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dppm and hydrido-bridged dinuclear complexes of iridium. Synthesis and structures of $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-X})]^{2+}$ (X = Cl, OMe, OH, or H)

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Reaction of $[IrCp^*Cl(\mu\text{-H})]_2$ **1** (Cp* = pentamethylcyclopentadienyl) with two equivalents of bis(diphenylphosphino)methane (dppm) gave an unidentate dppm complex IrCp*(H)(Cl)(dppm-*P*) **2**. This reacted with a half equivalent of $[IrCp^*Cl(\mu\text{-Cl})]_2$ **3** to give a dppm-bridged dinuclear complex $(Cl)(H)Cp^*Ir(\mu\text{-dppm})IrCp^*Cl_2$ **4**, in which the two metal centers are distal. Reaction of **4** with two equivalents of AgOTf (OTf = O_3SCF_3) gave a dppm, hydride and chloride-bridged diiridium complex $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-Cl})][OTf]_2$ **5a**. Complex **5a** reacted with sodium methoxide in methanol to give $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OMe})][OTf]_2$ **6a**. This reacted with water in refluxing acetone to give a diiridium complex $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OH})][OTf]_2$ **7a**. Heating complex **6a** in refluxing toluene gave $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})_2][OTf]_2$ **8a**. The structures of the anion exchanged complexes $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-X})][BPh_4]_2$ [X = Cl **5b**, OMe **6b**, OH **7b** or H **8b**] have been confirmed by X-ray analysis.

Introduction

Recently, much attention has focused on the chemistry of multinuclear transition-metal complexes[1] with the metal atoms kept in close proximity in expectation of co-operative reactivities of those metals, which could not be realized by a single metal center. Bis(diphenylphosphino)methane (dppm) is one of the most commonly adopted ligands in order to lock the metal atoms in position and to prevent dissociation to mononuclear species.[2] While many hundreds of complexes containing two bridging dppm, $M(\mu\text{-dppm})_2M$, have been reported,[3] there have been relatively few dinuclear complexes with a single bridging dppm ligand.[4]

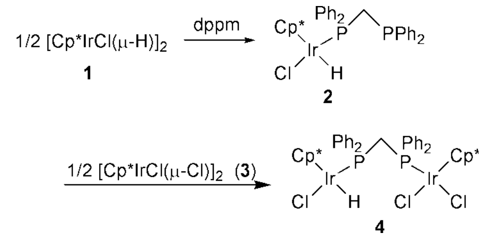
On the other hand, the chemistry of mononuclear iridium complexes is also of interest, because of their roles in the activation of small molecules.[5] Especially, cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) iridium complexes are of great interest, and their remarkable reactivities (such as carbon–hydrogen bond activation) have been revealed.[6] Investigations on mononuclear cyclopentadienyl and pentamethylcyclopentadienyl iridium complexes have widely been performed and their fundamental properties revealed, however relatively little is known about dinuclear cyclopentadienyl and pentamethylcyclopentadienyl iridium complexes.

In this paper we report the synthesis and structures of novel dppm and hydrido-bridged diiridium complexes with a pentamethylcyclopentadienyl ligand on each iridium center. These complexes are, to the best of our knowledge, the first examples of dppm-bridged diiridium complexes with pentamethylcyclopentadienyl ligands and two iridium atoms in close proximity.

Results and discussion

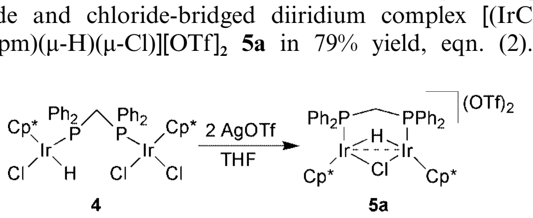
Synthesis of $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-Cl})][OTf]_2$ 5a

Reaction of the hydrido-bridged dinuclear complex $[IrCp^*Cl(\mu\text{-H})]_2$ **1** with two equivalents of dppm in tetrahydrofuran gave an unidentate dppm complex IrCp*(H)(Cl)(dppm-*P*) **2**, eqn. (1). Formation of **2** was spectroscopically confirmed, but isolation was not carried out. Addition of a half equivalent of chloro-bridged dinuclear complex $[IrCp^*Cl(\mu\text{-Cl})]_2$ **3** to the solution of **2** gave a dppm-bridged dinuclear complex $(Cl)(H)Cp^*Ir(\mu\text{-dppm})IrCp^*Cl_2$ **4** in 85% yield, (eqn. 1). The ^1H NMR spectrum of **4** showed two resonance signals for non-equivalent Cp* protons (δ 1.28 and 1.53). A signal for hydride was observed at δ −13.59 as doublet [$^2J(PH) = 36.6$ Hz]. Since the solubility of **4** in common organic solvents was extremely poor, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR could not be measured. Considering the structure of the closely related complex $(IrCp^*Cl_2)_2(\mu\text{-dppm})$, reported by Keim and co-workers,[7] the two iridium centers in **4** would not be in close proximity and there would be no interaction between them.



(1)

To eliminate chloride ligands and generate a co-ordinatively unsaturated species, reactions of complex **4** with silver salt were carried out. Treatment with two equivalents of AgOTf (OTf = triflate, *i.e.* trifluoromethanesulfonate) in THF gave a dppm, hydride and chloride-bridged diiridium complex $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-Cl})][OTf]_2$ **5a** in 79% yield, eqn. (2). ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR data of **5a** are summarized in Table 1. These data indicated that **5a** has a symmetrical



(2)

Table 1 NMR Spectral data (in $CDCl_3$) for compounds **5a**–**8a**[a]

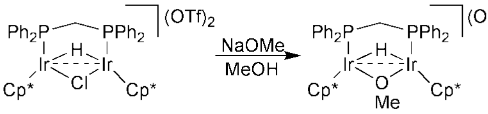
Signal	**5a**	**6a**	**7a**	**8a**
^1H				
Ir–H–Ir	−18.42 [1 H, t, ^2J(PH) 11.9]	−17.93 [1 H, t, ^2J(PH) 11.9]	−17.76 [1 H, t, ^2J(PH) 11.9]	−17.24 [2 H, t, ^2J(PH) 9.2]
C_5Me_5	1.75 (30 H, s)	1.72 (30 H, s)	1.77 (30 H, s)	1.62 (30 H, s)
PCH_2P	2.82 [1 H, td, ^2J(PH) 11.9, ^2J(HH) 13.8]	1.45 (1 H, m)	1.73 (1 H, overlapped by C_5Me_5)	3.47 [2 H, t, ^2J(PH) 11.9]
	3.41 [1 H, td, ^2J(PH) 10.1, ^2J(HH) 13.8]	3.48 (1 H, m)	3.29 [1 H, td, ^2J(PH) 11.9, ^2J(HH) 12.8]	
OMe		4.38 (3 H, s)		
OH			6.08 (1 H, s)	
Ph	7.27–7.55 (20 H)	7.21–7.56 (20 H)	7.27–7.52 (20 H)	7.24–7.55 (20 H)
^{13}C-{^1H}				
C_5*Me*$_5$	10.1 (s)	9.9 (s)	9.9 (s)	10.5 (s)
PCH_2P	27.8 [t, ^1J(PC) 29.0]	19.0 [t, ^1J(PC) 29.0]	23.3 [t, ^1J(PC) 26.9]	40.2 [t, ^1J(PC) 31.3]
OMe		77.2 (s)		
C$_5Me_5$	99.1 (s)	96.8 (s)	96.1 (s)	99.9 (s)
CF_3SO_3	121.0 [q, ^1J(FC) 321]	121.0 [q, ^1J(FC) 321]	120.9 [q, ^1J(FC) 321]	121.0 [q, ^1J(FC) 321]
Ph	121.8–135.8	123.0–135.4	123.2–135.7	126.1–134.7
^{31}P-{^1H}				
P	11.3 (s)	16.9 (s)	14.2 (s)	41.7 (s)

[a] Given as chemical shift (δ) [relative intensity, multiplicity, *J*/Hz].

structure in solution. The ^1H NMR spectrum showed a single resonance signal of the Cp* protons at δ 1.75 together with those due to the non-equivalent methylene protons of dppm (δ 2.82 and 3.41) and phenyl protons (δ 7.27–7.55). A signal for metal hydride was observed at δ −18.42 as a triplet [^2J(PH) = 11.9 Hz] coupling to the two phosphorus atoms, indicating that the hydride bridges the two metal centers. In ^{31}P-{^1H} NMR only a single resonance signal at δ 11.3 was observed.

Synthesis of $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OMe})][OTf]_2$ 6a

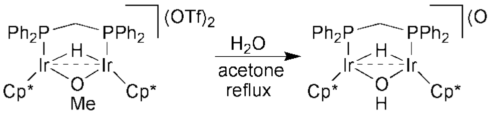
The complex **5a** reacted with sodium methoxide in methanol to give a dppm, hydride and methoxo-bridged diiridium complex $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OMe})][OTf]_2$ **6a** in 83% yield, eqn. (3). ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR data are summarized in Table 1. Signal patterns for Cp*, dppm and metal hydride of **6a** were similar to those of **5a**, suggesting that **6a** also has a symmetrical structure. A signal for bridging methoxy group was found at δ 4.38 in ^1H NMR, at δ 77.2 in ^{13}C-{^1H} NMR. In ^{31}P-{^1H} NMR a signal for phosphorus of dppm appeared at δ 16.9. The reaction of **5a** with sodium methoxide would proceed *via* substitution of chloride ligand by methoxide. Reaction of **5a** with sodium ethoxide was also attempted, but a very complicated mixture of several complexes was obtained.



5a **6a** (3)

Reaction of complex 6a with water: formation of $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OH})][OTf]_2$ 7a

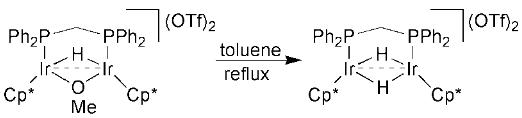
The bridging methoxy ligand in **6a** was substituted by hydroxy ligand in the reaction of **6a** with water in refluxing acetone to give a diiridium complex $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OH})][OTf]_2$ **7a** in 35% yield, eqn. (4). ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR data of **7a** are summarized in Table 1. In ^1H NMR a new signal appeared at δ 6.08, which was assigned to hydroxy proton because it disappeared upon adding a drop of D_2O. Although the proton of a hydroxy group bridging two metal centers is ordinarily observed in the upfield region,[3i,j,4f] that of **7a** was found at extremely low field. The reason for this low-field shift is not clear. One possible explanation would be that deprotonation of the hydroxy group could occur affording a oxide bridged complex in solution, but no clear evidence was given by crystal structure analysis of **7b** (see below). In ^{31}P-{^1H} NMR a signal for phosphorus of dppm was found at δ 14.2.



6a **7a** (4)

Synthesis of $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})_2][OTf]_2$ 8a

Heating complex **6a** in refluxing toluene for 17 hours gave a dppm and dihydrido-bridged complex $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})_2][OTf]_2$ **8a** in 82% yield, eqn. (5). ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR data of **8a** are summarized in Table 1. In ^1H NMR the signal for the methoxy group of the starting complex **6a** disappeared. The bridging hydrides were found at δ −17.24 as a triplet [^2J(PH) = 9.2 Hz], which integrated to two hydrides. A single signal for the methylene protons of dppm in **8a** was found at δ 3.47 as a triplet [^2J(PH) = 11.9 Hz], in contrast with the result that two signals were obtained for **5a**, **6a** and **7a**. In ^{31}P-{^1H} NMR a signal for phosphorus of dppm appeared at δ 41.7, which shifted to lower field of those of **5a**, **6a** and **7a**. It has been reported that the NMR signal of phosphorus incorporated in a five-membered ring shifts to lower field.[8] Considering the crystal structure determination of **8b** (see below), the shorter distance between the two iridium centers in **8a** than those in **5a**, **6a** and **7a** could make it possible to construct a five-membered ring by dppm and two iridium atoms. In order to ascertain the origin of the second hydride, synthesis of **8a** was performed using toluene-d_8 as a solvent. No incorporation of deuterium was observed. So the formation of **8a** from **6a** would proceed *via* β-hydrogen elimination from bridging methoxy ligand, although formaldehyde could not be detected.



6a **8a** (5)

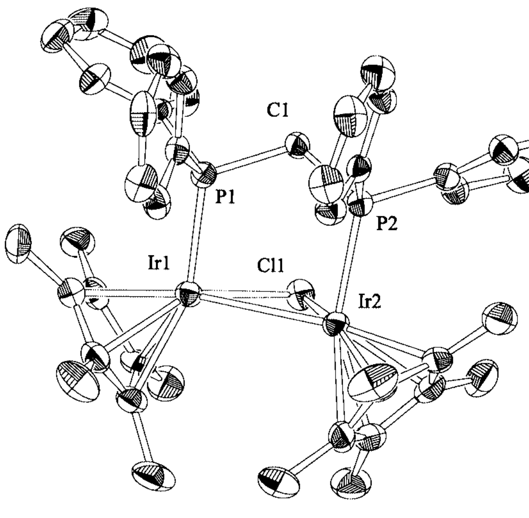
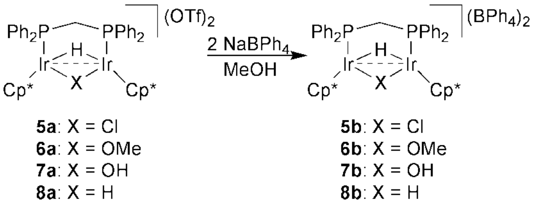


Fig. 1 An ORTEP[9] drawing of the cation $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-Cl})]^{2+}$ in complex **5b**. Hydrogen atoms are omitted for clarity.

In contrast to the present reaction, Riera and co-workers have reported that the reaction of a dppm and dihydrido-bridged dimanganese complex with aldehydes afforded dppm, hydride and alkoxo-bridged dimanganese complexes.[4b]

Crystal structure analysis of dppm and hydrido-bridged diiridium complexes $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-X})]^{2+}$ 5–8

To obtain crystals suitable for X-ray analysis, the triflate complexes **5a**–**8a** were converted into tetraphenylborate complexes **5b**–**8b** by anion exchange reaction with sodium tetraphenylborate, eqn. (6). NMR spectra of **5b**–**8b** were essentially the same as those of the corresponding triflate complexes. The structures of **5b**–**8b** were elucidated through X-ray diffraction studies. The molecular geometry and atom-numbering systems are shown in Figs. 1–4, and the results obtained are summarized in Tables 2 and 3.



(6)

The complex **5b** contains a diiridium core bridged by dppm and a chlorine atom. Although the location of the bridging hydrogen atom could not be determined, it should be situated on the Ir(1)–Cl(1)–Ir(2) plane, which is nearly perpendicular to the plane defined by the phosphorus and iridium atoms. The geometry around each iridium center is described as three-legged piano stool, which is general in Cp^*Ir^{III} complexes, assuming that the bridging hydride exists at the position mentioned above. The dppm methylene group is folded toward the bridging chloride atom. The complex **5b** would be a 34-electron one, if the bridging hydride is regarded as a two-electron ligand. The iridium–iridium distance is relatively large (3.0079(9) Å). This value is outside the range of normal iridium–iridium bonding distances, thereby the degree of direct metal–metal interaction is ambiguous.

The structures of **6b**, **7b** and **8b** are similar to that of **5b** except for the bridging group X. It should be noted that the distances between the two iridium centers decrease in the order **5b** > **6b**, **7b** > **8b**. In complex **6b** the carbon atom of the bridging methoxo group is directed out of the Ir(1)–O(1)–Ir(2) plane. The Ir(1)–O(1) and Ir(2)–O(1) distances are 2.167(6) and 2.144(6) Å, respectively. In **7b** the Ir(1)–O(1) and Ir(2)–O(1) distances are equal [2.130(5) Å]. The hydrogen atom of the hydroxy group was not refined well, nonetheless it was clearly defined on Fourier difference maps with O(1)–H(93) 0.99 Å. No significant interaction of the hydroxy hydrogen atom H(93)

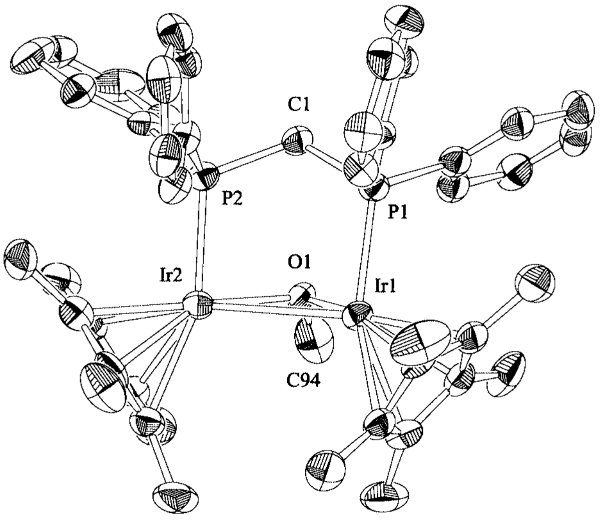


Fig. 2 An ORTEP drawing of the cation $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OMe})]^{2+}$ in the complex **6b**. Hydrogen atoms are omitted for clarity.

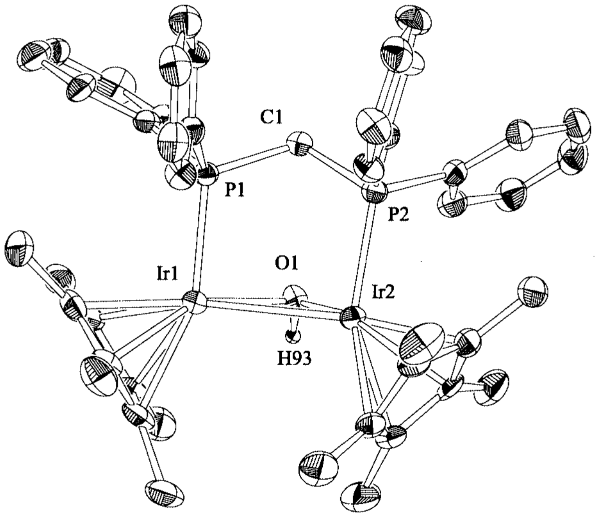


Fig. 3 An ORTEP drawing of the cation $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-OH})]^{2+}$ in the complex **7b**. Hydrogen atoms except for hydroxy proton are omitted for clarity.

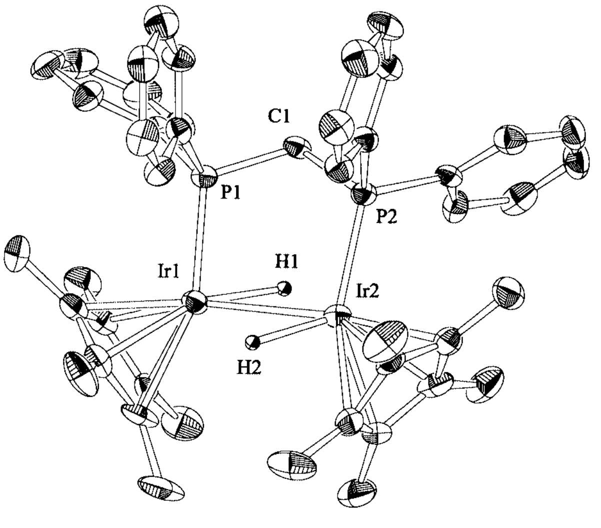


Fig. 4 An ORTEP drawing of the cation $[(IrCp^*)_2(\mu\text{-dppm})(\mu\text{-H})_2]^{2+}$ in the complex **8b**. Hydrogen atoms except for metal hydrides are omitted for clarity.

Table 2 Selected interatomic distances (Å) and angles (°) in the complexes **5b**–**8b**

	5b	**6b**	**7b**	**8b**
Ir(1) · · · Ir(2)	3.0079(9)	2.953(1)	2.9334(5)	2.818(1)
Ir(1)–P(1)	2.308(3)	2.314(2)	2.309(2)	2.302(2)
Ir(2)–P(2)	2.313(3)	2.307(2)	2.306(2)	2.296(2)
Ir(1)–Cl(1)	2.406(3)			
Ir(2)–Cl(1)	2.423(3)			
Ir(1)–O(1)		2.167(6)	2.130(5)	
Ir(2)–O(1)		2.144(6)	2.130(5)	
P(1)–C(1)	1.84(1)	1.832(8)	1.836(8)	1.813(9)
P(2)–C(1)	1.83(1)	1.825(8)	1.832(8)	1.838(9)
O(1)–C(94)		1.21(1)		
Ir(2)–Ir(1)–P(1)	89.06(7)	92.22(6)	90.31(5)	91.53(7)
Ir(2)–Ir(1)–Cl(1)	51.72(7)			
Ir(2)–Ir(1)–O(1)		46.4(1)	46.5(1)	
P(1)–Ir(1)–Cl(1)	91.7(1)			
P(1)–Ir(1)–O(1)		81.7(2)	86.6(2)	
Ir(1)–Ir(2)–P(2)	91.98(7)	90.06(6)	92.33(5)	93.35(7)
Ir(1)–Ir(2)–Cl(1)	51.21(6)			
Ir(1)–Ir(2)–O(1)		47.1(2)	46.5(1)	
P(2)–Ir(2)–Cl(1)	87.1(1)			
P(2)–Ir(2)–O(1)		86.7(2)	81.6(2)	
Ir(1)–Cl(1)–Ir(2)	77.07(8)			
Ir(1)–O(1)–Ir(2)		86.5(2)	87.0(2)	
Ir(1)–P(1)–C(1)	112.2(3)	112.6(3)	110.8(3)	111.3(3)
Ir(2)–P(2)–C(1)	113.0(3)	111.3(3)	112.7(2)	112.8(3)
P(1)–C(1)–P(2)	113.5(5)	114.0(4)	113.1(4)	112.4(5)
Ir(1)–O(1)–C(94)		118.9(7)		
Ir(2)–O(1)–C(94)		120.7(7)		

with other atoms (as in hydrogen bonding) were observed, while ^{1}H NMR spectra of **7a** and **7b** in solution show signals for the hydroxy proton at unusually lower field [δ 6.08 (**7a**), 5.04 (**7b**)]. In the complex **8b** the iridium–iridium distance is 2.818(1) Å, significantly shorter than that of **5b**, in agreement with the observation of a low-field shift in ^{31}P-{^{1}H} NMR of **8a** and **8b** (see above). Two metal hydrides were located from Fourier difference maps and the Ir(1)–H(1), Ir(1)–H(2), Ir(2)–H(1) and Ir(2)–H(2) bond distances were 1.75, 1.99, 1.96 and 1.70 Å, respectively. The complex **8b** would be a 32-electron one, so there should be bonding interaction between the two iridium atoms.

In conclusion, novel dppm and hydrido-bridged dinuclear complexes of iridium were prepared and their structures confirmed by X-ray analyses. These complexes are, to the best of our knowledge, the first examples of dppm-bridged diiridium complexes with the pentamethylcyclopentadienyl ligand and two iridium atoms in close proximity. Since complexes **5**–**8** would generate co-ordinatively unsaturated species by bridge splitting reaction, unique reactivities of the dinuclear complexes are expected. Further investigation on the reactivities of these complexes is in progress.

Experimental

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. Melting points were determined under air on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Infrared spectra were taken on a HORIBA FT-300 spectrometer, ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} spectra with JEOL EX-270 and A-500 spectrometers. Solvents were distilled under an argon atmosphere with appropriate drying agents (solvent/drying agent): tetrahydrofuran/Na–benzophenone, diethyl ether/Na-benzophenone, methanol/Mg, chloroform/P_2O_5, toluene/CaH_2. The compounds [IrCp*Cl(μ-H)]$_2$ **1**[10] and [IrCp*Cl(μ-Cl)]$_2$ **3**[11] were prepared by literature methods. Other reagents were used as obtained from commercial sources.

Preparations

IrCp*(H)(Cl)(dppm-*P*) 2. A mixture of compound **1** (0.504 g, 0.692 mmol) and dppm (0.555 g, 1.44 mmol) was placed in a reactor. Tetrahydrofuran (7 cm^3) was added and the solution stirred at room temperature for 20.5 h. Formation of **2** was confirmed by ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR, but isolation was not carried out. δ_H (C_6D_6) −12.87 (1 H, d, ^2J(PH) 38.5 Hz, Ir-H), 1.62 (15 H, s, C_5Me_5), 3.87–4.08 (2 H, m, PCH_2P) and 6.99–8.11 (20 H, Ph). δ_C (C_6D_6) 9.3 (s, $C_5\mathit{Me}_5$), 32.3 [dd, ^1J(PC) 36.2, 32.1, PCH_2P], 92.7 [d, ^2J(PC) 3.1 Hz, C_5Me_5] and 127.1–140.7 (Ph). δ_P (C_6D_6) −23.7 [d, ^2J(PP) 59.5, $IrPCH_2\mathit{P}$] and 7.4 [d, ^2J(PP) 59.5 Hz, $Ir\mathit{P}CH_2P$].

(Cl)(H)Cp*Ir(μ-dppm)IrCp*Cl$_2$ 4. To a tetrahydrofuran solution of compound **2** generated *in situ* from **1** (0.692 mmol) and dppm (1.44 mmol), **3** (0.552 g, 0.693 mmol) was added and the solution stirred at room temperature for 30 min. The resulting yellow precipitate was filtered off, washed with diethyl ether (12 cm^3), and dried to give **4** (1.34 g, 85%) as a yellow powder, mp 116.4 °C (decomp.) (Found: C, 46.63; H, 4.67; Cl, 9.21%. $C_{45}H_{53}Cl_3Ir_2P_2$ requires C, 47.14; H, 4.66; Cl, 9.28%); $\tilde{\nu}$/cm^{-1} (KBr) 2081w (Ir-H). δ_H ($CDCl_3$) −13.59 [1 H, d, ^2J(PH) 36.6, Ir-H], 1.28 (15 H, s, C_5Me_5), 1.53 (15 H, s, C_5Me_5), 4.62 [2 H, t, ^2J(PH) 9.2 Hz, PCH_2P] and 6.94–7.51 (20 H, Ph).

[(IrCp*)$_2$(μ-dppm)(μ-H)(μ-Cl)][OTf]$_2$ 5a. A mixture of compound **4** (0.505 g, 0.440 mmol) and AgOTf (0.227 g, 0.883 mmol) was placed in a reactor. Tetrahydrofuran (20 cm^3) was added, and the solution stirred at room temperature for 35 min. After evaporation of the solvent the residue was chromatographed on silica gel. Elution with methanol followed by evaporation of the solvent gave **5a** (0.479 g, 79%) as a red-orange powder, mp 237.3 °C (decomp.) (Found: C, 40.47; H, 3.69; Cl, 2.59%. $C_{47}H_{53}ClF_6Ir_2O_6P_2S_2$ requires C, 41.09; H, 3.89; Cl, 2.58%).

[(IrCp*)$_2$(μ-dppm)(μ-H)(μ-Cl)][BPh$_4$]$_2$ 5b. A mixture of compound **5a** (0.203 g, 0.148 mmol) and $NaBPh_4$ (0.100 g, 0.292 mmol) was placed in a reactor. Methanol (5 cm^3) was added and the solution stirred at room temperature for 30 min. The resulting orange product was filtered off, washed with methanol (6 cm^3) and dried. Extraction with acetone (17 cm^3) and recrystallization from acetone–diethyl ether gave **5b** (0.174 g, 69%) as red crystals, mp 206.9 °C (decomp.) (Found: C, 64.87; H, 5.44; Cl, 2.16%. $C_{93}H_{93}B_2ClIr_2P_2$ requires C, 65.16; H, 5.47; Cl, 2.07%). δ_H (acetone-d$_6$) −18.37 [1 H, t, ^2J(PH) 11.9, Ir-H-Ir], 1.78 (30 H, s, C_5Me_5), 3.49 [2 H, t, ^2J(PH) 11.0, PCH_2P], 6.74–6.91, 7.23–7.60 (60 H, Ph). δ_C (acetone-d$_6$) 10.2 (s, $C_5\mathit{Me}_5$), 26.0 [t, ^1J(PC) 30.0 Hz, PCH_2P], 99.8 (s, C_5Me_5), 122.1–136.9, 164.2–165.4 (Ph). δ_P (acetone-d$_6$) 11.8 (s).

[(IrCp*)$_2$(μ-dppm)(μ-H)(μ-OMe)][OTf]$_2$ 6a. To a solution of compound **5a** (0.535 g, 0.389 mmol) in methanol (25 cm^3) was added a solution of NaOMe (15.5 cm^3, 35.2 M in methanol) at room temperature and stirred for 2.2 h. After evaporation of the solvent the residue was extracted with 15 cm^3 of chloroform. Evaporation of the solvent gave **6a** (0.439 g, 83%) as a red powder, mp 109.8 °C (decomp.). Elemental analyses for **6a** were unsatisfactory because of a small amount of contaminant.

[(IrCp*)$_2$(μ-dppm)(μ-H)(μ-OMe)][BPh$_4$]$_2$ 6b. Reaction of compound **6a** with $NaBPh_4$ according to a similar procedure to the above gave **6b** as orange crystals, mp 109.1 °C (decomp.) (Found: C, 66.03; H, 5.69%. $C_{94}H_{96}B_2Ir_2OP_2$ requires C, 66.03; H, 5.66%). δ_H (acetone-d$_6$) −17.85 [1 H, t, ^2J(PH) 11.9, Ir-H-Ir], 1.77 (30 H, s, C_5Me_5), 2.14 [1 H, td, ^2J(PH) 11.9, ^2J(HH) 13.8, $PC\mathit{H}HP$], 3.36 [1 H, td, ^2J(PH) 11.9, ^2J(HH) 13.8 Hz, $PCH\mathit{H}P$], 4.42 (3 H, s, OMe) and 6.74–7.61 (60 H, Ph). δ_C (acetone-d$_6$) 10.1 (s, $C_5\mathit{Me}_5$), 17.2 [t, ^1J(PC) 30.0 Hz, PCH_2P], 77.2 (s, OMe),

Table 3 Summary of crystal data, collection data, and refinement of complexes **5b**, **6b**, **7b** and **8b**

	5b	**6b**	**7b**	**8b**
Formula	$C_{93}H_{93}B_2ClIr_2P_2$	$C_{94}H_{96}B_2Ir_2OP_2$	$C_{93}H_{94}B_2Ir_2OP_2$	$C_{93}H_{94}B_2Ir_2P_2$
M	1714.22	1709.80	1695.77	1679.77
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a/Å	26.484(7)	26.481(9)	26.435(2)	26.362(6)
b/Å	11.022(5)	11.13(1)	10.988(3)	11.023(8)
c/Å	27.760(5)	27.771(9)	27.771(2)	27.701(8)
β/°	107.93(1)	107.96(3)	108.701(5)	108.50(2)
V/Å^3	7710(4)	7788(7)	7641(2)	7634(5)
Z	4	4	4	4
μ/cm^{-1}	35.81	35.13	35.80	35.81
T/K	296	291	291	296
No. reflections measured	19013	19124	18752	18756
No unique data, R_{int}	18614, 0.097	18730, 0.045	18365, 0.058	18365, 0.080
No. reflections used	10359	8238	11263	11200
R	0.058	0.040	0.049	0.062
R_w	0.061	0.037	0.056	0.071

97.8 (s, C_5Me_5), 122.1–136.9, 164.2–165.4 (Ph). δ_P (acetone-d$_6$) 17.6 (s).

[(IrCp*)$_2$(μ-dppm)(μ-H)(μ-OH)][OTf]$_2$ 7a. A solution of compound **6a** (0.173 g, 0.126 mmol) in acetone (10 cm^3) and water (0.1 cm^3) was refluxed for 24 h. After evaporation of the solvent the residue was chromatographed on silica gel. Elution with chloroform and methanol (4:1) followed by evaporation of the solvent gave **7a** (0.0595 g, 35%) as an orange powder, mp 238.5 °C (decomp.) (Found: C, 41.93; H, 3.93%. $C_{47}H_{54}F_6Ir_2O_7P_2S_2$ requires C, 41.65; H, 4.02%).

[(IrCp*)$_2$(μ-dppm)(μ-H)(μ-OH)][BPh$_4$]$_2$ 7b. Reaction of compound **7a** with NaBPh$_4$ according to a similar procedure to the above gave **7b** as orange crystals, mp 219.2 °C (decomp.) (Found: C, 65.69; H, 5.57%. $C_{93}H_{94}B_2Ir_2OP_2$ requires C, 65.87; H, 5.59%). δ_H (acetone-d$_6$) −17.58 [1 H, t, ^2J(PH) 11.9 Hz, Ir-H-Ir], 1.77 (30 H, s, C_5Me_5), 2.31 (1 H, m, PCHHP), 3.36 (1 H, m, PCHHP), 5.04 (1 H, s, OH) and 6.74–7.65 (60 H, Ph). δ_C (acetone-d$_6$) 10.2 (s, C_5Me_5), 18.9 [t, ^1J(PC) 27.9 Hz, PCH$_2$P], 97.1 (s, C_5Me_5), 122.2–137.0, 164.3–165.5 (Ph). δ_P (acetone-d$_6$) 15.6 (s).

[(IrCp*)$_2$(μ-dppm)(μ-H)$_2$][OTf]$_2$ 8a. A suspension of compound **6a** (1.04 g, 0.759 mmol) in toluene (20 cm^3) was refluxed for 17 h. Evaporation of the solvent gave **8a** (0.836 g, 82%) as a brown powder, mp 249.8–253.5 °C. Elemental analyses for **8a** were unsatisfactory because of a small amount of contaminant.

[(IrCp*)$_2$(μ-dppm)(μ-H)$_2$][BPh$_4$]$_2$ 8b. Reaction of compound **8a** with NaBPh$_4$ according to a similar procedure to the above gave **8b** as dark orange crystals, mp 223.5 °C (decomp.) (Found: C, 66.05; H, 5.45%. $C_{93}H_{94}B_2Ir_2P_2$ requires C, 66.50; H, 5.64%). δ_H (acetone-d$_6$) −17.16 [2 H, t, ^2J(PH) 10.1, Ir-H-Ir], 1.64 (30 H, s, C_5Me_5), 3.85 [2 H, t, ^2J(PH) 11.9 Hz, PCH$_2$P] and 6.74–7.59 (60 H, Ph). δ_C (acetone-d$_6$) 10.9 (s, C_5Me_5), 39.6 [t, ^1J(PC) 33.1 Hz, PCH$_2$P], 101.2 (s, C_5Me_5), 122.2–137.0, 164.4–165.5 (Ph). δ_P (acetone-d$_6$) 48.0 (s).

Crystallography

The crystal data and experimental details for compounds **5b**, **6b**, **7b** and **8b** are summarized in Table 3. Diffraction data were obtained with a Rigaku AFC-7R diffractometer for **5b** and a Rigaku AFC-5S for **6b**, **7b** and **8b**. The reflection intensities were monitored by three standard reflections every 150 measurements. Reflection data were corrected for Lorentz-polarization effects. Absorption corrections were empirically applied. The structures were solved by heavy-atom Patterson methods,[12,13] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. All refinements were continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from ref. 14. The hydrogen atoms were located on idealized positions except for that of the hydroxy group in **7b** and metal hydrides in **8b**, which were defined on Fourier difference maps. All hydrogen atoms were not refined. Metal hydrides in **5b**–**7b** were not located. The calculations were performed using the program system TEXSAN.[15]

CCDC reference number 186/1947.

See http://www.rsc.org/suppdata/dt/b0/b001239o/ for crystallographic files in .cif format.

References

1 A. F. Heyduk and D. G. Nocera, *Chem. Commun.*, 1999, 1519; T. Iwasa, H. Shimada, A. Takami, H. Matsuzaka, Y. Ishii and M. Hidai, *Inorg. Chem.*, 1999, **38**, 2851; M. V. Jiménez, E. Sola, A. P. Martínez, F. J. Lahoz and L. A. Oro, *Organometallics*, 1999, **18**, 1125; D. A. Vicic and W. D. Jones, *Organometallics*, 1999, **18**, 134; K. Tani, A. Iseki and T. Yamagata, *Angew. Chem., Int. Ed.*, 1998, **37**, 3381; M. A. Arthurs, J. Bickerton, S. R. Stobart and J. Wang, *Organometallics*, 1998, **17**, 2743; H. Matsuzaka, K. Ariga, H. Kase, T. Kamura, M. Kondo, S. Kitagawa and M. Yamasaki, *Organometallics*, 1997, **16**, 4514; D. M. Heinekey, D. A. Fine and D. Barnhart, *Organometallics*, 1997, **16**, 2530; Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe and M. Hidai, *Organometallics*, 1997, **16**, 151.

2 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, 99; B. Chaudret, B. Delavaux and R. Poilblanc, *Coord. Chem. Rev.*, 1988, **86**, 191.

3 (*a*) R. A. Stockland, Jr., G. K. Anderson and N. P. Rath, *J. Am. Chem. Soc.*, 1999, **121**, 7945; (*b*) J. R. Torkelson, R. McDonald and M. Cowie, *Organometallics*, 1999, **18**, 4134; (*c*) Y. Gao, J. Kuncheria, G. P. A. Yap and R. J. Puddephatt, *Chem. Commun.*, 1998, 2365; (*d*) K.-B. Shiu, S.-W. Jean, H.-J. Wang, S.-L. Wang, F.-L. Liao, J.-C. Wang and L.-S. Liou, *Organometallics*, 1997, **16**, 114; (*e*) F. A. Cotton, C. A. James and R. L. Luck, *Inorg. Chem.*, 1991, **30**, 4370; (*f*) S. J. Chen and K. R. Dunbar, *Inorg. Chem.*, 1990, **29**, 529; (*g*) R. McDonald, B. R. Sutherland and M. Cowie, *Inorg. Chem.*, 1987, **26**, 3333; (*h*) P. E. Fanwick, W. S. Harwood and R. A. Walton, *Inorg. Chem.*, 1987, **26**, 242; (*i*) B. R. Sutherland and M. Cowie, *Organometallics*, 1985, **4**, 1637; (*j*) K.-W. Lee and T. L. Brown, *Organometallics*, 1985, **4**, 1025; (*k*) H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1983, 838.

4 (*a*) M. A. Alvarez, M. E. García, V. Riera and M. A. Ruiz, *Organometallics*, 1999, **18**, 634; (*b*) F. J. G. Alonso, M. G. Sanz, X. Y. Liu, A. Oliveira, M. A. Ruiz, V. Riera and C. Bois, *J. Organomet. Chem.*, 1996, **511**, 93; (*c*) V. Riera, M. A. Ruiz, F. Villafañe, Y. Jeannin and C. Bois, *J. Organomet. Chem.*, 1988, **345**, C4; (*d*) V. Riera, M. A. Ruiz, A. Tiripicchio and M. T. Camellini, *J. Organomet. Chem.*, 1986, **308**, C19; (*e*) K.-W. Lee, W. T. Pennington, A. W. Cordes and T. L. Brown, *J. Am. Chem. Soc.*, 1985, **107**, 631; (*f*) K.-W. Lee, W. T. Pennington, A. W. Cordes and T. L. Brown, *Organometallics*, 1984, **3**, 404; (*g*) F. Faraone, G. Bruno, S. L. Schiavo and G. Bombieri, *J. Chem. Soc., Dalton*

Trans., 1984, 533; (*h*) G. M. Dawkins, M. Green, A. G. Orpen and F. G. A. Stone, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 41.

5 G. J. Leigh and R. L. Richards, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 5, p. 541; J. D. Atwood, in *Comprehensive Organometallic Chemistry II*, eds. E. W. Abel, F. G. A. Stone, G. Wilkinson and J. D. Atwood, Pergamon, Oxford, 1995, vol. 8, p. 303.

6 B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, *Acc. Chem. Res.*, 1995, **28**, 154 and references therein; B. A. Arndtsen and R. G. Bergman, *Science*, 1995, **270**, 1970.

7 W. Keim, P. Kraneburg, G. Dahmen, G. Deckers, U. Englert, K. Linn, T. P. Spaniol and G. Raabe, *Organometallics*, 1994, **13**, 3085.

8 P. Garrou, *Chem. Rev.*, 1981, **81**, 229.

9 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

10 D. S. Gill and P. M. Maitlis, *J. Organomet. Chem.*, 1975, **87**, 359.

11 J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

12 PATTY, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

13 DIRDIF 94, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1994.

14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4; J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781; *International Tables for X-Ray Crystallography*, Kluwer, Boston, MA, 1992, vol. C.

15 TEXSAN for Windows, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1997.