{183}W–^{13}C correlation experiment was used to identify the coupling (^1J) in **5** (Fig. 5). There is a considerable difference in chemical shifts between the apical tungsten atom (−1613 ppm, CD_2Cl_2) and the axial Cp-ligated tungsten atoms (−2289 ppm, CD_2Cl_2). ^{183}W data for a well-defined basal tungsten

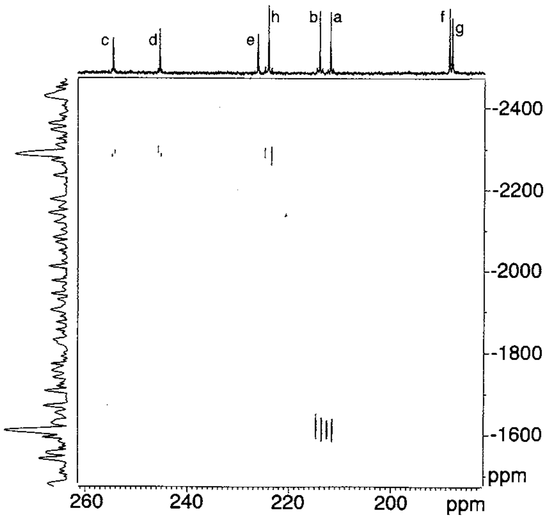

Fig. 5. ^{183}W–^{13}C correlation NMR spectroscopic study of $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-}dppm)(CO)_5]$ (**5**).

atom with a radially ligated cyclopentadienyl group are needed to ascertain whether or not tungsten NMR will be a useful technique to definitively assign the configurations of clusters of this type.

Cluster **6** is also fluxional on the NMR timescale, with scrambling commencing above 213 K in CD_2Cl_2. However, it slowly decomposes above 318 K, preventing a complete study by variable-temperature NMR. In the ^{31}P- and ^{13}C-spectra of **6** in CD_2Cl_2 (Figs. 6 and 7, respectively), all exchange processes are stopped at 213 K. At this temperature four resonances are observed in the ^{31}P-NMR spectrum corresponding to the presence of two configurations. The ^{13}C-NMR spectrum at this temperature contains 13 resonances, with the upfield resonance integrating as four coincident resonances, two from each configuration. As with **5**, the presence of carbonyl resonances in the bridging carbonyl region (254.5, 242.9 ppm major isomer; 250.5, 246.9 ppm minor isomer) excludes the possibility of an all-terminal carbonyl geometry, and the lack of carbonyl resonances in the Ir axial/apical region is consistent with a WIr_2 basal plane and diaxially bridging dppe ligands. The location of the cyclopentadienyl ligands is, as above, the remaining ambiguity but, following the arguments above, an apical Cp, axial Cp geometry is likely for both isomers, with the apical Cp inclined to the W_2Ir faces. The NMR spectra are consistent with the presence of the two isomers displayed in Fig. 4(a). The isomers **6a** and **6b** are similar, having the Cp ligand inclined to the W_2Ir faces. Isomers **6a** and **6b** differ in the conformation of the diphosphine backbone with respect to the location of the cyclopentadienyl ligands; isomer **6a** has the methylene attached to the phosphorus which is ligated to the iridium in the W_2Ir face containing the cyclopentadienyl ligand located ‘out’ rather than ‘in’, with respect to the basal plane: see Fig. 4(b).

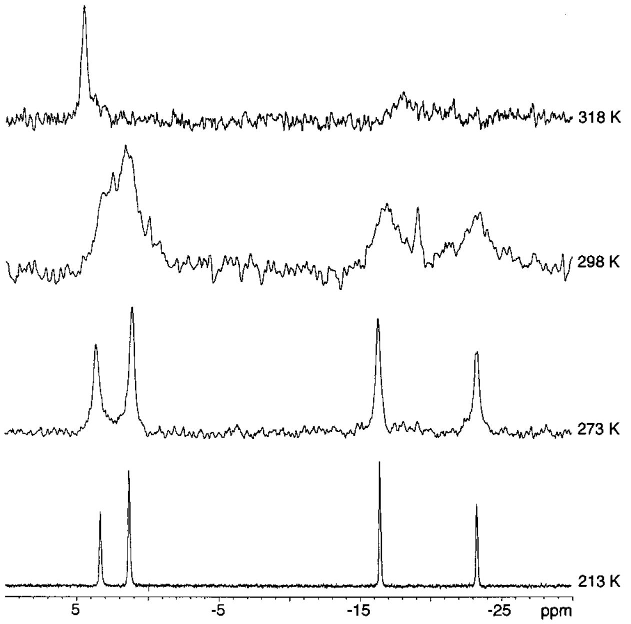

Fig. 6. Variable-temperature ^{31}P-NMR study of $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-}dppe)(CO)_5]$ (**6**).

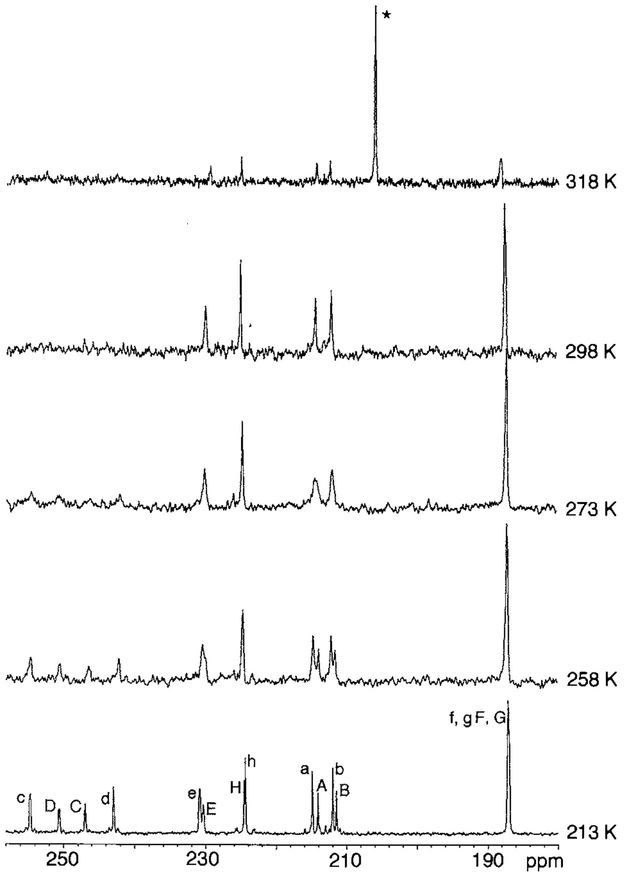

Fig. 7. Variable-temperature ^{13}C-NMR study of $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-}dppe)(CO)_5]$ (**6**).

It is possible to assign most of the resonances belonging to the two isomers in solution, with the uncertainties unimportant for the subsequent ligand scrambling discussion. Resonances for the major isomer are observed at 254.5 (d or c), 242.9 (c or d), 230.8 (e), 224.5 (h), 214.8 (a or b), 211.9 (b or a) and 186.9 (f and g) ppm, with relative intensities 1:1:1:1:1:1:2, with the signals at 254.5 (92 Hz), 242.9 (92 Hz), 224.5 (184 Hz), 214.8 (157 Hz) and 211.9 (163 Hz) ppm showing the expected satellite coupling to ^{183}W. Distinguishing between carbonyls a and b, and between c and d, was not possible based on the available information but, as above with **5**, a more precise assignment is of no importance for the discussion of the fluxionality of **6**. Resonances for the minor isomer are observed at 250.5 (C or D), 246.9 (D or C), 230.3 (E), 224.3 (H), 214.0 (A or B), 211.4 (B or A) and 186.9 (F and G) ppm, with the relative intensities 1:1:1:1:1:1:2, the specific assignments following those outlined above for the major isomer.

Ligand fluxionality commences upon warming the mixture of isomers of **6**. A ^{13}C-{^{1}H} EXSY study at 208 K is shown in Fig. 8. EXSY experiments use a NOESY sequence that allows for a 'mixing time' during which the observed nuclei may migrate to another site. The off-diagonal cross-peaks in the 2D experiment occur between the shifts of exchanging sites [13]. A contour plot of **6** reveals site exchanges at 208 K corresponding to c or d$\leftrightarrow$D or C, d or c$\leftrightarrow$C or D, a or b$\leftrightarrow$A or B and b or a$\leftrightarrow$B or A, suggestive of interconversion of **6a** and **6b**. In principle, flexing of the diphosphine backbone, a 'waggling' of the CpW(CO)$_2$ group so as to place the Cp ligand over both W$_2$Ir faces, or complete tripodal rotation of the CpW(CO)$_2$ group will all interconvert **6a** and **6b**. However, diphosphine backbone flexing has been shown to be a very high energy process in related tetrairidium clusters; for phosphines with variable oligomethylene backbone, flexing as proposed here does not become important until the backbone is lengthened to that of a butylene linkage [14]. We therefore reject diphosphine backbone flexing as the source of the low-energy process. It may also be significant that the processes rendering the phosphorus atoms equivalent occur at a similar temperature for **5** and **6** which, though not conclusive, suggests the same process is operative.

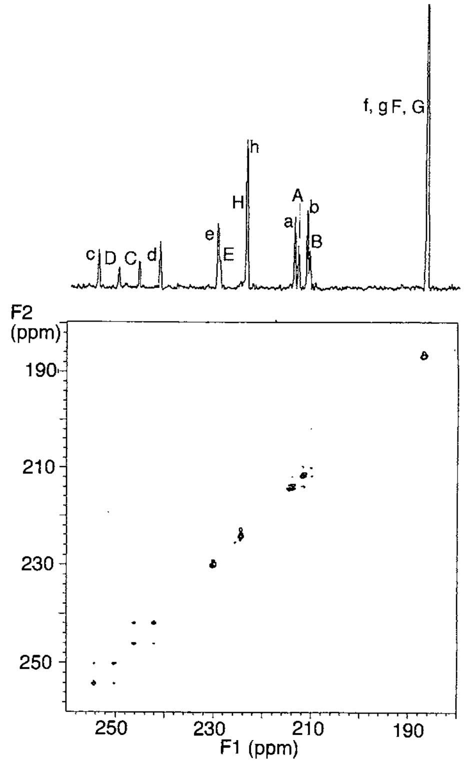

Fig. 8. ^{13}C-NMR EXSY spectrum of [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppe)(CO)$_5$] (**6**) at 208 K.

For clusters such as **5** and **6** with triaxial, apical geometries, carbonyl exchange via a 'merry-go-round' of the basal carbonyls may be expected. This process has been well documented in tetrairidium clusters with tripodal face-capping ligands [15–18]. Surprisingly, this was not observed up to the temperature at which **6** begins to decompose. The tripodal ligands in the tetrairidium derivatives are held in a fixed geometric relationship which is truly triaxial, but a bidentate ligand and monodentate ligand occupying axial sites would be expected to be displaced somewhat to minimize steric repulsion, and a consequent 'semiaxial' ligand would raise the energy barrier for the putative 'merry-go-round' process. We have structurally characterized a number of derivatives with cyclopentadienyl ligands in formally axial, but effectively semiaxial, sites [5,8]; significantly, no examples with a 'merry-go-round' fluxional process have thus far been identified. It is therefore likely that the semiaxial Cp ligation in **6** observed in the incomplete structural study [12] raises the barrier for 'merry-go-round' exchange significantly.

2.3. Reactions of [CpWIr$_3$(CO)$_{11}$] (1) with bidentate ligands

We have previously reported studies of the reactions of [CpWIr$_3$(CO)$_{11}$] (**1**) with the flexible bidentate phosphines dppe and dppm [4,9]. It was of interest to extend these studies to embrace both a rigid diphosphine and a redox-active phosphine. The reaction of [CpWIr$_3$(CO)$_{11}$] (**1**) with the bidentate phosphine 1,2-bis(diphenylphosphino)benzene (pdpp) proceeds in dichloromethane at room temperature to afford the cluster [CpWIr$_3$(μ-CO)$_3$(μ-pdpp)(CO)$_6$] (**7**) as the sole reaction product in reasonable yield (62%). The cluster was characterized by a combination of IR, ^{1}H- and ^{31}P-NMR spectroscopies, mass spectrometry and satisfactory microanalyses. The infrared spectrum suggests the presence of edge-bridging carbonyl ligands. The ^{1}H-NMR spectrum contains signals assigned to Cp and Ph groups in the appropriate ratio. The FAB mass spectrum contains a molecular ion followed by sequential loss of eight carbonyls. The above data are consistent with the formulation [CpWIr$_3$(μ-CO)$_3$(μ-pdpp)-(CO)$_6$], a composition analogous to those of the previously reported bidentate phosphine adducts [CpWIr$_3$(μ-CO)$_3$(μ-L)(CO)$_6$] (L = dppm, dppe, dppa) [4] . The variable-temperature ^{31}P-NMR spectra of **7** were investigated, as the rigid backbone of the bis(1,2-diphenylphosphino)benzene ligand may modify the diaxially ligating bidentate ligand coordination geometry from that observed with **2** and **3**. The ^{31}P-NMR spectrum of **7** at room temperature reveals the presence of a broad signal at 15.0 ppm. Signals at 22.2 and 6.1 ppm, ratio 1:1, are resolved on cooling to 181 K. Cluster **7** is therefore assigned a geometry shown in Fig. 4, with the Cp ligand inclined over the WIr$_2$ faces remote from the diphosphine. Cluster **7** differs in behaviour from the related clusters [CpWIr$_3$(μ-CO)$_3$(μ-L)(CO)$_6$] [L = dppe (**2**), dppm (**3**)], for which the configuration with the Cp ligand inclined over the WIr$_2$ face including the diphosphine was also observed, a result indicating that the diphosphine ligand can control conformational preference. Coalescence of the phosphorus resonances observed on increasing temperature is, as with **5** and **6**, presumably due to either CpW(CO)$_2$ 'waggling' or complete tripodal rotation.

Introduction of a redox-active ligand onto a tungsten–triiridium cluster is also of interest. Reaction of [Ir$_4$(CO)$_{11}$Br]$^-$ with a stoichiometric amount of the phosphole complex [Fe(η^5-C$_5$H$_5$)(η^5-P$_3$C$_2$Bu$^t_2$] affords [Ir$_4$(CO)$_{11}$(η^1-[Fe(η^5-C$_5$H$_5$)(η^5-P$_3$C$_2$Bu$^t_2$])], which loses CO to give [Ir$_4$(μ-CO)$_3$(μ-η^2-[Fe(η^5-C$_5$H$_5$)(η^5-P$_3$C$_2$Bu$^t_2$])(CO)$_7$] [19] . Similar attempts at reacting the isolobal [CpWIr$_3$(CO)$_{11}$] (**1**) with the phosphole complex at room temperature were unsuccessful, and heating **1** and the phosphole complex in refluxing thf caused decomposition of the cluster.

3. Conclusions

Extending bidentate phosphine chemistry of [CpWIr$_3$(CO)$_{11}$] (**1**) from the previously reported dppe and dppm adducts to embrace pdpp results in a product of analogous composition [CpWIr$_3$(CO)$_9$(L$_2$)], but one in which the configuration distribution has changed. The bidentate phosphine adducts (**5** and **6**) of the isolobally-related ditungsten–diiridium cluster **4** are accessible in good yield. Both [CpWIr$_3$(μ-CO)$_3$(μ-dppm)(CO)$_6$] (**3**) and [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppm)(CO)$_5$] (**5**) exist in one conformation with diaxially ligated dppm, but only **3** undergoes carbonyl exchange by a merry-go-round mechanism. Both [CpWIr$_3$(μ-CO)$_3$(μ-dppe)(CO)$_6$] (**2**) and [Cp$_2$W$_2$Ir$_2$(μ-CO)$_3$(μ-dppe)(CO)$_5$] (**6**) exist in two conformations corresponding to puckering of the bidentate phosphine ethylene bridge with respect to the location of the apical cyclopentadienyl group, but only the former undergoes carbonyl exchange by a merry-go-round process. All five clusters **2**, **3**, **5**, **6** and **7** undergo a fluxional process corresponding to a 'waggling' or complete tripodal rotation of the apical CpW(CO)$_2$ group.

4. Experimental

All reactions were performed under an atmosphere of dry nitrogen (high-purity grade, CIG), although no special precautions were taken to exclude air during work-up. The reaction solvent dichloromethane was dried over CaH$_2$; all other solvents were reagent grade, and used as received. Petroleum ether refers to a fraction of boiling point range 60–80°C. The products of thin-layer chromatography were separated on 20 × 20 cm^2 glass plates coated with Merck GF$_{254}$ silica gel (0.5 mm). [Cp$_2$W$_2$Ir$_2$(CO)$_{10}$] (**4**) was prepared by the published procedure [20]. Dppe (Aldrich), dppm (Aldrich) and pdpp (Strem) were purchased commercially and used as received. [Fe(η^5-C$_5$H$_5$)(η^5-P$_3$C$_2$Bu$^t_2$] was obtained from Dr M. H. Benvenutti and Professor J. Nixon (University of Sussex, UK). Samples required for fluxionality studies were prepared from ^{13}CO-enriched (95%) **4**, the latter obtained by stirring a solution of the complex in CH$_2$Cl$_2$ under 1.2 atm ^{13}CO at 25 °C for 60 h.

Infrared spectra were recorded on a Perkin–Elmer System 2000 Fourier transform spectrophotometer with a solution cell employing NaCl windows. ^{1}H-NMR spectra were recorded on a Varian Gemini 300 spectrometer (300 MHz). The ^{13}C- and ^{31}P-NMR spectra were recorded on a Varian VXR300S spectrometer (^{13}C-spectra at 75 MHz, ^{31}P-spectra at 121 MHz) and were proton decoupled. The ^{183}W–^{13}C correlation experiment was recorded on a Bruker DMX600 (^{183}W at 24.9 MHz, ^{13}C at 150.9 MHz). Spectra were run in CD$_2$Cl$_2$, CDCl$_3$ or acetone-*d*$_6$ (Cambridge Isotope Laboratories); chemical shifts in ppm are referenced to internal residual solvent for ^{1}H- and ^{13}C-NMR spectra (^{1}H, CHCl$_3$ = 7.25 ppm; ^{13}C, CD$_2$Cl$_2$ = 53.8 ppm, acetone-*d*$_6$ = 29.8 ppm, CDCl$_3$ = 77.0 ppm) and external 85% H$_3$PO$_4$ (0.0 ppm) for ^{31}P-NMR spectra. ^{183}W shifts were measured relative to hypothetical external WF$_6$ (WF$_6$ = 0 ppm) using Ξ = 4.161733 using the formula X nucleus reference frequency = Ξ × ^{1}H zero ppm frequency/100 [21]. The ^{13}C-{^{1}H} EXSY experiments were carried out using the standard NOESY pulse sequence with the mixing time set to 0.05 s. The ^{13}C-NMR spectra were recorded with a recycle delay of 3–5 × the longest T_1. 2D-NMR spectra were recorded utilizing a recycle delay of 1–3 × the longest T_1. T_1 measurements were performed using the inversion-recovery technique.

Mass spectra were obtained at the Australian National University on a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, matrix 3-nitrobenzyl alcohol). Peaks were recorded as m/z based on ^{183}W assignments and are reported in the form: m/z (assignment, relative intensity). Elemental microanalyses were performed by the Microanalysis Service Unit in the Research School of Chemistry, Australian National University.

4.1. Reaction of $[Cp_2W_2Ir_2(CO)_{10}]$ with dppm

A red solution of $[Cp_2W_2Ir_2(CO)_{10}]$ (20.0 mg, 0.0172 mmol) and dppm (6.6 mg, 0.0172 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature (r.t.) for 20 h. The dark brown solution was then evaporated to dryness. The resultant brown residue was dissolved in CH_2Cl_2 (ca. 1 ml) and chromatographed (3:1 CH_2Cl_2–petroleum ether eluant), affording two bands. The contents of the first band were identified as **4** (2.1 mg, 11%). Crystallization of the contents of the second band, R_f 0.65, from CH_2Cl_2/MeOH afforded dark brown crystals of $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-dppm})(CO)_5]$ (**5**) (19.4 mg, 76%). Analytical data for **5**: IR ($c\text{-}C_6H_{12}$) 2003vs, 1990s, 1979s, 1971m, 1960s, 1952m, 1911m, 1870w cm^{-1}; ^1H-NMR ($CDCl_3$, 298 K) δ 7.54–7.39 (m, 20H, Ph), 4.56 [s (br), 10H, C_5H_5], 3.48 [s (br), 2H, CH_2]; ^{13}C-NMR (CD_2Cl_2, 213 K) **5** 254.4 [c or d; s, 85%, d, 15% $J(WC) = 84$ Hz; 1], 245.5 [d or c; s, 85%, d, 15%, $J(WC) = 84$ Hz; 1], 226.2 (e; s; 1), 224.0 [h, s, 85%, d, 15%, $J(WC) = 191$ Hz; 1], 214.0 [a or b; s, 85%, d, 15%, $J(WC) = 156$ Hz; 1], 211.9 [b or a; s, 85%, d, 15%, $J(WC) = 158$ Hz; 1], 188.5 (f or g; s; 1), 187.9 (g or f; s; 1) ppm. ^{13}C-NMR (CD_2Cl_2, 213 K) δ 133.2–127.9 (Ph), 88.7 (C_5H_5), 87.6 (C_5H_5) ppm, other signals not observed; ^{31}P-NMR (CD_2Cl_2, 213 K) δ −21.9 (d, $J_{PP} = 48$ Hz, 1P), −45.8 (d, $J_{PP} = 48$ Hz, 1P); FAB MS 1491 ($[M]^+$, 33), 1463 ($[M–CO]^+$, 22), 1435 ($[M–2CO]^+$, 35), 1407 ($[M–3CO]^+$, 100), 1379 ($[M–4CO]^+$, 47), 1351 ($[M–5CO]^+$, 92), 1323 ($[M–6CO]^+$, 36). Anal. Calc.: C 34.64, H 2.16%. Found: C 34.89, H 2.26%.

4.2. Reaction of $[Cp_2W_2Ir_2(CO)_{10}]$ with dppe

A red solution of $[Cp_2W_2Ir_2(CO)_{10}]$ (20.0 mg, 0.0172 mmol) and dppe (6.9 mg, 0.0173 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 20 h. The dark brown solution was then evaporated to dryness. The resultant brown residue was dissolved in CH_2Cl_2 (ca. 1 ml) and chromatographed (4:1 CH_2Cl_2–petroleum ether eluant), affording two bands. The contents of the first band were identified as **4** (1.6 mg, 8%). Crystallization of the contents of the second band, R_f 0.60, from CH_2Cl_2/MeOH afforded dark brown crystals of $[Cp_2W_2Ir_2(\mu\text{-}CO)_3(\mu\text{-dppe})(CO)_5]$ (**6**) (20.3 mg, 80%). Analytical data for **6**: IR ($c\text{-}C_6H_{12}$) 2007s, 2002vs, 1992w, 1978s, 1973s, 1954m, 1916s, 1859m cm^{-1}; ^1H-NMR ($CDCl_3$, 298 K) δ 7.53–7.38 (m, 20H, Ph), 4.73 [s (br), 10H, C_5H_5], 3.98 [s (br), 4H, CH_2]; ^{13}C-NMR (CD_2Cl_2, 213 K) **6a** 254.5 [d or c; s, 85%, d, 15%, $J(WC) = 92$ Hz; 0.67], 242.9 [c or d; s, 85%, d, 15%, $J(WC) = 92$ Hz; 0.67], 230.8 (e; s; 0.67), 224.5 [h; s, 85%, d, 15%, $J(WC) = 184$ Hz; 0.67], 214.8 [a or b; s, 85%, d, 15%, $J(WC) = 157$ Hz; 0.67], 211.9 [b or a; s, 85%, d, 15%, $J(WC) = 163$ Hz; 0.67], 186.9 (f and g; s; 1.34) ppm. **6b** 250.5 [C or D; s, 85%, d, 15%, $J(WC) = 92$ Hz; 0.33], 246.9 [D or C; s, 85%, d, 15%, $J(WC) = 92$ Hz; 0.33], 230.3 (E; s; 0.33], 224.3 [H; s, 85%, d, 15%, $J(WC) = 184$ Hz; 0.33], 214.0 [A or B; s, 85%, d, 15%, $J(WC) = 159$ Hz; 0.33], 211.4 [B or A; s, 85%, d, 15%, $J(WC) = 154$ Hz; 0.33], 186.9 (F and G; s; 0.66) ppm. ^{13}C-NMR (CD_2Cl_2, 213 K) δ 131.3–128.5 (Ph), 88.7 (C_5H_5), 88.4 (C_5H_5), 87.9 (C_5H_5), 87.6 (C_5H_5) ppm, other signals not observed; ^{31}P-NMR (CD_2Cl_2, 213 K) δ 3.3 (s, 0.33P), 1.3 (s, 0.67P), −16.4 (s, 0.67P), −23.3 (s, 0.33P); FAB MS 1505 ($[M]^+$, 45), 1477 ($[M–CO]^+$, 13), 1449 ($[M–2CO]^+$, 20), 1421 ($[M–3CO]^+$, 100), 1393 ($[M–4CO]^+$, 28), 1365 ($[M–5CO]^+$, 60), 1337 ($[M–6CO]^+$, 45), 1309 ($[M–7CO]^+$, 50). Anal. Calc.: C 35.12, H 2.28%. Found: C 34.72, H 1.91%.

4.3. Reaction of $[CpWIr_3(CO)_{11}]$ (**1**) with pddp

A red solution of $[CpWIr_3(CO)_{11}]$ (20.0 mg, 0.0176 mmol) and pdpp (7.9 mg, 0.0177 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 20 h. The dark brown solution was then evaporated to dryness. The resultant brown residue was dissolved in CH_2Cl_2 (ca. 1 ml) and chromatographed (3:2 CH_2Cl_2–petroleum ether eluant), affording two bands. The contents of the first band were identified as **1** (1.5 mg, 7.5%) by solution IR spectroscopy. Crystallization of the contents of the second band, R_f 0.51, from CH_2Cl_2/MeOH afforded orange crystals of $[CpWIr_3(\mu\text{-}CO)_3(\mu\text{-pdpp})(CO)_6]$, **7** (16.6 mg, 62%). Analytical data for **7**: IR ($c\text{-}C_6H_{12}$) 2062w, 2054w, 2047vs, 2023vs, 1987s, 1984s, 1961w, 1921w, 1811w cm^{-1}; ^1H-NMR ($CDCl_3$) δ 7.62–7.27 (m, 24H, Ph), 4.99 (s, 5H, C_5H_5); ^{31}P-NMR ($CDCl_3$, 181 K) δ 22.2 (s, 1P), 6.1 (s, 1P); MS 1524 ($[M]^+$, 15), 1496 ($[M–CO]^+$, 40), 1468 ($[M–2CO]^+$, 14), 1440 ($[M–3CO]^+$, 100), 1412 ($[M–4CO]^+$, 18), 1384 ($[M–5CO]^+$, 28), 1356 ($[M–6CO]^+$, 57), 1328 ($[M–7CO]^+$, 40), 1300 ($[M–8CO]^+$, 7). Anal. Calc: C 34.15, H 1.93. Found: C 34.72, H 2.01%.

4.4. Attempted reactions of $[CpWIr_3(CO)_{11}]$ (**1**) with $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$

4.4.1. Attempt I

A dark orange solution of $[CpWIr_3(CO)_{11}]$ (20.0 mg, 0.0176 mmol) and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ (6.2 mg, 0.0176 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 24 h. No apparent reaction was observed. The solution was slowly heated and refluxed for 16 h. An IR spectrum indicated no reaction had occurred.

4.4.2. Attempt II

A dark orange solution of $[CpWIr_3(CO)_{11}]$ (20.0 mg, 0.0176 mmol) and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$ (10.0 mg, 0.0284 mmol) in thf (20 ml) was refluxed for 20 h. Monitoring the reaction by IR showed a decrease in the intensity of the ν(CO) bands, but with no other changes in the pattern. Chromatography yielded no tractable products.

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References

[1] R.D. Adams, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 10, Pergamon, Oxford, UK, 1995.

[2] S.M. Waterman, N.T. Lucas, M.G. Humphrey, Adv. Organomet. Chem. (1999) in press.

[3] S.M. Waterman, M.G. Humphrey, D.C.R. Hockless, J. Organomet. Chem. 582 (1999) 310.

[4] J. Lee, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, Organometallics 12 (1993) 3468.

[5] S.M. Waterman, M.G. Humphrey, V.-A. Tolhurst, B.W. Skelton, A.H. White, Organometallics 15 (1996) 934.

[6] N.T. Lucas, I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, M.P.S. Perera, M.L. Williams, J. Organomet Chem. 540 (1997) 147.

[7] N.T. Lucas, M.G. Humphrey, P.C. Healy, M.L. Williams, J. Organomet. Chem. 545 (1997) 519.

[8] S.M. Waterman, M.G. Humphrey, D.C.R. Hockless, J. Organomet. Chem. 555 (1998) 25.

[9] S.M. Waterman, M.G. Humphrey, D.C.R. Hockless, J. Organomet. Chem. 565 (1998) 81.

[10] S.M. Waterman, M.G. Humphrey, Organometallics 18 (1999) 3116.

[11] S.M. Waterman, J. Lee, M.G. Humphrey, G.E. Ball, D.C.R. Hockless, Organometallics 18 (1999) 2440.

[12] B.W. Skelton, A.H. White (1998) unpublished results.

[13] A.E. Derome, Modern NMR Techniques for Chemistry Research, Pergamon, Oxford, 1987, p. 239.

[14] A. Strawczynski, R. Ros, R. Roulet, D. Braga, C. Gradella, F. Grepioni, Inorg. Chim. Acta 170 (1990) 17.

[15] A. Strawczynski, C. Hall, G. Bondietti, R. Ros, R. Roulet, Helv. Chim. Acta 77 (1994) 754.

[16] G. Suardi, A. Strawczynski, R. Ros, R. Roulet, Helv. Chim. Acta 73 (1990) 154.

[17] A. Orlandi, U. Frey, G. Suardi, A.E. Merbach, R. Roulet, Inorg. Chem. 31 (1992) 1304.

[18] J.A. Clucas, M.M. Harding, B.S. Nicholls, A.K. Smith, J. Chem. Soc. Chem. Commun. (1984) 319.

[19] M.H.A. Benvenutti, P.B. Hitchcock, J.F. Nixon, M.D. Vargas, Chem. Commun. (Cambridge) (1996) 441.

[20] J.R. Shapley, S.J. Hardwick, D.S. Foose, G.D. Stucky, J. Am. Chem. Soc. 103 (1981) 7383.

[21] R.K. Harris, Nuclear Magnetic Resonance Spectroscopy: a Physicochemical View, Pitman, London, 1983, p. 230.