

Short Communication

Synthesis and structure of the dimer $[\text{Ir}_2\text{Cl}_2\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2]$

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Abstract

$[\text{Ir}(\text{CO})(\text{dppm})]_2$ reacts with PhICl_2 to afford the molecular complex $[\text{Ir}_2\text{Cl}_2\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2]$. A crystal structure reveals a *syn* arrangement of chloride as well as carbonyl ligands on adjacent metal atoms. The complex is monoclinic, space group $C2/c$, with $a = 43.497(12)$, $b = 12.932(3)$, $c = 21.619(6)$ Å, $\beta = 104.26(2)^\circ$ and $Z = 8$.

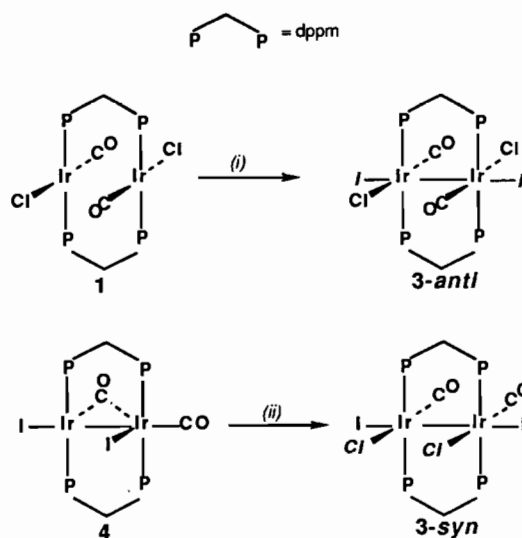
Introduction

We have recently shown that halogenation of *trans*- $[\text{IrCl}(\text{CO})(\text{dppm})]_2$ (**1**) ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) yields molecular compounds $[\text{Ir}_2\text{Cl}_2\text{X}_2(\text{CO})_2(\mu\text{-dppm})_2]$ ($\text{X} = \text{Cl}$ (**2**), I (**3**)) which were believed to be symmetrical species on the basis of NMR spectroscopic results [1]. In particular, $[\text{Ir}_2\text{Cl}_2\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2]$ (**3**) could exist either as the *anti* or *syn* isomer wherein steric congestion in the equatorial plane is relieved by *trans* disposition of the iodide ligands across the metal–metal bond. The symmetric *anti* isomer (**3-anti**) would be the result of iodine attack to the *exo* sides of the metal centres in the starting face-to-face structure [2] of **1** (Scheme 1). After some unfruitful attempts, we are now able to report on the formation of the *syn* isomer (**3-syn**) along with the correct structural assignment for the *anti* isomer.

Experimental

All experiments were performed under nitrogen in dried solvents.

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Scheme 1. (i) I_2 ; (ii) PhICl_2 .

$[\text{Ir}_2\text{Cl}_2\text{I}_2(\text{CO})_2(\mu\text{-dppm})_2]$ (**3-syn**)

Solid PhICl_2 [**3**] (0.5 mg, 0.034 mmol) was added in one portion to an orange suspension of $[\text{Ir}(\text{CO})(\text{dppm})]_2$ [**4**] (50 mg, 0.034 mmol) in CH_2Cl_2 (5 cm^3). Immediately a dark orange solution was obtained. After 1 h of stirring, diethyl ether was added dropwise until an orange precipitate formed. The solid was recrystallized from acetone–diethyl ether to give the product in 70% yield.

Anal. Calc. for $\text{C}_{52}\text{H}_{44}\text{Cl}_2\text{I}_2\text{Ir}_2\text{O}_2\text{P}_4 \cdot \text{C}_3\text{H}_6\text{O}$: C, 41.50; H, 3.16. Found: C, 41.20; H, 3.14%. IR spectrum (Nujol mull): $\nu(\text{CO})$ 2021 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 5.74 [2H, m, $^2J(\text{HH})$ 14.7, $J(\text{PH})$ 6.7 Hz, $\text{P}-\text{CH}_2-\text{P}$], 4.96 [2H, br m, $J(\text{PH}) \approx 2.6$ Hz, $\text{P}-\text{CH}_2-\text{P}$]. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $\text{CH}_2\text{Cl}_2/\text{acetone-d}_6(20\%)$, 85% H_3PO_4 external standard): δ -22.1(s).

X-ray diffraction study

Crystal data. $\text{C}_{52}\text{H}_{44}\text{Cl}_2\text{I}_2\text{Ir}_2\text{O}_2\text{P}_4 \cdot 1.5\text{C}_3\text{H}_6\text{O}$, crystals grown from acetone solution, $M_r = 1592.4$, monoclinic, space group $C2/c$, $a = 43.497(12)$, $b = 12.932(3)$, $c = 21.619(6)$ Å, $\beta = 104.26(2)^\circ$, $U = 11786(5)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.795$ g cm^{-3} , $F(000) = 6036$, $T = 296$ K, orange single crystal (0.20 × 0.42 × 0.18 mm) sealed in Lindemann capillary, $\mu(\text{Mo K}\alpha) = 57.69$ cm^{-1} ; 10356 independent reflections, 5624 with $I > 3\sigma(I)$.

Intensity data were collected on a Siemens R3m/V diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω scan technique with 2θ ranging from 3.0 to 50.0°. Data were corrected

for absorption (XABS [5]) and Lorentz-polarization effects. The structure was solved by Patterson and Fourier methods. One phenyl ring of a bridging dpmm ligand was constrained to a rigid, planar hexagon ($C-C=1.395 \text{ \AA}$) and C atoms were assigned isotropic thermal parameters. All remaining non-H atoms were anisotropic, 581 parameters in the model, final $R=0.077$ and $R'=0.082$ with $w^{-1}=[\sigma^2(F_o)+0.001F_o^2]$. The rather high R values are a consequence of the poor quality of the crystal and disorder in the acetone solvate molecules.

All calculations were performed with SHELXTL PLUS [5] and PARST [6] programs.

Results and discussion

Orange CH_2Cl_2 suspensions of $[\text{IrI}(\text{CO})(\text{dpmm})]_2$ (**4**) rapidly afford deep orange solutions of **3-syn** when treated with phenyl iodide dichloride (a synthon for molecular chlorine [7, 8]) at room temperature.

Compound **3-syn** has a solution ^1H NMR spectrum characteristic of '*trans,trans*- $\text{M}_2(\mu\text{-dpmm})_2$ ' structures with a different ligand environment on each side of the $\text{M}_2\text{P}_4\text{C}_2$ ring. A typical AB quartet with superimposed phosphorus coupling ($J(\text{AB})$ 14.7 Hz) is indeed observed in the region of methylene protons. In contrast, isomer **3-anti** shows a single resonance for the methylene protons of coordinated dpmm [1]. On the other hand, the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance occurs as a singlet at very similar δ values for both isomers (**3-anti**: -25.9 [1], **3-syn**: -22.1 ppm).

In the solid state the molecular structure of **3-syn** is characterized by the presence of the expected mutually *trans* dpmm ligands bridging the pseudo-octahedral iridium atoms. A perspective view of **3-syn** is given in Fig. 1, which also includes some selected bond parameters.

Owing to steric crowding, the coordination environments of the metal centres are forced to be staggered with torsion angles averaging 27.5° . Despite this, the chloride and carbonyl ligands on adjacent iridium atoms are involved in close transannular contacts: $\text{Cl}(1)\cdots\text{Cl}(2)$ $3.384(9) \text{ \AA}$, $\text{C}(1)\cdots\text{C}(2)$ $2.91(4) \text{ \AA}$. The Ir-Ir separation at $2.859(2) \text{ \AA}$ is consistent with a single bond between two Ir(II) centres and it is within the range observed for related compounds [1, 9–12].

Finally, the Ir-I bonds opposite the metal-metal bond have slightly different lengths with respect to each other ($\text{Ir}(1)-\text{I}(1)$ $2.710(3)$, $\text{Ir}(2)-\text{I}(2)$ $2.815(2) \text{ \AA}$). Since steric requirements are similar on both metal centres, steric congestion at the metal cannot account for such a difference. The only noticeable discrepancy is in the Ir-Ir-I angle value ($\text{Ir}(1)-\text{Ir}(2)-\text{I}(2)$ $174.3(1)^\circ$, $\text{Ir}(2)-\text{Ir}(1)-\text{I}(1)$ $178.0(1)^\circ$). On the other hand, unusual

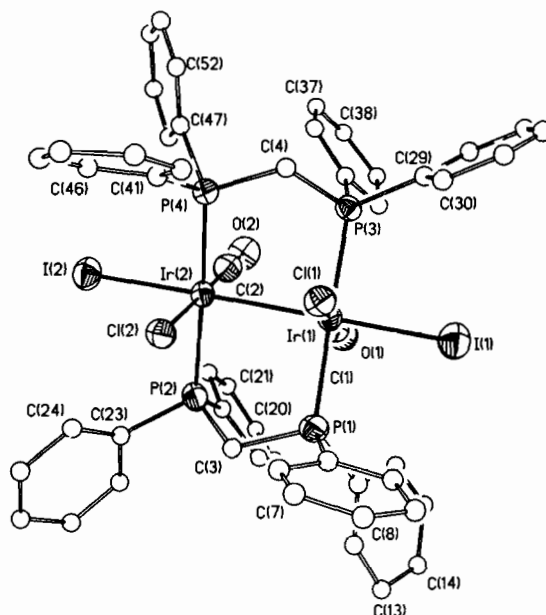


Fig. 1. Perspective view of $[\text{Ir}_2\text{Cl}_2\text{I}_2(\text{CO})_2(\mu\text{-dpmm})_2]$ (**3-syn**). Thermal ellipsoids are shown at the 30% level except for carbon atoms of phenyl rings which are arbitrarily sized circles. Important bond distances (\AA): $\text{Ir}(1)-\text{Ir}(2)$ $2.859(2)$, $\text{Ir}(1)-\text{Cl}(1)$ $2.403(6)$, $\text{Ir}(2)-\text{Cl}(2)$ $2.400(7)$, $\text{Ir}(1)-\text{I}(1)$ $2.710(3)$, $\text{Ir}(2)-\text{I}(2)$ $2.815(2)$, $\text{Ir}(1)-\text{P}(1)$ $2.376(7)$, $\text{Ir}(1)-\text{P}(3)$ $2.390(6)$, $\text{Ir}(2)-\text{P}(2)$ $2.373(6)$, $\text{Ir}(2)-\text{P}(4)$ $2.377(5)$, $\text{Ir}(1)-\text{C}(1)$ $1.87(3)$, $\text{Ir}(2)-\text{C}(2)$ $1.81(3)$. Bond angles ($^\circ$): $\text{P}(1)-\text{Ir}(1)-\text{P}(3)$ $172.1(2)$, $\text{P}(2)-\text{Ir}(2)-\text{P}(4)$ $170.8(1)$, $\text{Ir}(1)-\text{Ir}(2)-\text{I}(2)$ $174.3(1)$, $\text{Ir}(2)-\text{Ir}(1)-\text{I}(1)$ $178.0(1)$, $\text{Cl}(1)-\text{Ir}(1)-\text{C}(1)$ $179.0(7)$, $\text{Cl}(2)-\text{Ir}(2)-\text{C}(2)$ $177.5(9)$, $\text{Ir}(1)-\text{C}(1)-\text{O}(1)$ $178.1(24)$, $\text{Ir}(2)-\text{C}(2)-\text{O}(2)$ $177.8(25)$.

intra or intermolecular contacts are not observed. All other bond distances and angles within the structure are as expected.

Supplementary material

All the crystallographic material (atomic coordinates, bond lengths, bond angles and thermal parameters) is available from the Cambridge Crystallographic Data Center.

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