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Bis(diphosphino)methanide and hydride derivatives of $Ir_4(CO)_{12}$

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The reaction of $[Ir_4(CO)_{10}(\mu\text{-}(Ph_2P)_2CH_2)]$ with dried KOH forms $[Ir_4(CO)_{10}(\mu\text{-}(Ph_2P)_2CH)]^-$ which subsequently converts into $[Ir_4(CO)_9(\mu_3\text{-}(Ph_2P)_2CH)]^-$, a rare example of an Ir cluster with an Ir–C bond (average 2.274(8) Å). The same reaction with the weaker base 1,8-diazobicyclo[5.4.0]undec-7-ene or with K_2CO_3 in wet CH_2Cl_2 under CO affords the anion $[HIr_4(CO)_9(\mu\text{-}(Ph_2P)_2CH_2)]^-$, a hydride-cluster with an unusually long Ir–H distance (2.08(6) Å at 90 K). Intramolecular CO scrambling is observed in CD_2Cl_2 solution above 200 K, preserving the terminal–axial position of the hydride ligand.

Introduction

The hydrido-derivatives of $Ir_4(CO)_{12}$ reported to date are the anions $[HIr_4(CO)_{11}]^-$,[1] and $[H_2Ir_4(CO)_{10}]^{2-}$,[2] as well as the neutral orthometalled species $[HIr_4(CO)_7(Ph_2PCH{=}CHPPh_2)(PhC_6H_4PCH{=}CHPPh_2)]$.[3] The examples of clusters containing Ir–C(alkyl) bonds are $[Ir_4(CO)_{11}(CH_2CO_2CH_3)]^-$ and $[Ir_4(CO)_{10}(CH_2CO_2CH_3)_2]^{2-}$.[4] Clusters containing Ir=C bonds are the carbene complexes $[Ir_4(CO)_{12-n}(\overline{COCH_2CH_2O})_n]$ (n = 1–3) derived from the nucleophilic attack of the coordinated CO ligands of $Ir_4(CO)_{12}$ by oxirane.[5] The classical organometallic reactions used for the preparation of metal alkyls failed to give any well defined derivatives from $Ir_4(CO)_{12}$. An idea for obtaining new clusters with Ir–C bonds is therefore to deprotonate a methylene group which is part of a bidentate ligand already bonded to Ir and form an Ir–C bond by intramolecular displacement of carbon monoxide.

The bidentate ligand bis(diphenylphosphino)methane (dppm) has widely been used in coordination and organometallic chemistry.[6] Its deprotonated form, bis(diphenylphosphino)methanide, $[(Ph_2P)_2CH)]^-$, has also received some attention because of its ability to act as a two-, four- or six-electron donor ligand, being a versatile building block for the construction of heterometallic species.[7] We report here a simple way to obtain a new class of methanide complexes derived from deprotonation of the dppm ligand of $[Ir_4(CO)_{10}(\mu\text{-dppm})]$[8] or alternatively, depending on the choice of the base, a way to obtain new hydrido derivatives of Ir_4 clusters.

Results and discussion

The reaction of $[Ir_4(CO)_{10}(\mu\text{-dppm})]$ (**1**) with two equivalents of bis(triphenyphosphoranylidene)ammonium chloride (PPNCl) and an excess of KOH (dry powder) in CH_2Cl_2 at −20 °C gives rapidly a first product which could only be observed in solution, and was identified as $[Ir_4(CO)_{10}(\mu\text{-}(Ph_2P)_2CH)]^-$ on the basis of its NMR characteristics (see Experimental section). After *ca.* 30 minutes, intramolecular coordination of the methanide moiety is completed, affording the yellow product $[PPN][Ir_4(CO)_9(\mu_3\text{-}(Ph_2P)_2CH)]$ (**2**) (yield 76%) by the overall equation:

$$[Ir_4(CO)_{10}(\mu\text{-dppm})] + 2\,KOH + PPNCl \longrightarrow [PPN][Ir_4(CO)_9(\mu_3\text{-}(Ph_2P)_2CH)] + KCl + KHCO_3$$

The same reaction, but with a large excess of the weaker base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (or more slowly with K_2CO_3) in wet CH_2Cl_2 under CO gave orange crystals of the hydrido-cluster $[PPN][HIr_4(CO)_9(\mu\text{-dppm})]$ (**3**) (yield 86%) by the overall reaction:

$$[Ir_4(CO)_{10}(\mu\text{-dppm})] + DBU + H_2O + PPNCl \longrightarrow [PPN][HIr_4(CO)_9(\mu\text{-dppm})] + CO_2 + [DBUH]Cl$$

The crystal structures of **2** and **3** were determined by X-ray analysis (see below).

Crystal structures of $[PPN][Ir_4(CO)_9(\mu_3\text{-}(Ph_2P)_2CH)]\cdot CH_2Cl_2$ and $[PPN][HIr_4(CO)_9(\mu\text{-dppm})]$

The structure of the anionic part of **2** and the labelling scheme are shown in Fig. 1. Some relevant interatomic distances are reported in Table 1. Crystallographic data for **2**·CH_2Cl_2 and **3** are reported in Table 2.

The anion of **2** has approximate C_s symmetry with all terminal CO's. The $[(Ph_2P)_2CH)]^-$ ligand is face bridging with the plane P(3)–C(32)–P(2) eclipsed relative to the plane Ir(4)–Ir(2)–Ir(3). The mean value of the Ir–Ir distances (2.700(1) Å) is signif-

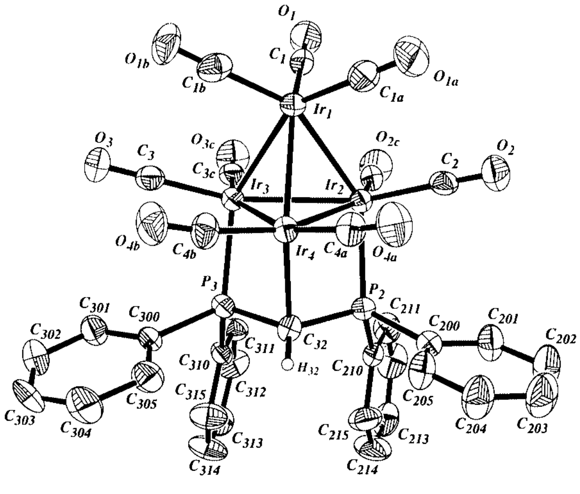

Fig. 1 ORTEP[15] representation at the 30% probability level of $[Ir_4(CO)_9(\mu_3\text{-}(Ph_2P)_2CH)]^-$.

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Table 1 Bond lengths [Å] for **2** and **3**

	2	**3**
Ir(1)–C(1)	1.864(12)	1.889(6)
Ir(1)–C(1A)	1.879(14)	1.888(7)
Ir(1)–C(1B)	1.917(13)	1.889(7)
Ir(1)–Ir(2)	2.7066(5)	2.7448(3)
Ir(1)–Ir(3)	2.7080(5)	2.7598(4)
Ir(1)–Ir(4)	2.7179(6)	2.7860(4)
Ir(2)–C(2C)	1.892(13)	
Ir(2)–C(2)	1.899(12)	1.856(7)
Ir(2)–C(23)		2.053(6)
Ir(2)–C(24)		2.176(7)
Ir(2)–P(2)	2.287(2)	2.275(2)
Ir(2)–Ir(4)	2.6703(6)	2.7426(4)
Ir(2)–Ir(3)	2.7359(5)	2.6847(3)
Ir(3)–C(3)	1.872(12)	1.859(7)
Ir(3)–C(3C)	1.873(12)	
Ir(3)–C(23)		2.103(6)
Ir(3)–C(34)		2.151(7)
Ir(3)–P(3)	2.299(2)	2.291(2)
Ir(3)–Ir(4)	2.6620(6)	2.7276(4)
Ir(4)–H(4)		2.08(6)
Ir(4)–C(4)		1.855(7)
Ir(4)–C(4B)	1.869(12)	
Ir(4)–C(4A)	1.871(12)	
Ir(4)–C(24)		2.046(7)
Ir(4)–C(34)		2.064(6)
Ir(4)–C(32)	2.274(8)	
Ir(4)–P(3)	2.931(2)	
Ir(4)–P(2)	2.956(2)	
O(1)–C(1)	1.164(12)	1.168(8)
O(1A)–C(1A)	1.178(13)	1.152(8)
O(1B)–C(1B)	1.141(12)	1.131(8)
O(2)–C(2)	1.137(12)	1.170(8)
O(2C)–C(2C)	1.147(12)	
O(23)–C(23)		1.173(7)
O(24)–C(24)		1.167(8)
O(3)–C(3)	1.157(12)	1.160(8)
O(3C)–C(3C)	1.168(12)	
O(34)–C(34)		1.172(8)
O(4)–C(4)		1.153(9)
O(4A)–C(4A)	1.150(12)	
O(4B)–C(4B)	1.142(11)	
P(2)–C(32)	1.786(9)	1.843(6)
C(32)–H(32A)		0.97
C(32)–H(32B)		0.97
P(2)–C(200)	1.818(10)	1.829(6)
P(2)–C(210)	1.840(10)	1.817(6)
P(3)–C(32)	1.792(9)	1.829(6)
P(3)–C(310)	1.822(9)	1.836(6)
P(3)–C(300)	1.841(9)	1.841(6)
C(32)–H(32)	1.01	

Table 2 Crystallographic data for compounds **2**·CH_2Cl_2 and **3**

	2·CH_2Cl_2	**3**
Formula	$C_{71}H_{53}Cl_2Ir_4NO_9P_4$	$C_{70}H_{53}Ir_4NO_9P_4$
M	2027.72	1944.81
Crystal size/mm		0.5 × 0.4 × 0.3
T/K	293(2)	90(3)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	12.6694(8)	10.2149(8)
b/Å	26.479(2)	18.4724(13)
c/Å	20.7990(13)	33.772(3)
β/°	94.0210(10)	94.578(9)
V/Å^3	6960.4(8)	6352.3(8)
Z	4	4
D_c/g cm^{-3}	1.935	2.034
F(000)	3840	3680
μ/mm^{-1}	7.848	8.259
$2\theta_{max}$/°	51.0	51.88
Reflections collected/unique	28587/11402	49085/12165
Variables	821	797
R_1	0.0554	0.0412
wR_2	0.823	0.838

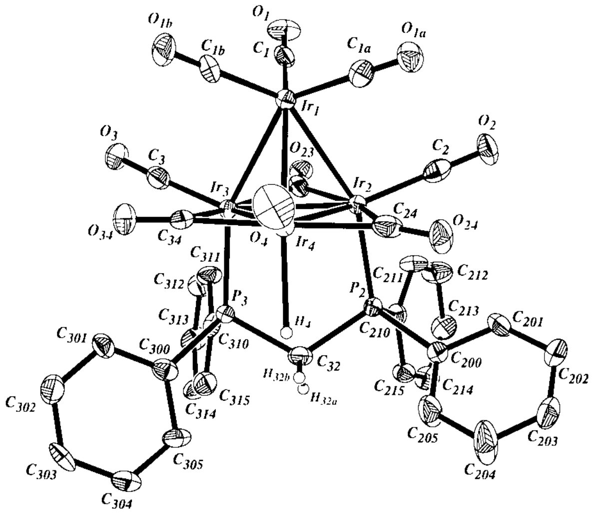

Fig. 2 ORTEP representation at the 50% probability level of $[Ir_4(CO)_9(\mu\text{-dppm})]^-$.

icantly shorter than that found for $[Ir_4(CO)_7(\mu\text{-CO})_3(\mu\text{-}(Ph_2P)_2CHMe)]$ (**1′**) (2.729(1) Å).[9] A DFT calculation on $Rh_4(CO)_{12}$ and $IrRh_3(CO)_{12}$ has shown that unbridged metal–metal bonds are shorter than CO-bridged ones.[10] This conclusion seems to be also valid for the present, substituted clusters. The metal tetrahedron is not regular, as the three Ir–Ir distances of the Ir(2)–Ir(3)–Ir(4) face bearing the $[(Ph_2P)_2CH)]^-$ ligand differ by more than 0.06 Å, the longest being that between the Ir-atoms bearing the P-atoms and the shortest being the other two bonds of that face. All the bond distances (and bond angles) of the Ir_2P_2C ring are smaller than the corresponding ones in **1′**, probably denoting the better donor properties of the deprotonated ligand relative to the neutral dppm ligand. As expected, the average Ir–C distance (2.274(8) Å) is longer than the Ir=C(carbene) distances of 1.94–2.06 Å in $[Ir_4(CO)_{12-n}(COCH_2CH_2O)_n]$ (n = 1–3),[5] but also longer than the Ir–C distances found in $[Ir_4(CO)_{11}(CH_2CO_2Me)]^-$ and $[Ir_4(CO)_{10}(CH_2CO_2Me)_2]^{2-}$ (2.15–2.19 Å).[4]

The anionic structure of **3** and the labelling scheme are shown in Fig. 2. Some relevant interatomic distances are reported in Table 1. The anion has approximate C_s symmetry with the mirror plane defined by atoms Ir(1) and Ir(4), and the methylene group. Three CO's are edge-bridging, defining the basal face Ir(2)–Ir(3)–Ir(4). The P-atoms of the dppm ligand are in axial positions relative to the basal face. The comparison between corresponding bond distances of **3** and **2** gives the same trends as that described above between **1'** and **2**. Due to the presence of 3 edge-bridging CO's, the mean value of the Ir–Ir distance (2.769(3) Å) is longer than that of **2**. Likewise, the interatomic distances in the Ir_2P_2C ring (mean Ir–P 2.283, mean P–C 1.836 Å) in **3** are longer than those in **2** (2.293 and 1.789 Å, respectively). The value for the Ir–H distance (2.08(6) Å at 90 K) is unusually large, both relative to the range found in monometallic complexes (1.5–1.9 Å)[11] and to the calculated range (1.54–1.60 Å).[12] The temperature was low enough to locate this H–atom during the refinement down to 4.16%. However, a neutron diffraction experiment will be undertaken to verify this value.

Behaviour of clusters 2 and 3 in solution

Complex **2** is thermally stable in CH_2Cl_2 solution up to room temperature. It reverts back to **1** upon adding 1 equivalent of HCl under CO. It converts to **3** upon adding excess DBU and 1 equivalent of H_2O under CO, or to the deuterido-analog of **3** when replacing H_2O by D_2O.

Its geometry in solution is similar to that found in the solid, as deduced from IR, ^1H-, ^{31}P- and ^{13}C-NMR spectroscopy (see Experimental section). A 2D–COSY spectrum of an enriched

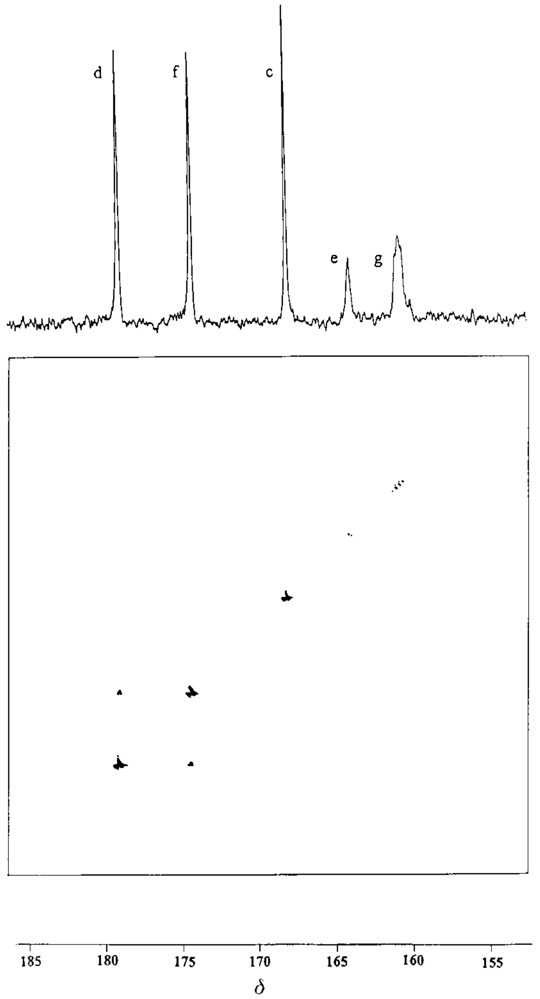

Fig. 3 2D-COSY spectrum of **2** in CD_2Cl_2 at 193 K (see Fig. 4 for the carbonyl labelling scheme).

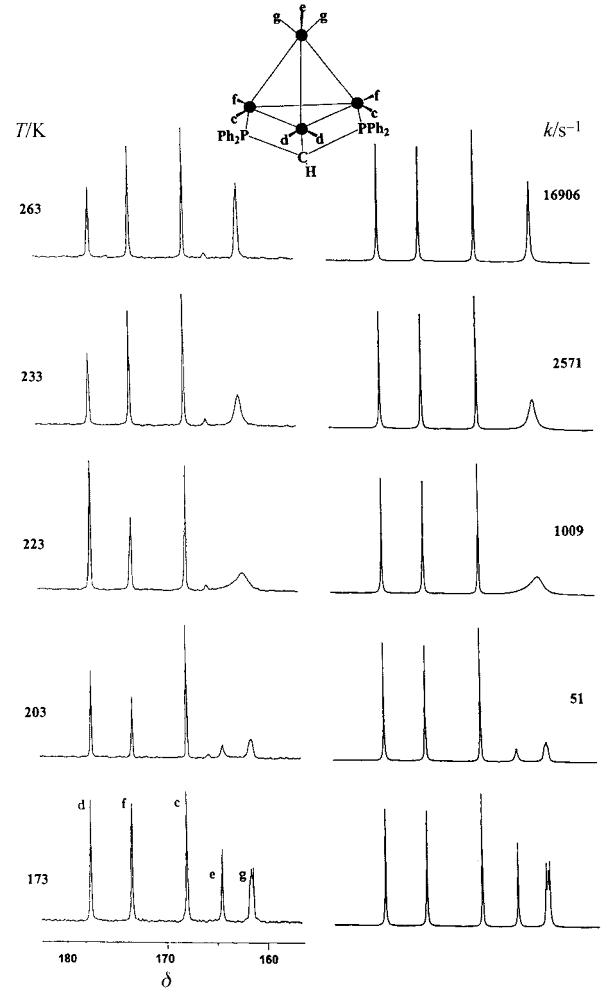

Fig. 4 Experimental (left) and calculated (right) VT ^{13}C-NMR spectra of **2** in CD_2Cl_2.

sample of **2** in ^{13}CO (*ca.* 30%) at 193 K (Fig. 3) shows the pseudo-*trans* coupling between carbonyls d and f, the signal at 177.2 ppm being due to carbonyls d closest to the CH^- group, and shows also that the apical CO's e and g (respectively at 163.4 and 160.4 ppm) are already in the slow exchange domain.

The only exchange mechanism in CD_2Cl_2 for compound **2**, noticeable above 203 K, is the rotation of the apical carbonyls, as shown by the variable temperature ^{13}C-NMR spectra (Fig. 4, left) which were simulated using a two-site exchange matrix (Fig. 4, right). Regression of the Eyring plot ln(k/T) *vs.* $1/T$ gave a value of 43.1 ± 0.6 kJ mol^{-1} for the free enthalpy of activation at 298 K for the rotation of the apical carbonyls about the local C_3 axis.

The geometry of **3** in solution is similar to that found in the solid, as deduced from IR, ^{1}H-, ^{31}P- and ^{13}C-NMR spectroscopy (see Experimental section). The ^{1}H-NMR spectrum at 210 K shows the CH_2 group of the dppm ligand as an ABX_2 spin system due to the inequivalence of the two methylene protons: whereas the H_B proton shows the expected chemical shift at 2.69 ppm, the H_A proton is abnormally deshielded at 6.03 ppm. This pattern is quite similar to that found for **1**;[8] therefore, the conformation of the dimetallacyclopentane ring must be that found in solid **1′**[9] (where a methyl group replaces the H_B proton of dppm). The hydride ligand is coordinated in an axial position, replacing the unique axial CO in **1** (−15.7 ppm). This is deduced from the presence of three resonances in the ^{13}C-NMR limiting spectrum of a ^{13}CO enriched sample of **3** (*ca.* 30% enrichment) in the region of radial CO's (the two P-atoms and the H-atom must therefore occupy axial positions). Cluster **3** is fluxional in solution, as shown by the variable temperature ^{13}C-NMR spectra (Fig. 5, left). The first process of CO scrambling, starting at *ca.* 200 K, is the merry-go-round of the basal carbonyls a, b, d and f.

The second process is the rotation of apical carbonyls, which could not be simulated due to the similar δ values of carbonyls g and e. Simulation of the merry-go-round was effected with a four sites exchange matrix (Fig. 5, right). Regression of the function ln(k/T) *vs.* $1/T$ gave a value of 39.4 ± 1.4 kJ mol^{-1} for the free enthalpy of activation at 298 K, which is quite similar to that found for anionic Ir_4 clusters such as $[Ir_4(CO)_{11}X]^-$ (X = Br, I, NCS, NO_2).[13]

Experimental

Unless otherwise stated, all the operations were carried out under nitrogen, all solvents were dried by conventional methods prior to use. PPNCl (Fluka) was used as received. KOH (Fluka) was dried at 150 °C under reduced pressure (10^{-4} mm Hg). DBU (Aldrich) was dried with KOH and distilled. $[Ir_4(CO)_{10}(\mu\text{-dppm})]$ was prepared as described in the literature,[8] as well as ^{13}CO enriched derivatives of **2** and **3** (*ca.* 30% enrichment).[14] Infrared spectra were recorded from 0.1 mm CaF_2 cells previously purged with N_2 on a Perkin-Elmer FT-IR 2000 spectrometer. Elemental analyses were performed at the Analytische Laboratorien, Lindlar, Germany. ^{1}H-,^{31}P- and ^{13}C-NMR spectra were recorded on a Bruker AC200 spectrometer, using the residual proton peaks and carbon resonances of deuterated solvents as chemical shift references for ^{1}H- and ^{13}C-NMR spectra. ^{31}P-NMR spectra were referenced to external 85% H_3PO_4. ^{13}C-NMR and 2D-^{13}C-NMR spectra were recorded in 10 mm o.d. tubes on a Bruker WH360 spectrometer. COSY experiment: 256 t_1 increments with 2K transients, spectral

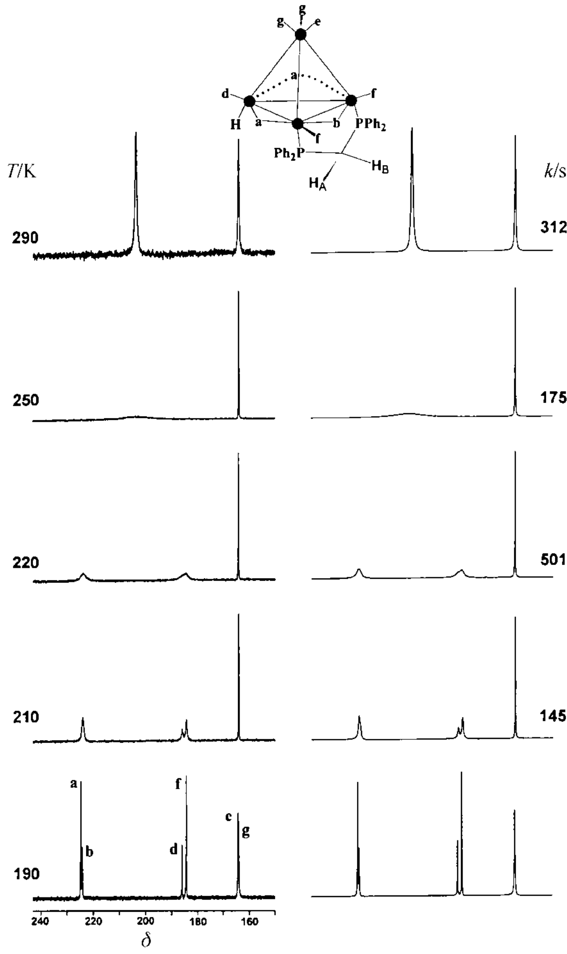

Fig. 5 Experimental (left) and calculated (right) VT ^{13}C-NMR spectra of **3** in CD_2Cl_2.

width 2840.9 Hz in the F_2 domain and 1420.5 Hz in the F_1 domain.

Bis(triphenylphosphoranylidene)ammonium *tetrahedro*-nonacarbonyl{μ_3-bis(diphenylphosphino)methanido}tetrairidate (2) ([PPN][$Ir_4(CO)_9(\mu_3$-$(Ph_2P)_2CH)$])

Dry KOH powder (0.20 g) and PPNCl (0.37 g, 0.64 mmol) were added to a solution of **1** (0.40 g, 0.28 mmol) in CH_2Cl_2 (15 cm^3) under N_2 at −20 °C. After a few minutes the deprotonated intermediate $[Ir_4(CO)_{10}(\mu$-$(Ph_2P)_2CH)]^-$ was formed but could not be isolated. δ_C (CD_2Cl_2, 210 K): 231.2 (1 CO, s), 214.7 (2 CO, m), 185.2 (2 CO, radial, s), 174.3 (1 CO, radial, s), 166.4 (1 CO, s), 159.8 (1 CO, s), 159.0 (2 CO, m). δ_P (CD_2Cl_2, 210 K): −59.2 (PPh_2). The suspension was stirred for 35 minutes, filtered, and cold isopropanol (80 cm^3) added. The yellow precipitate was recrystallised at −30 °C from CH_2Cl_2/isopropanol, and the crystals of **2** washed with cold isopropanol and pentane (0.41 g, 76%) (Found: C, 43.14; H, 2.69; N, 0.71; P, 6.32; Ir, 39.75%. $C_{70}H_{51}Ir_4NO_9P_4$ requires C, 43.27; H, 2.65; N, 0.72; P, 6.38; Ir, 39.57%). ν_{max}/cm^{-1} (CH_2Cl_2): 2034s, 1983vs, 1924w ν(CO). δ_H (CD_2Cl_2, 298 K): 7.7–6.6 (50 H, m, Ph); 3.95 [1 H, t, ^2J(P,H) 5.5 Hz, CH]. δ_P (CD_2Cl_2, 298 K): 21.0 (PPN$^+$), −44.4 (PPh_2). δ_C (CD_2Cl_2, 173 K): 177.1 (2 CO, s, d), 172.8 (2 CO, s, f), 167.0 (2 CO, s, c), 163.3 (1 CO, s, e), 160.2 (2 CO, m, g). Suitable crystals of **2** for an X-ray diffraction study were obtained by slow diffusion of hexane in a CH_2Cl_2 solution at 0 °C.

Bis(triphenylphosphoranylidene)ammonium *tetrahedro*-nonacarbonyl(hydrido){μ-bis(diphenylphosphino)methane}tetrairidate (3) ([PPN][$HIr_4(CO)_9(\mu$-dppm)])

A solution of **1** (0.27 g, 0.19 mmol) and PPNCl (0.21 g, 0.37 mmol) in CH_2Cl_2 (20 cm^3) under CO was cooled to −10 °C and DBU (600 µl, 4 mmol) was added. The solution was stirred for 2 h, then cold isopropanol (20 cm^3) was added and the volume of the mixture reduced by half. The orange precipitate was recrystallised at −30 °C from CH_2Cl_2 (+PPNCl)/isopropanol and the crystals of **3** were washed with cold isopropanol and pentane (0.32 g, 87%) (Found: C, 43.08; H, 2.71; N, 0.69; P, 6.28; Ir, 39.70%. $C_{70}H_{53}Ir_4NO_9P_4$ requires C, 43.23; H, 2.75; N, 0.72; P, 6.37; Ir, 39.53%). ν_{max}/cm^{-1} (CH_2Cl_2): 2010m, 1960vs, 1827vs, 1766 m ν(CO). δ_H (CD_2Cl_2, 210 K): 7.6–7.0 (50 H; m, Ph); 6.03 [1 H, dt, $^2J(H_A,H_B)$ 12.8 Hz, ^2J(P,H) 10.3 Hz, H_A], 2.69 [1 H, dt, $^2J(H_A,H_B)$ 12.8 Hz, ^2J(P,H) 12.8 Hz, H_B)], −15.7 (Ir-H). δ_P (CD_2Cl_2, 210 K): 20.1 (PPN$^+$), −52.9 (PPh_2). δ_C (CD_2Cl_2, 200 K): 225.0 (2 CO; s, a), 224.5 (1 CO, s, b), 186.7 (1 CO, s, d), 185.1 (2 CO, s, f), 165.0 (1 CO, s, e) 164.9 (2 CO, m, g). Suitable crystals of **3** for an X-ray diffraction study were obtained by slow diffusion of hexane in a CH_2Cl_2 solution at 0 °C.

X-Ray crystallography

Compound 2. A yellow crystal was brought onto a Bruker SMART CCD system equipped with Mo radiation. All non-hydrogen atoms were refined anisotropically, and all hydrogens were made to ride on their associated carbons.

Compound 3. An orange crystal of which the habitus consisted of {100}, {001} pinacoids, (10, $\bar{2}$), (0, $\bar{1}$ 0) pedions and a (161) fracture plane was cooled, using an Oxford Cryostream, to 90 K, the temperature of the data collection which took place on a Stoe IPDS system equipped with Mo radiation. All non-hydrogen atoms were refined anisotropically, and all hydrogens but H_4 were made to ride on their associated carbons. The hydrogen H_4 was difficult to find in difference maps and isotropically refined to a position surprisingly far away from Ir_4 [2.08(6) Å].

CCDC reference number 186/1923.

See http://www.rsc.org/suppdata/dt/a9/a909881j/ for crystallographic files in .cif format.

Acknowledgements

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