

Preliminary Communication

A novel octa-substituted iridium carbonyl derivative containing the dehydrogenated dppf ligand ( $\text{dppf} = \text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2$ ): synthesis and crystal structure of  $[\text{H}_4\text{Ir}_4(\text{CO})_4\{\text{Fe}(\text{C}_5\text{H}_3\text{PPh}_2)(\text{C}_5\text{H}_4\text{P}(\text{Ph})\text{C}_6\text{H}_4)\}_2]$

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**Abstract**

The octa-substituted iridium carbonyl derivative  $[\text{H}_4\text{Ir}_4(\text{CO})_4\{\text{Fe}(\text{C}_5\text{H}_3\text{PPh}_2)(\text{C}_5\text{H}_4\text{P}(\text{Ph})\text{C}_6\text{H}_4)\}_2]$  prepared from  $[\text{Ir}_4(\text{CO})_{12}]$  and dppf consists of a tetrahedral  $\text{Ir}_4$  unit and two tetradentate dehydrogenated dppf ligands formed upon ortho-metallation of a cyclopentadienyl and a phenyl ring with each iridium atom coordinated by a carbonyl group, a phosphorus and an *ortho*-carbon of the dehydrogenated cyclopentadienyl or phenyl group.

**Keywords:** Crystal structures; Iridium complexes; Carbonyl complexes; Hydride complexes; Diphosphine complexes; Cluster complexes

Mono- to hexa-substituted derivatives for the phosphine containing iridium carbonyl have been published so far. The di-substituted to hexa-substituted derivatives containing monodentate phosphines were prepared from  $[\text{Ir}_4(\text{CO})_{12}]$  and the corresponding ligands by the thermolytic method or substitution method with  $[\text{Me}_3\text{PhCH}_2\text{N}][\text{H}\text{Ir}_4(\text{CO})_{11}]$  or  $[\text{Me}_3\text{PhCH}_2\text{N}]_2[\text{Ir}_4(\text{CO})_{10}]_2$  as intermediate [1]. The mono-, di- and tetra-substituted products with diphosphines were synthesized from  $[\text{Ir}_4(\text{CO})_{12}]$  or  $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$  and dppm, dppe, dppp or *cis*-dppe ( $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ;  $n=1$ , dppm;  $n=2$ , dppe;  $n=3$ , dppp; *cis*-dppe = *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ ) [2]. The tri-substituted derivatives containing triphosphines,  $\text{HC}(\text{PPh}_2)_3$  and  $\text{CH}_3\text{Si}(\text{PEt}_2)_3$ , were prepared by the thermolytic method or chemical oxidation method with  $\text{Me}_3\text{NO}$  as initiator [3]. The reported hepta-substitution derivative  $[\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})]$ , which has no phosphine ligand, was the major product of the reaction between  $[\text{Ir}_4(\text{CO})_{12}]$  and 1,5-cyclooctadiene; however, the four metal atoms do not retain the tetrahedral unit and are described as a butterfly geometry associated with alkyne adducts of tetrametallic clusters or as a *closo*-octahedral arrangement of the  $\text{M}_4\text{C}_2$  framework from X-ray crystallographic analysis [4]. In the present work, the unusual octa-substituted derivative was isolated from the reaction of  $[\text{Ir}_4(\text{CO})_{12}]$  and dppf in refluxed toluene and was character-

ized by IR,  $^{31}\text{P}$  NMR and X-ray single crystal structure determination.

The title compound was prepared as follows. A mixture of  $[\text{Ir}_4(\text{CO})_{12}]$  (0.110 g, 0.10 mmol) and dppf (0.110 g, 0.20 mmol) in toluene (20  $\text{cm}^3$ ) was refluxed under nitrogen atmosphere over a period of 8 h. After the mixture had been evaporated to dryness under diminished pressure, the crude product was recrystallized from  $\text{CH}_2\text{Cl}_2$ /*n*-hexane. The title compound was crystallized and filtered first owing to its low solubility in  $\text{CH}_2\text{Cl}_2$  (0.012 g, 5.5%;  $\nu_{\text{max}}$  1973s,  $\text{br cm}^{-1}$  (CO);  $\delta_{\text{p}}$  ( $\text{CDCl}_3$ ):  $-34.0$ ,  $-42.2$  ppm). The other products were further separated by column chromatography.

The crystal data for the title compound are:  $\text{C}_{72}\text{H}_{56}\text{Ir}_4\text{Fe}_2\text{O}_4\text{P}_4 \cdot 2\text{CH}_2\text{Cl}_2$ ,  $M_r = 2159.5$ , light yellowish orange crystals ( $0.11 \times 0.13 \times 0.21$  mm) prepared from dichloromethane/*n*-hexane by the evaporation method, monoclinic, space group  $P2_1/c$ ,  $a = 19.153(5)$ ,  $b = 10.933(4)$ ,  $c = 33.339(4)$  Å,  $\beta = 93.49(2)^\circ$ ,  $V = 6968(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.059$  g  $\text{cm}^{-3}$ ,  $F(000) = 4096$ , Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å),  $\mu(\text{Mo } K\alpha) = 8.21$   $\text{mm}^{-1}$ ,  $T = 298$  K, unit cell: 25 reflections,  $2\theta$  range  $23.08$ – $32.22^\circ$ . The  $\omega/2\theta$  mode was employed with scan width =  $0.60 + 0.35 \tan\theta$ . Three standard reflections monitored every 2 h: variation on  $I$  was  $< 3\%$ . Of 12 457 reflections measured ( $3.0 < 2\theta < 49.9^\circ$ ;  $h, k, l$ :  $-22$  to  $22$ ,  $0$  to  $12$ ,  $0$  to  $39$ , respectively), 12 223 were unique, giving 7074 observed ( $I > 2.5\sigma(I)$ ). An absorption

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correction was made according to experimental  $\psi$  scans (maximum, minimum transmission factors = 0.999, 0.505). The structure was solved by direct methods. All isotropic H atoms were calculated after isotropic refinement and included in the structure factor calculation but not refined. Non-hydrogen atoms were refined with anisotropic thermal parameters. The weighting scheme,  $w = 1/\sigma^2(F_o)$ , was employed with  $\sigma(F_o)$  from counting statistics. The last least-squares cycle was calculated with 152 atoms, 830 parameters and 7074 reflections with maximum shift/e.s.d. = 0.003. The quantity minimized was  $\sum w(KF_o - F_c)^2$ , final  $R$ ,  $R_w$  and  $S$  being 0.040, 0.038, and 1.82. The peaks in the final  $\Delta F$  map were 2.500 to  $-1.900 \text{ e } \text{Å}^{-3}$ . The peaks greater than  $1.00 \text{ e } \text{Å}^{-3}$  are near the iridium atoms. Correction for secondary extinction was made with coefficient = 0.20(2) (length in  $\mu\text{m}$ ). Atomic scattering factors were taken from Ref. [5]. The computing and graphic program used were the NRCVAX package [6] and ORTEP [7].

All the published phosphine iridium carbonyl derivatives, except  $[\text{Ir}_4(\text{CO})_9(\text{HC}(\text{PPh}_2)_3)]$  [3c], contain bridging carbonyl groups identified by the CO stretching absorption in the range  $1700\text{--}1860 \text{ cm}^{-1}$ , although the starting material  $[\text{Ir}_4(\text{CO})_{12}]$  has only terminal carbonyls [8]. A structure having no bridging CO groups for the title compound may be attributed to the bulk and rigidity of the  $\text{HC}(\text{PPh}_2)_3$  and the dpfp ligands and to the formation of the bridged metal hydrides for the title compounds. According to the IR study [1c, 1d, 1f, 2a], the increase in the substitution number accompanies the decrease in CO stretching frequency for the iridium derivatives containing only phosphorus as coordination atoms (CO peak with highest frequency:  $2062\text{--}2072$ ,  $2029\text{--}2046$ ,  $1981\text{--}2008$  and  $1960 \text{ cm}^{-1}$  for di-, tri-, tetra- and hexa-substituted derivatives, respectively). The frequency of CO absorption for the title compound ( $1973 \text{ cm}^{-1}$ ), which is higher than that for the hexa-substituted derivative  $[\text{Ir}_4(\text{CO})_6(\text{PPh}_3)_4(\mu_3\text{-PPh})]$  [1d], may be due to the coordinated *ortho*-carbon of the cyclopentadienyl or phenyl group and there are no bridging CO groups in the molecule.

The molecule shown in Fig. 1 possesses unusual features arising from the intramolecular reaction. The dpfp ligands become tetradentate ligands on the tetrahedron base since one *ortho*-cyclopentadienyl and one *ortho*-phenyl carbon atom undergo metallation by insertion of iridium atoms. Consequently two CO ligands are replaced by the newly formed Ir–C bonds and the H atoms migrate to the cluster surface. The six Ir–Ir bonds are divided into 3 classes: Ir(1)–Ir(2), Ir(3)–Ir(4) (2.7097(9), 2.708(1) Å); Ir(1)–Ir(3), Ir(2)–Ir(4) (2.8643(9), 2.889(1) Å); Ir(1)–Ir(4), Ir(2)–Ir(3) (2.9533(9), 2.937(1) Å). The four larger bond lengths are due to the formation of bridged metal hydrides and to the steric hindrance between the two dpfp ligands, especially between phenyl ring B and H and between rings D and F. The hydridic nature was assumed from electron counting, a significant elongation of the four Ir–Ir bonds and the presence of electron density peaks above the long edges. The carbonyl group C(1)–O(1) and C(2)–O(2) as well as C(3)–O(3)

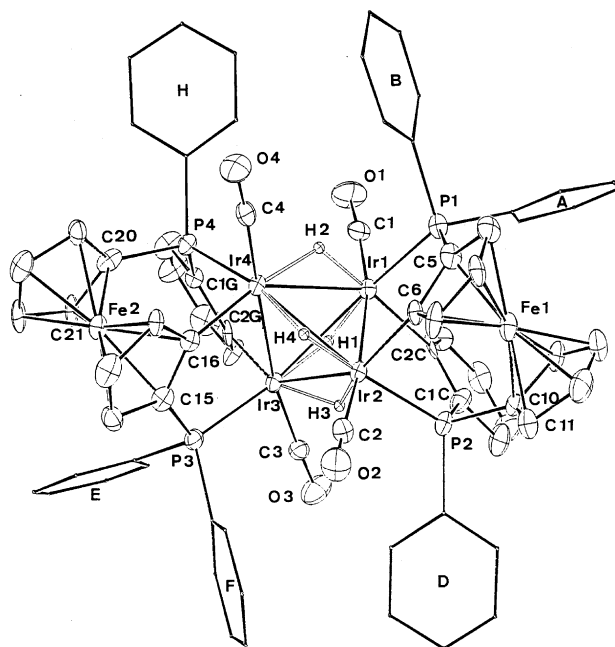


Fig. 1. The molecular structure of the title compound. Selected bond lengths (Å) and angles ( $^\circ$ ): Ir(1)–Ir(2) 2.7097(9), Ir(1)–Ir(3) 2.8643(9), Ir(1)–Ir(4) 2.9533(9), Ir(2)–Ir(3) 2.937(1), Ir(2)–Ir(4) 2.889(1), Ir(3)–Ir(4) 2.708(1), Ir(1)–P(1) 2.308(4), Ir(2)–P(2) 2.286(4), Ir(3)–P(3) 2.295(4), Ir(4)–P(4) 2.284(4), Ir(1)–C(1) 1.86(2), Ir(2)–C(2) 1.87(2), Ir(3)–C(3) 1.90(2), Ir(4)–C(4) 1.90(1), Ir(1)–C(2C) 2.12(1), Ir(2)–C(6) 2.07(1), Ir(3)–C(2G) 2.11(1), Ir(4)–C(16) 2.09(1), Ir(2)–Ir(1)–Ir(3) 63.53(3), Ir(2)–Ir(1)–Ir(4) 61.17(2), Ir(3)–Ir(1)–Ir(4) 55.46(2), Ir(1)–Ir(2)–Ir(3) 60.80(2), Ir(1)–Ir(2)–Ir(4) 63.58(2), Ir(3)–Ir(2)–Ir(4) 55.38(2), Ir(1)–Ir(3)–Ir(2) 55.67(2), Ir(1)–Ir(3)–Ir(4) 63.94(2), Ir(2)–Ir(3)–Ir(4) 61.40(3), Ir(1)–Ir(4)–Ir(2) 55.25(2), Ir(1)–Ir(4)–Ir(3) 60.61(2), Ir(2)–Ir(4)–Ir(3) 63.22(3).

and C(4)–O(4) are at the *trans* position of the attaching Ir–Ir bonds with OC–Ir–Ir bond angles of  $169.2(5)$ ,  $173.7(5)$  and  $170.0(4)$ ,  $178.4(4)^\circ$ , respectively. The Ir–CO bond lengths (1.86(2), 1.87(2), 1.89(2) and 1.90(1) Å) are shorter than the other Ir–C bond lengths (2.12(1), 2.11(1), 2.07(1) and 2.09(1) Å), since the carbonyl group is known to be a better  $\pi$ -acceptor than the others. As a whole, the molecule is quite symmetrical with the same bonding mode around Ir(1) and Ir(3) and around Ir(2) and Ir(4) and there seems to be a pseudo two-fold rotational axis through the middle point of Ir(1)–Ir(3) and of Ir(2)–Ir(4).

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