Chemistry of Iridium Carbonyl Clusters. Synthesis and Chemical Characterization of the Hexanuclear Anions $[Ir_6(CO)_{15}(CO_2R)]^-$ (R = Me or Et) and $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$. Crystal and Molecular Structure of $[N(PPh_3)_2][Ir_6(\mu\text{-}CO)_4(CO)_{11}(CO_2Me)]$ †

Luigi Garlaschelli and Maria Carlotta Malatesta
Dipartimento di Chimica Inorganica e Metallorganica, Via G. Venezian 21, 20133 Milano, Italy
Secondo Martinengo
Centro di Studio Sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, 20133 Milano, Italy
Francesco Demartin, Mario Manassero, and Mirella Sansoni
Istituto di Chimica Strutturistica Inorganica dell'Universita' di Milano, Via G. Venezian 21, 20133 Milano Italy

---

The anions $[Ir_6(CO)_{15}(CO_2R)]^-$ (R = Me or Et) and $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$ have been prepared by reacting $[Ir_6(CO)_{16}]$ with Na(OR) in dry alcohol under an atmosphere of carbon monoxide. The reaction of $[Ir_6(CO)_{15}(CO_2Me)]^-$ with primary and secondary alcohols such as EtOH and Pr^iOH gives rise to specific alcoholysis. The anions $[Ir_6(CO)_{15}(CO_2R)]^-$ (R = Me or Et) and $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$ react with acids in tetrahydrofuran solution to give quantitatively $[Ir_6(CO)_{16}]$. The chemical and spectroscopic characterization of the hexanuclear anions is reported. Crystals of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 10.813(3), b = 16.613(3), c = 16.061(2) Å, α = 97.96(1), β = 96.20(1), γ = 94.58(2)°, and Z = 2. The X-ray structure has been solved by the heavy-atom method and refined by least squares to a final conventional R of 0.033 for 5 291 independent observed reflections. The anion consists of a slightly distorted octahedron of iridium atoms with eleven terminal and four edge-bridging CO groups and a methoxycarbonyl group σ-bonded to a metal atom. The Ir–Ir bond lengths are in the range 2.703(1)—2.870(1) Å, with an average value of 2.793 Å. Other average bond distances are $Ir\text{–}C_{terminal}$ 1.878 and $C\text{–}O_{terminal}$ 1.135 Å.

Several hexanuclear anionic and neutral carbonyl clusters of iridium have been reported. In 1970 Malatesta *et al.*[1] reported the synthesis of $[Ir_6(CO)_{16}]$ and $[Ir_6(CO)_{15}]^{2-}$. Only recently $[Ir_6(CO)_{16}]$ has been isolated and crystallographically characterized in two different isomeric forms: a red isomer isostructural with $[Rh_6(CO)_{16}]$, with four face-bridging carbonyl groups, and a black isomer with four asymmetrical edge-bridging carbonyl groups.[2] In the last six years the structural analysis of $[NMe_3(CH_2Ph)]_2[Ir_6(CO)_{15}]$[3] and the synthesis and X-ray structure analysis of the clusters $[Ir_6(CO)_{16-x}L_x]$ [x = 4, L = $P(OPh)_3$;[4] x = 5, L = $P(OMe)_3$[5]] and $[PPh_4][Ir_6(CO)_{15}\{C(O)Et\}]$[6] {obtained by reacting the red isomer of $[Ir_6(CO)_{16}]$ with different nucleophiles} have been reported. All these compounds show an octahedral framework of metal atoms with CO distributions different from that of the parent $[Ir_6(CO)_{16}]$ compound.

Few clusters, with four or more metal atoms, containing an alkoxycarbonyl group have been synthesized and structurally characterized *via* X-ray analysis: $[PPh_3(CH_2Ph)][Ir_4(CO)_{11}(CO_2Me)]$[7] and $[PPh_4][Rh_6(CO)_{15}(CO_2Me)]$,[8] which contain a σ-bonded methoxycarbonyl group, are obtained by nucleophilic attack of an alkoxy group on a positively polarized carbon atom of a CO group bonded to the metal; $[Os_5H(CO)_{14}C(CO_2Et)]$[9] and $[Os_5I(CO)_{14}C(CO_2Me)]$,[9] containing a bridging alkoxycarbonyl group, are obtained by nucleophilic attack of a molecule of alcohol. Two more tetranuclear alkoxycarbonyl derivatives, $[M_4(CO)_{11}(CO_2Me)]^-$ (M = Rh[10] or Co[11]), have been formulated only on the basis of spectroscopic and chemical data.

We report now the synthesis and chemical characterization of the new anions $[Ir_6(CO)_{15}(CO_2R)]^-$ (R = Me or Et) and $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$, obtained by reacting $[Ir_6(CO)_{16}]$ with Na(OR). The complete results of the X-ray structure analysis of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ (**1**) are also reported.

Results

Synthesis of $[Ir_6(CO)_{15}(CO_2R)]^-$ (R = Me *or* Et) *and* $[Ir_6(CO)_{14}(CO_2Me)_2]^{2-}$.—The red isomer of $[Ir_6(CO)_{16}]$ reacts with Na(OMe) (mol ratio 1:1.5) in dry methanol at room temperature under a carbon monoxide atmosphere to produce an orange solution containing the anion $[Ir_6(CO)_{15}(CO_2Me)]^-$ [equation (1)]. The reaction is carried out under a carbon monoxide atmosphere in order to stabilize the product; under nitrogen some brown decomposition products, not yet characterized, are observed.

$$[Ir_6(CO)_{16}] + Na(OMe) \longrightarrow Na[Ir_6(CO)_{15}(CO_2Me)] \quad (1)$$

The orange anion $[Ir_6(CO)_{15}(CO_2Me)]^-$ can be isolated from the alcoholic solution by addition of an aqueous solution of bulky cations such as $[N(PPh_3)_2]^+$, $[NEt_4]^+$, or $[NMe_4]^+$.

The ethoxy derivative $[Ir_6(CO)_{15}(CO_2Et)]^-$ can be obtained by reacting $[Ir_6(CO)_{16}]$ with Na(OEt) in dry ethanol and can be isolated in similar way.

The i.r. spectrum of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ (**1**) in

---

* Bis(triphenylphosphine)iminium 1,2;1,3;2,6;4,5-tetra-μ-carbonyl-1,2,2,3,3,4,4,5,5,6,6-undecacarbonyl-1-methoxycarbonyl-*octahedro*-hexairidate(1 –).

Supplementary data available (No. SUP 56426, 7 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Infrared (cm^{-1})[a] and ^{1}H n.m.r.[b] spectral data

Compound	ν(C–O)	δ/p.p.m.			
		OCH$_3$	OCH$_2$	CH$_3$	C$_6$H$_5$
(**1**) [N(PPh$_3$)$_2$][Ir$_6$(CO)$_{15}$(CO$_2$Me)]	2 085w 2 040vs 2 035vs 1 795m 1 660w[c] 1 045w[c]	3.45(s)			7—8(m)
(**2**) [N(PPh$_3$)$_2$][Ir$_6$(CO)$_{15}$(CO$_2$Et)]	2 085w 2 045vs 2 030vs 1 795m 1 655w 1 030w[c]		3.98(q)[d]	1.17(t)[d]	7—8(m)
(**3**) [PPh$_4$]$_2$[Ir$_6$(CO)$_{14}$(CO$_2$Me)$_2$]	2 050w 2 010(sh) 2 000vs 1 785s 1 765m 1 645w 1 035w[c]	3.31(s)			7—8(m)

[a] In thf solution; v = very, s = strong, m = medium, w = weak, sh = shoulder. [b] CDCl$_3$ solution; s = singlet, t = triplet, q = quartet, m = multiplet. [c] Stretching of C–O–R group (R = Me or Et). [d] J(H–H) = 7 Hz.

tetrahydrofuran (thf) (Table 1) shows both terminal (2 085w, 2 040vs, and 2 035vs cm^{-1}) and bridging (1 795 cm^{-1}) carbonyl groups in agreement with the structure analysis (see later). The two weak absorptions at 1 660 and 1 045 cm^{-1} are attributable to the methoxycarbonyl group. The latter band is more easily observed in a Nujol mull spectrum when no absorption bands of the counter cations are present. The ^{1}H n.m.r. spectrum of (**1**) (25 °C, CDCl$_3$) shows a singlet at δ 3.45 p.p.m. (due to the resonance of the methyl group) with the correct intensity ratio (1 : 10) relative to the cation phenyl hydrogens in the range δ 7—8 p.p.m. (Table 1).

Complex [N(PPh$_3$)$_2$][Ir$_6$(CO)$_{15}$(CO$_2$Et)] (**2**) was fully characterized by i.r., ^{1}H n.m.r. spectroscopy and analytical data. The i.r. spectrum (Table 1) is analogous to that of compound (**1**) and this together with the ^{1}H n.m.r. spectrum and analytical data suggest for complex (**2**) the same structure as that found for (**1**).

The addition of a large excess of Na(OMe) to a suspension of [Ir$_6$(CO)$_{16}$] (3.5 : 1), in methanol, leads to the formation of a red solution from which, by addition of an aqueous solution of tetraphenylphosphonium bromide, it was possible to isolate a red product. On the basis of analytical and spectroscopic data this product can be formulated as [PPh$_4$]$_2$[Ir$_6$(CO)$_{14}$(CO$_2$Me)$_2$] (**3**); to date, we have been unable to obtain single crystals of suitable quality for a complete *X*-ray analysis. By monitoring the solution by i.r. spectroscopy during the Na(OMe) addition, it is possible to observe the intermediate formation of the mono(methoxycarbonyl) complex [Ir$_6$(CO)$_{15}$(CO$_2$Me)]$^-$, which, when the molar ratio of Na(OMe) *vs.* [Ir$_6$(CO)$_{16}$] is increased from 1 : 1 to 3.5 : 1 slowly converts to the bis(methoxycarbonyl) derivative (**3**). In spite of the presence of excess Na(OMe) the formation of complex (**3**) is not complete and some of the mono(methoxycarbonyl) derivative (10—15%) is always present in the final product as shown by ^{1}H n.m.r. spectroscopy. The presence of this mono(methoxycarbonyl) derivative cannot be detected, in the methanolic solution, by i.r. spectroscopy due to the partial superimposition of the absorption bands of this compound and compound (**3**).

The ^{1}H n.m.r. spectrum (CDCl$_3$, 25 °C) of compound (**3**) shows the presence of a singlet at δ 3.31 p.p.m., due to the resonance of the methoxycarbonyl groups of compound (**3**), and a second singlet at δ 3.45 p.p.m., due to the resonance of the methoxycarbonyl group of [Ir$_6$(CO)$_{15}$(CO$_2$Me)]$^-$ (*ca.* 15% of the total product). The presence of only one singlet for compound (**3**) suggests the equivalence of the two methoxycarbonyl groups in solution.

Chemical Characterization of the [Ir$_6$(CO)$_{15}$(CO$_2$R)]$^-$ (R = Me *or* Et) *Anions.*—The [Ir$_6$(CO)$_{15}$(CO$_2$R)]$^-$ (R = Me or Et) anions react instantaneously with the stoicheiometric amount of H$_2$SO$_4$ or with a very large excess of MeCO$_2$H in thf or acetonitrile solution to give quantitatively [Ir$_6$(CO)$_{16}$] [equation (2)]. This behaviour has already been observed in the case of the analogous hexanuclear rhodium derivative[12] and in the tetranuclear iridium[1] and rhodium[10] derivatives.

$$[Ir_6(CO)_{15}(CO_2R)]^- + H^+ \longrightarrow [Ir_6(CO)_{16}] + ROH \quad (2)$$

These anions can undergo, under mild conditions, alcoholysis as previously found in the tetranuclear derivative of iridium.[7] The alkoxy groups exchange quickly with primary alcohols such as MeOH and EtOH while with secondary alcohols such as Pr^{i}OH the reaction is slower and incomplete, as found by integration of the n.m.r. signals of the methyl group against the isopropyl group.

Unlike the rhodium analogues,[12] the [Ir$_6$(CO)$_{15}$(CO$_2$R)]$^-$ (R = Me or Et) anions are not very sensitive to water; they can be recovered without any modification after 24 h from a thf solution containing 2% water; this stability is in agreement with the tetranuclear iridium analogue.[7]

The anions react rapidly in wet alcohol with K$_2$CO$_3$ or Na$_2$CO$_3$ under a CO atmosphere to give the known anion [Ir$_6$(CO)$_{15}$]$^{2-}$.[1,3] By contrast the hydrolysis of [Ir$_4$(CO)$_{11}$(CO$_2$Me)]$^-$ gives [Ir$_4$H(CO)$_{11}$]$^-$.[7] We cannot exclude the possibility that the hydrolysis of [Ir$_6$(CO)$_{15}$(CO$_2$R)]$^-$ proceeds through the formation of the intermediate species [Ir$_6$H-

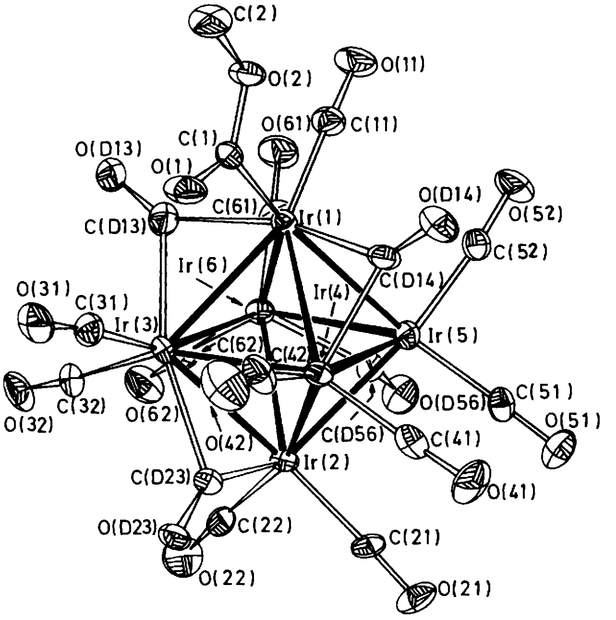

Figure. ORTEP view of the $[Ir_6(CO)_{15}(CO_2Me)]^-$ anion. Thermal ellipsoids are drawn with 30% probability

$(CO)_{15}]^-$, a species which is not easily detectable by i.r. spectroscopy owing to its instability in alkali media.[13]

Reactivity of $[PPh_4]_2[Ir_6(CO)_{14}(CO_2Me)_2]$ (**3**).—Compound (**3**) reacts with strong acids such as HCl in thf solution and is immediately and quantitatively transformed into $[Ir_6(CO)_{16}]$. On the other hand when (**3**) reacts with a slight excess of acetic acid, i.r. spectroscopy shows evidence of the formation of the intermediate monoester $[Ir_6(CO)_{15}(CO_2Me)]^-$. Complex (**3**) is stable for a prolonged period of time in wet solvents: it can be recovered without any modification after 24 h from a thf solution containing 5% water. Compound (**3**) is quickly transformed into $[Ir_6(CO)_{15}]^{2-}$ when treated with a methanolic solution of potassium hydroxide.

Description of the Structure of $[N(PPh_3)_2][Ir_6(\mu\text{-}CO)_4(CO)_{11}(CO_2Me)]$ (**1**).—Crystals of compound (**1**) consist of bulky $[N(PPh_3)_2]^+$ cations and $[Ir_6(CO)_{15}(CO_2Me)]^-$ anions with no unusual van der Waals interactions. A molecular plot of $[Ir_6(CO)_{15}(CO_2Me)]^-$ is shown in the Figure; selected bond distances and angles are given in Tables 2 and 3, respectively.

The anion, which lacks any idealized symmetry element, consists of an octahedral cluster of iridium atoms with eleven terminal, four edge-bridging CO groups and a σ-bonded methoxycarbonyl group, the last replacing a terminal CO ligand of the parent $[Ir_6(CO)_{16}]$.[3] Such a substitution results in a bonding mode for the bridging carbonyls which is different from that found in the red isomer of the parent $[Ir_6(CO)_{16}]$, and also in the black one in which the four edge-bridging CO groups are related by C_2 symmetry.[2]

In compound (**1**) each iridium atom is bonded to two terminal CO groups with the exception of Ir(1), which bears the methoxycarbonyl group. Moreover Ir(1) and Ir(3) are bonded to two edge-bridging carbonyls while the other metal atoms bond to one only. The two bridging CO groups bonded to Ir(3) are asymmetric, with the Ir(3)–C distances being the longer in both cases [mean Ir(3)–C = 2.222, mean Ir(1,2)–C = 2.035 Å]. The two remaining bridging CO groups are symmetric.

Table 2. Selected bond distances (Å) for the $[Ir_6(CO)_{15}(CO_2Me)]^-$ anion with estimated standard deviations (e.s.d.s) in parentheses

Ir–Ir

Ir(1)–Ir(3)	2.774(1)	Ir(2)–Ir(5)	2.778(1)
Ir(1)–Ir(4)	2.744(1)	Ir(2)–Ir(6)	2.794(1)
Ir(1)–Ir(5)	2.870(1)	Ir(3)–Ir(4)	2.794(1)
Ir(1)–Ir(6)	2.868(1)	Ir(3)–Ir(6)	2.832(1)
Ir(2)–Ir(3)	2.759(1)	Ir(4)–Ir(5)	2.826(1)
Ir(2)–Ir(4)	2.779(1)	Ir(5)–Ir(6)	2.703(1)
		Mean	2.793

$Ir\text{–}CO_2Me$

Ir(1)–C(1)	2.087(13)	C(1)–O(2)	1.290(15)
C(1)–O(1)	1.216(14)	O(2)–C(2)	1.456(15)

$Ir\text{–}C_{terminal}$		$C\text{–}O_{terminal}$	
Ir(1)–C(11)	1.859(15)	C(11)–O(11)	1.121(16)
Ir(2)–C(21)	1.903(15)	C(21)–O(21)	1.113(15)
Ir(2)–C(22)	1.869(16)	C(22)–O(22)	1.163(17)
Ir(3)–C(31)	1.876(15)	C(31)–O(31)	1.143(16)
Ir(3)–C(32)	1.895(17)	C(32)–O(32)	1.133(17)
Ir(4)–C(41)	1.861(16)	C(41)–O(41)	1.147(16)
Ir(4)–C(42)	1.909(16)	C(42)–O(42)	1.097(16)
Ir(5)–C(51)	1.859(16)	C(51)–O(51)	1.147(16)
Ir(5)–C(52)	1.875(16)	C(52)–O(52)	1.135(17)
Ir(6)–C(61)	1.864(15)	C(61)–O(61)	1.151(15)
Ir(6)–C(62)	1.891(16)	C(62)–O(62)	1.140(16)

$Ir\text{–}C_{bridging}$		$C\text{–}O_{bridging}$	
Ir(1)–C(D14)	2.095(16)	C(D14)–O(D14)	1.193(17)
Ir(4)–C(D14)	2.067(14)		
Ir(1)–C(D13)	2.044(16)	C(D13)–O(D13)	1.161(16)
Ir(3)–C(D13)	2.194(16)		
Ir(2)–C(D23)	2.026(14)	C(D23)–O(D23)	1.169(15)
Ir(3)–C(D23)	2.251(13)		
Ir(5)–C(D56)	2.078(16)	C(D56)–O(D56)	1.175(21)
Ir(6)–C(D56)	2.065(16)		

Table 3. Selected bond angles (°) for the $[Ir_6(CO)_{15}(CO_2Me)]^-$ anion with e.s.d.s in parentheses

Ir(1)–C(11)–O(11)	178.5(13)	Ir(2)–C(21)–O(21)	177.6(14)
Ir(2)–C(22)–O(22)	178.8(14)	Ir(3)–C(31)–O(31)	172.8(15)
Ir(3)–C(32)–O(32)	174.1(15)	Ir(4)–C(41)–O(41)	177.5(14)
Ir(4)–C(42)–O(42)	171.1(16)	Ir(5)–C(51)–O(51)	175.7(14)
Ir(5)–C(52)–O(52)	175.4(15)	Ir(6)–C(61)–O(61)	175.7(14)
Ir(6)–C(62)–O(62)	175.5(14)	Ir(1)–C(D14)–Ir(4)	82.5(6)
Ir(1)–C(D14)–O(D14)	138.8(11)	Ir(4)–C(D14)–O(D14)	136.6(12)
Ir(1)–C(D13)–Ir(3)	81.7(6)	Ir(1)–C(D13)–O(D13)	144.3(14)
Ir(3)–C(D13)–O(D13)	132.3(13)	Ir(2)–C(D23)–Ir(3)	80.1(15)
Ir(2)–C(D23)–O(D23)	140.1(12)	Ir(3)–C(D23)–O(D23)	133.5(12)
Ir(5)–C(D56)–Ir(6)	81.5(6)	Ir(5)–C(D56)–O(D56)	137.5(11)
Ir(6)–C(D56)–O(D56)	140.4(11)		

$Ir\text{–}CO_2Me$

Ir(1)–C(1)–O(1)	122.7(10)	Ir(1)–C(1)–O(2)	115.2(9)
O(1)–C(1)–O(2)	122.1(13)	C(1)–O(2)–C(2)	116.3(11)

The iridium methoxycarbonyl moiety (excluding the methyl hydrogens) is strictly planar within experimental error (see SUP No. 56426). The least-squares plane through atoms Ir(1), Ir(2), C(1), O(1), O(2), C(11), and O(11) is nearly perpendicular to that defined by atoms Ir(3), Ir(4), Ir(5), and Ir(6) (dihedral angle 90.8°) and asymmetrically bisects the vectors Ir(3)–Ir(4) and Ir(5)–Ir(6), so that atoms Ir(3,4,5,6) are 1.34, 1.45, 1.28, and 1.42 Å, respectively from this plane. In contrast, atoms C(D13) and C(D14) are nearly equidistant from the same plane (2.02

and 2.03 Å, respectively). Therefore it seems that the observed slight rotation of the plane around the Ir(1)—Ir(2) axis is likely to minimize non-bonded repulsions between the methoxycarbonyl ligand and the bridging carbonyl groups spanning edges Ir(1)–Ir(3) and Ir(1)–Ir(4).

The electronic interaction between the iridium atom and the alkoxycarbonyl group could be described in terms of a σ bond plus some contribution of a d_π–p_π interaction of the same type as suggested by Treichel *et al.*[14] and Coates *et al.*[15] for a metal–acyl bond. A comparison of the M–C bond distances in $[Rh_6(CO)_{15}(CO_2Me)]^-$ [Rh–C$_{ester}$ = 1.96(2) Å][8] and $[Rh_6(CO)_{15}\{C(O)Et\}]^-$ [Rh–C$_{acyl}$ = 2.06(2) Å][8] with those found in the analogous iridium derivatives {compound (**1**) Ir–C$_{ester}$ = 2.087(13) Å; $[Ir_6(CO)_{15}\{C(O)Et\}]^-$, Ir–C$_{acyl}$ = 2.078(12) Å[6]} and with the value found in the $[Ir_4(CO)_{11}(CO_2Me)]^-$ derivative [Ir–C$_{ester}$ = 2.20(4) Å][7] suggests that the d_π–p_π interaction is less in the iridium complexes than in the rhodium derivatives. Moreover assuming for iridium a covalent radius of 1.35 Å and for a sp^2-hybridized carbon a radius of 0.74 Å, the calculated Ir–C bond length of 2.09 Å is comparable with the experimental value found in complex (**1**). Therefore the Ir–C$_{ester}$ bond can be described as a pure σ covalent bond with scarce, if any, evidence of d_π–p_π interaction.

The Ir(1)–C(1) bond distance [2.087(13) Å] is comparable with that found in $[Ir_4(CO)_{11}(CO_2Me)]^-$[7] but longer than the Ir–C distances of the terminal CO groups owing to a smaller π acceptor ability of the methoxycarbonyl fragment with respect to the CO ligand. The pattern of bond lengths and angles for the methoxycarbonyl group is comparable to that found in $[Ir_4(CO)_{11}(CO_2Me)]^-$[7] and $[Rh_6(CO)_{15}(CO_2Me)]^-$.[8]

The stereochemistry of the cation agrees with several other independent determinations and has been discussed in detail by Dahl and co-workers.[16] Noteworthy features of the cation, which is in the common 'bent' form are: P–N–P 135.6(7)°, P–N 1.585(10) and 1.593(10) Å, mean P–C 1.796 and mean C–C 1.370 Å.

Experimental

All reactions were carried out under a carbon monoxide or nitrogen atmosphere using Schlenk-tube techniques. Solvents were purified and dried by standard methods. Infrared spectra (Table 1) were recorded on a Perkin-Elmer 781 spectrometer: the spectra were calibrated with polystyrene. Nuclear magnetic resonance spectra (internal reference $SiMe_4$) (Table 1) were recorded on a Bruker WP80 spectrometer at 80 MHz; chemical shifts (δ) are reported in p.p.m. downfield of the standard. $[Ir_6(CO)_{16}]$ was prepared as described in the literature.[2]

Synthesis of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ (**1**).—A suspension of $[Ir_6(CO)_{16}]$ (0.622 g, 0.39 mmol) in dry methanol (25 cm^3) was stirred at room temperature with 1.17 cm^3 of a 0.5 mol dm^{-3} solution of Na(OMe) in dry methanol {molar ratio $[Ir_6(CO)_{16}]$:Na(OMe) = 1:1.5} until all the $[Ir_6(CO)_{16}]$ had reacted (*ca.* 1 h). The resulting orange-yellow solution was poured into a stirred solution of $[N(PPh_3)_2]Cl$ (0.5 g) and KCl (0.5 g) in water (100 cm^3). The resulting orange precipitate was collected by filtration, washed with water (3 × 10 cm^3), and vacuum dried (0.635 g, 75%) (Found: C, 29.8, H, 1.5; N, 0.7. $C_{53}H_{33}Ir_6NO_{17}P_2$ requires C, 29.3, H, 1.5; N, 0.6%). Compound (1) is soluble and stable, under a nitrogen atmosphere, for a prolonged period of time in CH_2Cl_2, $CHCl_3$, thf, or CH_3CN and is insoluble in aliphatic and aromatic hydrocarbons.

The $[PPh_3(CH_2Ph)]^+$, $[PPh_4]^+$, $[NMe_3(CH_2Ph)]^+$, $[NEt_4]^+$, and $[NMe_4]^+$ salts were obtained similarly. For the larger cations there was an immediate precipitation whereas concentration was necessary in order to induce precipitation of the products containing the smaller cations.

Synthesis of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Et)]$ (**2**).—This compound was prepared as described for derivative (**1**) but using dry ethanol (30 cm^3), $[Ir_6(CO)_{16}]$ (0.45 g, 0.28 mmol), and 0.65 cm^3 of a 0.65 mol dm^{-3} solution of Na(OEt) in ethanol {molar ratio $[Ir_6(CO)_{16}]$: Na(OEt) = 1 : 1.5}. The reaction was complete after *ca.* 1.5 h (0.428 g, 70%) (Found: C, 29.1; H, 1.4; N, 0.6. $C_{54}H_{35}Ir_6NO_{17}P_2$ requires C, 29.7; H, 1.6; N, 0.6%).

Synthesis of $[PPh_4]_2[Ir_6(CO)_{14}(CO_2Me)_2]$ (**3**).—A suspension of $[Ir_6(CO)_{16}]$ (0.423 g, 0.26 mmol) in dry methanol (20 cm^3) was stirred at room temperature with 1.9 cm^3 of a 0.5 mol dm^{-3} solution of Na(OMe) in dry methanol {molar ratio $[Ir_6(CO)_{16}]$:Na(OMe) = 1:3.5} until all the $[Ir_6(CO)_{16}]$ had reacted (*ca.* 20 min). The compound was isolated as described for complex (**1**) (0.42 g, 70%) (Found: C, 38.0; H, 1.9. $C_{66}H_{46}Ir_6O_{18}P_2$ requires C, 33.8; H, 2.0%). Compound (**3**) is soluble in thf, CH_3CN, or $CHCl_3$ and insoluble in aliphatic and aromatic hydrocarbons.

Reaction of $[PPh_3(CH_2Ph)][Ir_6(CO)_{15}(CO_2Me)]$ *with* EtOH.—$[PPh_3(CH_2Ph)][Ir_6(CO)_{15}(CO_2Me)]$ (0.32 g, 0.16 mmol) in dry ethanol (20 cm^3) was stirred for 45 min at 40 °C under a carbon monoxide atmosphere. After filtration from the hot solution of some by-products, the orange solution was cooled to −20 °C. The resulting orange microcrystalline compound was filtered off, washed with cold ethanol (2 × 10 cm^3), and vacuum dried. The product was recovered in *ca.* 75% yield. The ^{1}H n.m.r. spectrum ($CDCl_3$, 32 °C) showed a complete conversion from the methyl to the ethyl derivative.

Reaction of $[PPh_3(CH_2Ph)][Ir_6(CO)_{15}(CO_2Me)]$ *with* Pr^{i}OH.—A suspension of $[PPh_3(CH_2Ph)][Ir_6(CO)_{15}(CO_2Me)]$ (0.417 g, 0.21 mmol) in dry propan-2-ol (75 cm^3) was stirred for 45 min at 60 °C under a carbon monoxide atmosphere. After filtration from the hot solution of some by-products, the orange solution was cooled to −20 °C. The resulting orange compound was filtered off, washed with cold propan-2-ol (3 × 10 cm^3), and vacuum dried. The product was recovered in *ca.* 80% yield. The ^{1}H n.m.r. spectrum ($CDCl_3$, 32 °C) showed both methoxy [δ(OMe) = 3.45(s) p.p.m.] and isopropoxy [$\delta(OCHMe_2)$ = 1.25(d) p.p.m.; the septet expected for OC*H*Me$_2$ was not detected] signals in a 1:3 ratio in agreement with a 60% conversion.

Reaction of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ *with Acetic Acid.*—A solution of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ (0.38 g, 0.17 mmol) in thf (20 cm^3) was treated with acetic acid (2 cm^3) and the mixture stirred for 20 min. A red-orange precipitate of $[Ir_6(CO)_{16}]$ separated from the solution, which was filtered off and washed with thf (4 × 5 cm^3) and n-heptane. Yield 0.25 g (90%).

$[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Et)]$ (0.25 g, 0.11 mmol) reacts with acetic acid in a similar way to give $[Ir_6(CO)_{16}]$. Yield 0.15 g (85%).

Reaction of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ *with* K_2CO_3.—A suspension of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ (0.35 g, 0.16 mmol) in methanol (25 cm^3) containing 5% of water was stirred, under a carbon monoxide atmosphere, with K_2CO_3 (0.08 g, 0.6 mmol). After 3 h a solution of NaCl (0.5 g) and $[N(PPh_3)_2]Cl$ (0.5 g) in MeOH (2 cm^3) and water (75 cm^3) was added. The resulting brown compound was filtered off, washed with water (3 × 10 cm^3) and propan-2-ol (2 × 10 cm^3), and vacuum dried. Yield 90%. The product showed an i.r. spectrum

Table 4. Positional parameters for non-hydrogen atoms with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Ir(1)	0.224 25(5)	0.268 03(3)	0.209 57(3)	P(1)	0.502 1(3)	0.291 0(2)	0.796 5(2)
Ir(2)	−0.136 16(5)	0.196 83(3)	0.199 16(3)	P(2)	0.625 3(3)	0.250 1(2)	0.643 6(2)
Ir(3)	0.003 07(5)	0.316 18(3)	0.136 56(4)	N	0.594(1)	0.303 3(6)	0.727 7(6)
Ir(4)	0.039 03(5)	0.303 65(3)	0.309 03(3)	C(111)	0.353(1)	0.328 0(8)	0.769 3(8)
Ir(5)	0.080 39(5)	0.137 95(3)	0.266 31(3)	C(112)	0.321(2)	0.318(1)	0.689(1)
Ir(6)	0.049 94(5)	0.150 53(3)	0.099 49(3)	C(113)	0.200(2)	0.375(1)	0.671(1)
C(11)	0.373(1)	0.220 4(8)	0.200(1)	C(114)	0.121(2)	0.377(1)	0.729(1)
O(11)	0.462(1)	0.190 5(7)	0.194 8(9)	C(115)	0.150(2)	0.361(1)	0.807(1)
C(21)	−0.229(1)	0.160 5(9)	0.283 4(9)	C(116)	0.267(1)	0.334 9(9)	0.828 5(9)
O(21)	−0.286(1)	0.139 8(6)	0.331 2(7)	C(121)	0.469(1)	0.188 1(7)	0.814 6(8)
C(22)	−0.264(1)	0.165 3(9)	0.109 9(8)	C(122)	0.356(1)	0.143 8(9)	0.789 5(9)
O(22)	−0.345(1)	0.145 1(9)	0.055 3(7)	C(123)	0.337(2)	0.062(1)	0.801(1)
C(31)	0.037(1)	0.429 9(9)	0.147(1)	C(124)	0.437(2)	0.028(1)	0.835(1)
O(31)	0.016(1)	0.499 1(6)	0.148 5(8)	C(125)	0.553(2)	0.069(1)	0.859(1)
C(32)	−0.087(1)	0.308 6(9)	0.027 4(9)	C(126)	0.568(1)	0.150 7(9)	0.848 9(9)
O(32)	−0.132(1)	0.301 8(8)	−0.040 6(7)	C(131)	0.572(1)	0.349 3(8)	0.896 2(8)
C(41)	−0.016(1)	0.286 7(8)	0.411 6(9)	C(132)	0.539(1)	0.326 3(8)	0.970 8(9)
O(41)	−0.045(1)	0.275 8(8)	0.476 0(6)	C(133)	0.587(1)	0.375 2(9)	1.047(1)
C(42)	0.051(2)	0.419(1)	0.339(1)	C(134)	0.666(1)	0.443 5(9)	1.045 5(9)
O(42)	0.044(1)	0.484 4(6)	0.360 4(8)	C(135)	0.697(1)	0.466 8(9)	0.973(1)
C(51)	0.015(1)	0.099 2(8)	0.357 1(9)	C(136)	0.651(1)	0.418 5(8)	0.896 1(9)
O(51)	−0.031(1)	0.071 9(7)	0.409 6(6)	C(211)	0.640(1)	0.315 4(8)	0.566 2(9)
C(52)	0.227(1)	0.087 0(9)	0.286(1)	C(212)	0.627(2)	0.286(1)	0.481(1)
O(52)	0.320(1)	0.060 8(8)	0.296 5(9)	C(213)	0.647(2)	0.341(1)	0.420(1)
C(61)	0.185(1)	0.103 3(9)	0.056 3(9)	C(214)	0.675(2)	0.422(1)	0.447(1)
O(61)	0.268(1)	0.077 8(7)	0.026 3(7)	C(215)	0.683(2)	0.452(1)	0.534(1)
C(62)	−0.058(1)	0.125 9(9)	−0.003 2(8)	C(216)	0.665(1)	0.398 1(9)	0.594(1)
O(62)	−0.129(1)	0.108 4(7)	−0.062 3(7)	C(221)	0.511(1)	0.165 8(7)	0.598 5(8)
C(D14)	0.223(1)	0.283 1(8)	0.341 1(9)	C(222)	0.525(1)	0.088 9(9)	0.619 8(9)
O(D14)	0.296(1)	0.294 0(7)	0.403 8(7)	C(223)	0.427(2)	0.027(1)	0.595(1)
C(D13)	0.181(1)	0.292 1(9)	0.089(1)	C(224)	0.319(2)	0.044(1)	0.549(1)
O(D13)	0.223(1)	0.305 6(6)	0.028 1(6)	C(225)	0.305(2)	0.119(1)	0.526(1)
C(D23)	−0.156(1)	0.318 1(9)	0.216 6(9)	C(226)	0.402(2)	0.181 2(9)	0.553(1)
O(D23)	−0.232 1(8)	0.362 8(6)	0.228 5(6)	C(231)	0.772(1)	0.207 5(8)	0.663 1(8)
C(D56)	−0.008(1)	0.057 1(9)	0.162 9(8)	C(232)	0.836(1)	0.221 5(9)	0.743 3(9)
O(D56)	−0.054(1)	−0.010 8(5)	0.149 3(7)	C(233)	0.942(2)	0.182(1)	0.760(1)
C(1)	0.325(1)	0.382 8(8)	0.232 2(9)	C(234)	0.988(2)	0.136(1)	0.696(1)
O(1)	0.275 9(9)	0.446 0(6)	0.243 8(8)	C(235)	0.930(2)	0.125(1)	0.616(1)
O(2)	0.444 9(8)	0.382 1(6)	0.235 2(6)	C(236)	0.818(1)	0.159 7(9)	0.599(1)
C(2)	0.518(1)	0.461 4(9)	0.253(1)				

identical to that of an authentic sample of $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$.

In a similar way $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Et)]$ (0.31 g, 0.14 mmol) reacts with K_2CO_3 to give $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$. Yield 0.29 g (80%).

X-Ray Analysis of $[N(PPh_3)_2][Ir_6(CO)_{15}(CO_2Me)]$ (**1**).—Crystals of complex (**1**) suitable for *X*-ray analysis were obtained by slow diffusion of heptane (40 cm^3) into a dichloromethane (10 cm^3) solution containing the salt (0.20 g). The red-orange crystals are stable in air and have an elongated prismatic habit. A crystal of approximate dimensions 0.3 × 0.15 × 0.20 mm was used for the data collection.

Crystal data. $C_{53}H_{33}Ir_6NO_{17}P_2$, $M = 2\,170.99$, triclinic, space group $P\bar{1}$, $a = 10.813(3)$, $b = 16.613(3)$, $c = 16.061(2)$ Å, $\alpha = 97.96(1)$, $\beta = 96.20(1)$, $\gamma = 94.58(2)°$, $U = 2\,827$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, $D_c = 2.55$ g cm^{-3}, $Z = 2$, $D_m = 2.54(2)$ g cm^{-3}, $F(000) = 1\,972$, μ(Mo-K_α) = 141.4 cm^{-1}.

Intensity data. A single prismatic crystal was mounted on a NONIUS CAD-4 automated diffractometer and the setting angles of 25 accurately centred reflections, in the range $15 < 2\theta < 23.5°$, were used to determine accurate cell parameters and the orientation matrix by least-squares methods. 9 873 Independent reflections, corresponding to the $\pm h$, $\pm k$, l hemisphere, in the range $3 \leqslant \theta \leqslant 25°$ were collected with graphite-monochromated Mo-K_α radiation using an ω-scan technique, at a variable rate with maximum prescan rate of 5° min^{-1}, the scan width being $(1.2 + 0.35 \tan \theta)°$. The intensities of three standard reflections were measured every hour of the exposure and revealed a decrease in the scattering power of the crystal which at the end of the data collection was *ca.* 6%, evaluated on F_o.

Data reduction, structure solution and refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 5 291 independent reflections, with $I \geqslant 3\sigma(I)$, corrected for Lorentz, polarization, decay and absorption effects (the maximum, minimum, and average transmission factors were 1.00, 0.38, and 0.75 respectively, from an empirical correction based on a set of ψ scans of three reflections with χ values near to 90°).[17] The function minimized was $\Sigma w(F_o - k|F_c|)^2$. All the atoms of the anion and the phosphorus atoms of the cation were refined with anisotropic thermal parameters. The hydrogen atoms of the cation, located in their idealized positions, were introduced in the last cycles of the refinement but were not refined. The final conventional agreement factors R $[= \Sigma(F_o - k|F_c|)/\Sigma F_o]$ and $R'\{= [\Sigma w(F_o - k|F_c)^2/\Sigma wF_o]^{\frac{1}{2}}\}$ were 0.033 and 0.040 respectively. Weights were assigned to individual observations according to the formula $w = \sigma^{-2}(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (iI)^2]^{\frac{1}{2}}/Lp$, and i, the ignorance factor is equal to 0.04. Final positional parameters of the non-hydrogen atoms are given in Table 4.

All computations were made on a PDP 11/34 computer using the ENRAF-NONIUS Structure Determination Package (SDP) and the physical constants listed therein.[18]

Acknowledgements

We thank the Italian C.N.R. for financial assistance.

References

1 L. Malatesta, G. Caglio, and M. Angoletta, *Chem. Commun.*, 1970, 532; *J. Organomet. Chem.*, 1975, **94**, 99.

2 L. Garlaschelli, S. Martinengo, P. L. Bellon, F. Demartin, M. Manassero, M. Y. Chiang, C. Y. Wei, and R. Bau, *J. Am. Chem. Soc.*, 1984, **106**, 6664.

3 F. Demartin, M. Manassero, M. Sansoni, L. Garlaschelli, S. Martinengo, and F. Canziani, *J. Chem. Soc., Chem. Commun.*, 1980, 903.

4 F. Demartin, M. Manassero, M. Sansoni, L. Garlaschelli, U. Sartorelli, and F. Tagliabue, *J. Organomet. Chem.*, 1982, **234**, C39.

5 F. Demartin, M. Manassero, M. Sansoni, L. Garlaschelli, M. C. Malatesta, and U. Sartorelli, *J. Organomet. Chem.*, 1983, **248**, C17.

6 F. Demartin, M. Manassero, M. Sansoni, L. Garlaschelli, C. Raimondi, and S. Martinengo, *J. Organomet. Chem.*, 1983, **243**, C10.

7 L. Garlaschelli, S. Martinengo, P. Chini, F. Canziani, and R. Bau, *J. Organomet. Chem.*, 1981, **213**, 379.

8 G. Ciani, A. Sironi, P. Chini, and S. Martinengo, *J. Organomet. Chem.*, 1981, **213**, C37.

9 D. Braga, B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, J. N. Nicholls, and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1982, 966.

10 S. Martinengo, A. Fumagalli, P. Chini, V. G. Albano, and G. Ciani, *J. Organomet. Chem.*, 1976, **116**, 333.

11 G. Longoni, S. Campanella, A. Ceriotti, P. Chini, V. G. Albano, and D. Braga, *J. Chem. Soc., Dalton Trans.*, 1980, 1816.

12 P. Chini, S. Martinengo, and G. Giordano, *Gazz. Chim. Ital.*, 1972, **102**, 330.

13 L. Garlaschelli and S. Martinengo, unpublished work.

14 P. H. Treichel, R. L. Subkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177.

15 G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' 3rd edn., Methuen, London, 1967, vol. 2, p. 261.

16 L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Am. Chem. Soc.*, 1970, **92**, 7327.

17 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

18 ENRAF-NONIUS Structure Determination Package, Delft, 1979.

Received 17*th May* 1985; *Paper* 5/830