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Journal of Organometallic Chemistry 593–594 (2000) 63–68

Iridium clusters containing η^1 organic ligands: the synthesis and the solid state structure of $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$ and $[Ir_6(CO)_{14}(COOMe)_2]^{2-}$

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Received 2 April 1999; accepted 14 June 1999

Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

The cluster $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$ was obtained by reaction of $[HIr_4(CO)_{11}]^-$ and diphenylacetylene by refluxing in tetrahydrofuran (THF), with yields approaching 80%. The solid state structure was determined on the $[NEt_4]^+$ salt; the cluster possesses a tetrahedral metallic framework, with three edge bridging carbonyls. The vinyl fragment, having two phenyl rings in *cis*, is bound in axial position and donates only one electron to the cluster, since the C=C double bond (1.34 Å) does not interact with any iridium atom. The ^{13}C-NMR of the cluster, recorded at −90°C, allows full assignment of the signals. The cluster $[Ir_6(CO)_{14}(COOMe)_2]^{2-}$ was obtained by nucleophilic attack of MeONa on $[Ir_6(CO)_{16}]$, in anhydrous methanol at room temperature. The solid state structure was determined on its $[N(PPh_3)_2]^+$ salt. Two methoxycarbonyl fragments are on adjacent metal vertices of the octahedral framework. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iridium; Carbonyl clusters; Alkenyl ligand; Methoxycarbonyl ligand; ^{13}C-NMR; Solid state structure

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1. Introduction

The synthesis of clusters containing organic fragments is one of the most stimulating fields in organometallic chemistry [1]. On the light of the cluster-surface analogy [2], these compounds can be used to model the behaviour and the properties of metallic surfaces: the spectroscopic data and the detailed structural parameters obtained from molecular compounds can (a) help for the identification of reactive transients, (b) be used to calibrate the techniques of surface analysis [3], and (c) model the interactions between different adsorbed moieties [4]. Moreover, these organometallic molecules can be involved on their own in organic syntheses, either stoichiometric or catalytic [5,6]. For these purposes, triangular clusters of ruthenium and osmium are extraordinarily useful, since they are able to bind a huge variety of ligands, undergoing only small framework deformation [1,7]. Clusters of Group 9 metals are relatively less studied and, therefore, we pursued the synthesis and the characterisation of this type of compounds. Our investigations resulted into the isolation of $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$ (**1**) and $[Ir_6(CO)_{14}(COOMe)_2]^{2-}$ (**2**), showing that also tetra- and hexa-nuclear iridium compounds are useful substrates in this context. To our knowledge, **1** represents the only structurally characterised cluster containing an 'end-on' alkenyl ligand [7]. The cluster $[Ru_3(\mu_3\text{-ampy})(\eta^1\text{-PhC{=}CHPh})(CO)_9]$, which contains the same ligand with the same coordination, was previously characterised by NMR and IR spectroscopy [5].

Some reactivity and spectroscopic data on **2** were already reported, but difficulties in obtaining good quality crystals hampered the determination of its solid state structure [8].

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PII: S0022-328X(99)00344-7

2. Results

2.1. The syntheses

The hydridic anion $[HIr_4(CO)_{11}]^-$ (**3**) [9] is much more reactive than the homoleptic parent cluster $Ir_4(CO)_{12}$. For this reason, we are currently investigating the substitution reactions on **3**, which are expected to occur readily under mild conditions. Thus, the hydrido cluster **3** and diphenylacetylene were reacted in refluxing tetrahydrofuran (THF), observing the formation of a single new product, which was identified as $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$. The final product can be recovered easily by precipitation from dichloromethane/cyclohexane.

The alkenyl-substituted **1** must be originated by coordination of the diphenylacetylene, followed by insertion of the carbon–carbon triple bond into the Ir–H bond. However, according to infrared monitoring of the reaction mixture, the conversion of **3** to **1** is clean, and there is no evidence for any intermediate product, which could possibly have a lower number of carbonyl ligands, and the π-system of the organic fragment co-ordinated to an iridium atom. The presence of eleven carbonyls suggests that the acetylenic ligand is co-ordinated by the cluster without CO loss, through a possibly associative mechanism. On the basis of the process suggested for substitution on $Ir_4(CO)_{12}$ and its derivatives [10] we can conceive the following steps, which do not require carbonyl dissociation:

opening of the cluster in a butterfly intermediate

$\rightarrow \eta^2$ *coordination* $\rightarrow$ *insertion*

$\rightarrow$ *formation of the iridium–iridium bond.*

A different sequence such as:

CO loss $\rightarrow$ *acetylene coordination* $\rightarrow$ *insertion*

$\rightarrow$ *CO uptake*

is unlikely, since the whole process occurs with almost quantitative yields.

The synthesis of the octahedral cluster **2** was repeated according to the original procedure, i.e. by the nucleophilic attack of MeO^- on the red isomer of $Ir_6(CO)_{16}$. As already observed, when the reagents are mixed in stoichiometic amount, only $[Ir_6(CO)_{15}(COOMe)]^-$ (**4**) is formed. To drive the reaction to completeness, a large excess of methylate is needed (molar ratio MeO^-: $Ir_6(CO)_{16} > 6$). Even under these experimental conditions, the reaction is not complete, and variable amounts of the monosubstituted anion **4** are present. However, owing to their markedly different solubility in methanol and THF, dianion **2** and monoanion **4** can be separated easily. Crystals of $[N(PPh_3)_2]_2[Ir_6(CO)_{14}(COOMe)_2]$ were grown from CH_2Cl_2/C_6H_{12}. Some reactivity of dianion **2**, mainly its transformation into $[Ir_6(CO)_{15}]^{2-}$ or $Ir_6(CO)_{16}$, was already described [8].

2.1.1. The solid state structures

The solid state structure of the tetranuclear cluster **1**, shown in Fig. 1, was determined on the salt $[NEt_4][Ir_4(CO)_{11}(CPh{=}CHPh)]$ (**1a**). Selected bond distances and angles are listed in Table 1. The metallic framework is tetrahedral, with the edges of a triangular face bridged by three μ-CO groups. According to the usual definition for this arrangement [11], the alkenyl ligand is bound in a axial position with Ir(1)–C(12) = 2.13(1) Å, and points away from the cluster. The average Ir–Ir bond distance is 2.739 Å, with no significant differences between bridged and unbridged bonds [12]. The vinyl residue has the two phenyl rings in *cis* and, as expected for a double bond, the C(12)=C(13) distance is 1.34(1) Å, and the angles at the two carbon atoms are consistent with a sp^2 hybridisation. The bond distances involving Ir(1) follow peculiar trends: Ir–Ir bonds are systematically long (2.755 vs. 2.723 Å), Ir–CO are short, both for terminal and bridging ligands. The second effect can be reasonably explained by the poor π*-acidity of the organic fragment, compensated by a larger backdonation toward the carbonyls. As a result, CO(9) and CO(11) are slightly asymmetric. The Ir–C and C–O average distances are 1.90 and 1.13 Å (for terminal), 2.11 and 1.16 Å (for bridging ligands). All these distances are typical for monosubstituted tetrairidium clusters [13].

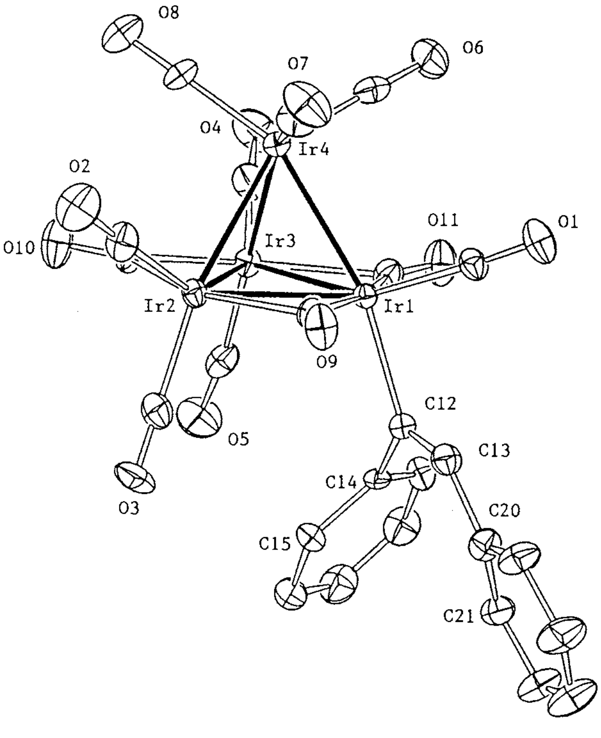

Fig. 1. The solid state structure of $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$ (**1**). The carbon atoms of the carbonyls have the same number as the oxygen to which they are attached.

Table 1
Selected bond lengths and angles in $[Ir_4(CO)_{11}(CPh=CHPh)]^-$ (**1**) with estimated standard deviations (e.s.d.) on the last figure in parentheses [a]

Bond lengths (Å)			
Ir–Ir			
Ir(1)–Ir(2)	2.750(1)	Ir(2)–Ir(3)	2.713(1)
Ir(1)–Ir(3)	2.757(1)	Ir(2)–Ir(4)	2.729(1)
Ir(1)–Ir(4)	2.758(1)	Ir(3)–Ir(4)	2.727(1)
$Ir–C_{term}$			
Ir(1)–C(1)	1.84(1)	Ir(3)–C(5)	1.90(1)
Ir(2)–C(2)	1.90(1)	Ir(4)–C(6)	1.91(1)
Ir(2)–C(3)	1.94(1)	Ir(4)–C(7)	1.92(1)
Ir(3)–C(4)	1.89(1)	Ir(4)–C(8)	1.92(1)
$Ir–C_{br}$			
Ir(1)–C(9)	2.00(1)	Ir(2)–C(10)	2.11(1)
Ir(1)–C(11)	2.06(1)	Ir(3)–C(10)	2.06(1)
Ir(2)–C(9)	2.22(1)	Ir(3)–C(11)	2.22(1)
Vinyl group			
Ir(1)–C(12)	2.13(1)	C(12)–C(14)	1.48(1)
C(12)–C(13)	1.34(1)	C(13)–C(20)	1.46(1)
C–O [b]			
$C_{term}–O_{term}$	1.13	$C_{br}–O_{br}$	1.16
Bond angles (°)			
Ir(1)–C(12)–C(13)	120(1)	$Ir–C_{term}–O_{term}$	176 [b]
Ir(1)–C(12)–C(14)	118(1)	$Ir–C_{br}–O_{br}$	140 [b]
C(12)–C(13)–C(20)	133(1)		

[a] Abbreviations: term, terminal; br, edge bridging.
[b] Average values.

The solid state structure of $[Ir_6(CO)_{14}(COOMe)_2]^{2-}$ is shown in Fig. 2, selected bond distances and angles are collected in Table 2. Two different salts have been analysed by X-ray: $[N(PPh_3)_2]_2[Ir_6(CO)_{14}(COOMe)_2] \cdot CH_2Cl_2$ (**2a**) and $[PPh_4]_2[Ir_6(CO)_{14}(COOMe)_2]$ (**2b**). In the latter salt (monoclinic, space group $P2_1/c$ (no. 14), $a = 25.326(3)$, $b = 28.352(5)$, $c = 20.496(3)$ Å, $\beta = 111.79(1)°$, $V = 13666(4)$ Å^3 and $Z = 8$.), the asymmetric unit contains two independent anions, and only one of them was found ordered; therefore, only the structure of **2a** is reported here. The cluster is octahedral, and the two methoxycarbonyl groups are on the adjacent metal atoms Ir(1) and Ir(2), being chemically unequivalent, since the molecule does not possess idealized symmetry elements. In the dianion **2** four carbonyls are edge bridging, the remaining terminal. Ir(1) and Ir(2) have two μ-CO and only one terminal group. All other iridium atoms have, instead, two terminal and one edge bridging ligands. Therefore, all the vertices of the octahedron receive five electrons from their ligands. The average Ir–Ir bond distance in **2** (2.809 Å) is typical for octahedral clusters [14], and individual data show the shortening effect of the bridging ligands: 2.749 versus 2.839 Å for unbridged bonds. The Ir–C and C–O average distances are 1.87 and 1.15 Å (for terminal), 2.08 and 1.17 Å (for bridging ligands). The methoxycarbonyl groups are bonded to their respective metal atoms with an average Ir–C distance of 2.07 Å, and the angles at C(1) and C(3) are well representative of sp^2 carbon atoms.

2.1.2. The ^{13}C-NMR

In order to confirm the nature of **1**, we recorded the ^{13}C-NMR on two different samples: the spectrum in the range 160–120 ppm shows ten sharp signals, attributable to the ten non-equivalent carbon atoms of the organic fragment. *J*-mode and bidimensional $^1H-^{13}C$ experiments unambiguously assign the signals at 156.6 and 139.7 ppm to the α and β carbon atoms of the alkenyl ligand, respectively; these values nicely match those reported for $[Ru_3(\mu_3\text{-ampy})(\eta^1\text{-}PhC{=}CHPh)(CO)_9]$ [5]. In addition, the peak at 5.9 ppm in the ^1H spectrum must be assigned to the $=C\underline{H}Ph$ hydrogen atom. A second sample was enriched in ^{13}CO (about 25%) and used for the NMR spectrum of the carbonyl ligands, recorded at −90°C in THF-d^8 (Fig. 3). Seven sharp signals appear at 211.3(2), 198.8(1), 180.4(1), 174.3(2), 163.3(2), 160.7(2), 157.9(1) ppm (relative intensities in parenthesis). The spectrum assesses definitely the presence of 11 CO groups under C_s symmetry, and can be interpreted easily on the basis of the typical trend for the chemical shifts of the carbonyl ligands of substituted $Ir_4(CO)_{11}L$ compounds, (bridging > radial > axial ≈ apical) [11].

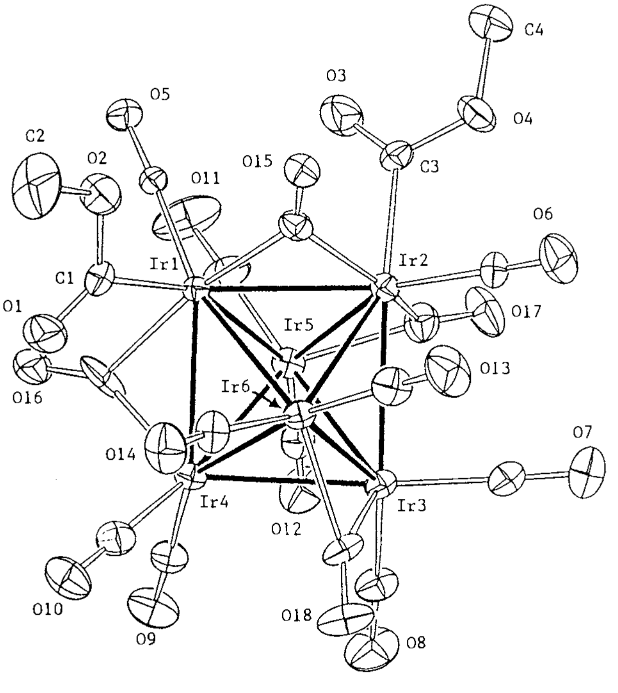

Fig. 2. The solid state structure of $[Ir_6(CO)_{14}(COOMe)_2]^{2-}$ (**2**). The carbon atoms of the carbonyls have the same number as the oxygen to which they are attached.

Table 2
Selected bond lengths and angles in $[Ir_6(CO)_{14}(COOMe)]^{2-}$ with estimated standard deviations (e.s.d.) on the last figure in parentheses [a]

Bond lengths (Å)			
Ir–Ir			
Ir(1)–Ir(2)	2.786(1)	Ir(2)–Ir(6)	2.884(1)
Ir(1)–Ir(4)	2.767(1)	Ir(3)–Ir(4)	2.799(1)
Ir(1)–Ir(5)	2.891(1)	Ir(3)–Ir(5)	2.794(1)
Ir(1)–Ir(6)	2.858(1)	Ir(3)–Ir(6)	2.704(1)
Ir(2)–Ir(3)	2.888(1)	Ir(4)–Ir(5)	2.815(1)
Ir(2)–Ir(5)	2.739(1)	Ir(4)–Ir(6)	2.785(1)
$Ir–C_{term}$			
Ir(1)–C(5)	1.87(1)	Ir(4)–C(10)	1.88(1)
Ir(2)–C(6)	1.88(1)	Ir(5)–C(11)	1.85(1)
Ir(3)–C(7)	1.86(1)	Ir(5)–C(12)	1.86(1)
Ir(3)–C(8)	1.89(1)	Ir(6)–C(13)	1.89(1)
Ir(4)–C(9)	1.91(1)	Ir(6)–C(14)	1.89(1)
$Ir–C_{br}$			
Ir(1)–C(15)	2.11(1)	Ir(3)–C(18)	2.05(1)
Ir(1)–C(16)	2.13(1)	Ir(4)–C(16)	1.99(1)
Ir(2)–C(15)	2.15(1)	Ir(5)–C(17)	2.04(1)
Ir(2)–C(17)	2.10(1)	Ir(6)–C(18)	2.10(1)
COOMe groups			
Ir(1)–C(1)	2.07(1)	C(1)–O(2)	1.37(2)
Ir(2)–C(3)	2.08(1)	C(3)–O(4)	1.34(1)
C(1)–O(1)	1.18(1)	O(2)–C(2)	1.47(2)
C(3)–O(3)	1.19(1)	O(4)–C(4)	1.45(2)
C–O [b]			
$C_{term}–O_{term}$	1.15	$C_{br}–O_{br}$	1.17
Bond angles (°)			
Ir(1)–C(1)–O(1)	128(1)	O(3)–C(3)–O(4)	118(1)
Ir(1)–C(1)–O(2)	112(1)	C(3)–Ir(2)–C(6)	90(1)
O(1)–C(1)–O(2)	120(1)	C(1)–O(2)–C(2)	114(1)
C(1)–Ir(1)–C(5)	89(1)	C(3)–O(4)–C(4)	117(1)
Ir(2)–C(3)–O(3)	127(1)	$Ir–C_{term}–O_{term}$	177 [b]
Ir(2)–C(3)–O(4)	115(1)	$Ir–C_{br}–O_{br}$	138 [b]

[a] Abbreviations: term, terminal; br, edge bridging.
[b] Average values.

3. Experimental

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under oxygen-free nitrogen atmosphere using the Schlenk-tube technique [15]. $[NEt_4][HIr_4(CO)_{11}]$ [9] and $Ir_6(CO)_{16}$ [16] were prepared by literature methods. Infrared spectra were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer, using calcium fluoride cells purged previously with N_2. Elemental analyses were carried out by the staff of Laboratorio di Analisi from the Dipartimento di Chimica Inorganica, Metallorganica e Analitica. ^{1}H- and ^{13}C-NMR spectra were recorded on a Brucker AC300 spectrometer and are reported in ppm downfield from the external standard $SiMe_4$.

3.1. Synthesis of $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$

$[NEt_4][HIr_4(CO)_{11}]$ (1.09 g; 0.9 mmol), $C_6H_5C{\equiv}CC_6H_5$ (0.28 g; 1.57 mmol) and THF (20 ml) were placed in a Schlenk tube and refluxed for about 3 h, while monitoring by infrared spectroscopy. At the end the solvent was evaporated in vacuum. The dark residue was washed with hexane, then extracted with the minimum amount of CH_2Cl_2 and filtered. The solution was layered with cyclohexane, yielding 1.0 g (80%) of well shaped crystals of $[NEt_4][Ir_4(CO)_{11}$-(CPh=CHPh)]. Calc. for $C_{33}H_{31}Ir_4NO_{11}$: C 28.6, H 2.25, N 1.01%; found: C 29.0, H 2.45, N 1.21%. ν(CO): 2062mw, 2024vs, 1988s(br), 1831m(br) cm^{-1}, in THF. FAB-MS (negative ions): $m/z = 1078$. ($[HIr_4(CO)_{11}]^-$), $1078 - 28x$ ($x = 1$–8, $[HIr_4(CO)_{11-x}]^-$), the parent peak at m/z = 1256 was not observed. ^{1}H-NMR: multiplet at 7.3–6.3 δ (10H, C_6H_5), 5.90 δ (1H, alkenyl =CH), 3.47 δ (q, 8H, CH_2), 1.39 δ (t, 12H, CH_3). ^{13}C-NMR (selected): 156.6 (alkenyl Ir–$\underline{C}$Ph=), 139.7 (alkenyl =$\underline{C}$HPh), in THF-d^8.

3.2. Synthesis of $[Ir_6(CO)_{14}(COOMe)_2]^{2-}$

$Ir_6(CO)_{16}$ (0.24 g; 0.15 mmol) was suspended in 15 ml of anhydrous methanol under a CO atmosphere. A solution approximately 0.43 M of MeONa was prepared by dissolving 50 mg of Na in 5 ml of anhydrous methanol. The latter solution was added in three portions (0.9 ml each, final ratio Ir_6:NaOMe = 1: 8). The course of the reaction was monitored via infrared. The cluster was isolated by addition of solid $[N(PPh_3)_2]Cl$ (1.0 g). An orange precipitate formed slowly, which was collected by filtration, washed with 2-propanol and dried in vacuum. The compound was analytically pure, as confirmed by ^{1}H-NMR and elemental analysis. Calc. for $C_{90}H_{66}Ir_6N_2O_{18}P_4$: C 39.4, H 2.43, N 1.02%; found: C 39.0, H 2.5, N 1.1%. Crystals for X-ray analysis were grown from CH_2Cl_2/cyclohexane. ν(CO): 2049w, 2010s, 2002vs, 1996s, 1935w, 1784m, 1768mw, 1643w

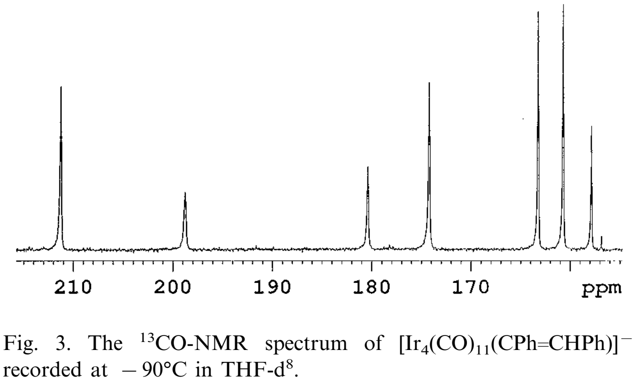

Fig. 3. The ^{13}CO-NMR spectrum of $[Ir_4(CO)_{11}(CPh{=}CHPh)]^-$, recorded at −90°C in THF-d^8.

Table 3
Crystal data and data collection parameters

Compound	**1a**	**2a**
Formula	$C_{33}H_{31}Ir_4NO_{11}$	$C_{91}H_{68}Cl_2Ir_6N_2O_{18}P_4$
Formula weight	1386.4	2825.6
Colour	Orange	Red
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	9.271(2)	14.220(2)
b (Å)	33.078(4)	15.443(3)
c (Å)	12.099(2)	24.988(3)
α (°)		94.92(1)
β (°)	90.82(1)	95.21(1)
γ (°)		117.06(1)
V (Å^3)	3710.0(7)	4816.3(1.5)
Z	4	2
$F(000)$	2528	2656
$D_{calc.}$ (g cm^{-3})	2.482	1.948
Crystal dimensions (mm)	$0.11\times0.45\times0.45$	$0.14\times0.31\times0.34$
μ(Mo–K$_\alpha$) (cm^{-1})	143.1	84.1
Min/max transmission	0.25–1.00	0.63–1.00
Scan mode	ω	ω
Frame width (°)	0.3	0.3
Time per frame (s)	20	25
No. of frames	1300	2500
Detector–sample distance (cm)	6.00	5.50
Theta range	2–25	2–25
Reciprocal space explored	$\pm h,\ +k,\ \pm l$	$\pm h,\ \pm k,\ \pm l$
Measured reflections (total; independent)	17873; 7141	52005; 20911
Unique observed reflections [$I>3\sigma(I)$]	5331	13315
Final R and R' [a]	0.032, 0.040	0.041, 0.062
No. of variables	443	1109
Goodness-of-fit [b]	1.13	1.41

[a] $R=[\Sigma(|F_o-k|F_c||)/\Sigma F_o]$, $R'=[\Sigma w(F_o-k|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

[b] $[\Sigma w(F_o-k|F_c|)^2/(N_o-N_v)]^{1/2}$, where $w=1/[\sigma(F_o)]^2$, $\sigma(F_o)=[\sigma^2(F_o^2)+(pF_o^2)^2]^{1/2}/2F_o$, N_o is the number of observations, N_v the number of variables, and p is the ignorance factor which is equal to 0.05 for **1a** and 0.06 for **2a**.

(COOMe) cm^{-1} in THF. ^{1}H-NMR: multiplet at 7.6–7.5 δ (60H, $[N(PPh_3)_2]^+$), 3.41 δ (6H, OCH_3), in CD_2Cl_2.

3.3. X-ray data collection and structure determination

Crystal data and other experimental details are summarised in Table 3. The diffraction experiments were carried out on a Siemens SMART CCD area-detector diffractometer at room temperature using Mo–K$_\alpha$ radiation ($\lambda=0.71073$ Å) with a graphite crystal monochromator in the incident beam and the generator working at 50 kV and 35 mA. Cell parameters and orientation matrix were obtained from the least-squares refinement of 115 (for **1a**) and 154 (for **2a**) reflections measured in three different sets of 15 frames each, in the range $2<\theta<23°$. At the end of data collections the first 50 frames, containing 498 reflections (for **1a**) and 590 reflections (for **2a**), were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT, and an absorption correction was applied (SADABS, written by G. Sheldrick) to the 17 873 collected reflections of **1a** (7141 of which are unique with $R_{int}=0.0467$ ($R_{int}=\Sigma\,|F_o^2-F_{mean}^2|/\Sigma\,F_o^2$)) and to the 52 005 collected reflections of **2a**, (20 911 of which are unique with $R_{int}=0.0275$).

The calculations were performed on an AST power premium 486/33 computer using the Personal Structure Determination Package (SDP) [17] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref. [18]. The structures were solved by SHELXS direct methods (contained in the Personal SDP) [17] and refined by full-matrix least-squares minimising the function $\Sigma\,w(F_o-kF_c)^2$ (refinement on F). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å, B 1.15 times that of the carbon atom to which they are attached) and not refined. In the final difference Fourier maps maximum residuals were 2.1(2) e Å^{-3} at 1.38 Å from Ir(4) for **1a**, and 5.9(2) e Å^{-3} at 1.06 Å from Ir(6) for **2a**.

4. Supplementary material

The atomic co-ordinates of the structure models has been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: hhtp://www.ccdd.cam.ac.uk)

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