A New Synthesis and the *X*-Ray Crystal Structure of Bis(trimethylbenzylammonium) Tri-μ-carbonyl-dodecacarbonyl-*octahedro*-hexairidate(2−)

By Francesco Demartin, Mario Manassero,* Mirella Sansoni, Luigi Garlaschelli,* and Secondo Martinengo

(*Istituto di Chimica Generale dell'Università e Centro del CNR, via G. Venezian* 21, 20133 *Milano, Italy*)

and Franco Canziani

(*Istituto di Chimica, Facoltà di Scienze, Università di Salerno,* 34100 *Salerno, Italy*).

Summary The $[Ir_6(CO)_{15}]^{2-}$ dianion, obtained by a two-step carbonylative reduction of K_2IrCl_6 in 2-methoxyethanol containing 10% of water, has been shown by *X*-ray diffraction to contain an octahedral Ir_6 cluster with twelve terminal and three symmetrical edge-bridging carbonyl groups.

Although a number of hexa- and octa-nuclear carbonyl clusters of iridium have been described since 1970,[1] none of their solid state structures has been directly established so far. As a part of a reinvestigation of the chemistry of these compounds, we report here an improved synthesis and the *X*-ray crystal structure of $[NMe_3CH_2Ph]_2[Ir_6(CO)_{15}]$, thus providing the second direct structure determination of a non-substituted carbonyl cluster of iridium reported to date [the first being that of the heavily disordered $Ir_4(CO)_{12}$].[2]

The $[Ir_6(CO)_{15}]^{2-}$ anion was prepared by treating a solution of $[Ir(CO)_2Cl_2]^-$ (0·05—0·1 M) in 2-methoxyethanol containing 10% of water† with a calculated amount of K_2CO_3 at 90 °C for 5 h under CO, according to the apparent stoicheiometry shown in equation (1). The corresponding $(NMe_3CH_2Ph)^+$ salt was obtained after concentration *in vacuo* by addition of an aqueous solution of $(NMe_3CH_2Ph)Cl$, and was recrystallized from tetrahydrofuran (THF) and propan-2-ol by slow diffusion. The overall yields were 70—75%; *cf.* 35—45% when the sparingly soluble $Ir_4(CO)_{12}$ is used as starting material.[1] The product was identified by i.r.‡ and elemental analysis data, and its molecular geometry has been established by a single-crystal *X*-ray diffraction study (dark-brown, air-sensitive triclinic prisms).

$$6[Ir(CO)_2Cl_2]^- + 12CO_3^{2-} + 7CO + 8H_2O = [Ir_6(CO)_{15}]^{2-} + 12Cl^- + 16HCO_3^- \qquad (1)$$

Crystal data: $M = 1723{\cdot}60$, space group $P\bar{1}$ (after refinement), $a = 22{\cdot}042(8)$, $b = 9{\cdot}806(4)$, $c = 10{\cdot}373(4)$ Å, $\alpha = 100{\cdot}65(3)$, $\beta = 95{\cdot}88(3)$, $\gamma = 99{\cdot}04(3)°$, $U = 2156$ Å^3, $D_m = 2{\cdot}95$, $D_c = 2{\cdot}89$ g cm^{-3} for $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 196{\cdot}3$ cm^{-1}. Data were collected on a BASIC diffractometer[3] with graphite-monochromatized Mo-K_α radiation in the 2θ range 6—50°. The structure was solved by conventional Patterson and Fourier methods on the basis of 4004 independent, absorption-corrected reflections having $I \geqslant 3\sigma(I)$. A block-matrix least-squares refinement, carried out after assigning anisotropic thermal parameters to all the atoms of the anion and constraining the phenyl rings of the cation to D_{6h} geometry, led to a current R value of 0·039.§

The structure of the $[Ir_6(CO)_{15}]^{2-}$ dianion consists of an essentially regular octahedron of metal atoms connected to

---

† Obtained by carbonylation in the same solvent of K_2IrCl_6 under CO at 110 °C for *ca.* 18 h, L. Garlaschelli, S. Martinengo, and F. Canziani, unpublished results.

‡ ν_{CO} (Nujol) broad bands at 1970s, 1770m, and 1730m cm^{-1}; ν_{CO} (THF) 1975vs, 1925w, 1775m, and 1730m cm^{-1}.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

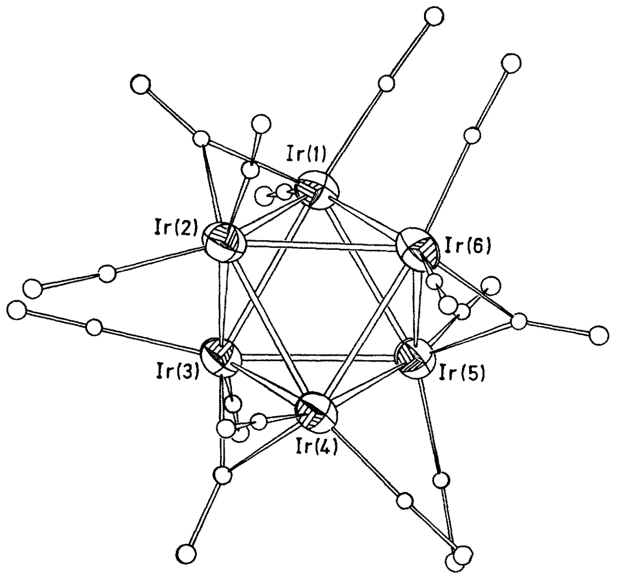

FIGURE A projection of $[Ir_6(CO)_{15}]^{2-}$ along the idealized three-fold axis Metal–metal bond lengths are Ir(1)–Ir(2) 2 730(1), Ir(3)–Ir(4) 2 735(1), Ir(5)–Ir(6) 2 743(1), Ir(1)–Ir(3) 2 766(1), Ir(1)–Ir(5) 2 797(1), Ir(1)–Ir(6) 2 822(1), Ir(2)–Ir(3) 2 779(1), Ir(2)–Ir(4) 2 792(1), Ir(2)–Ir(6) 2 789(1), Ir(3)–Ir(5) 2 782(1), Ir(4)–Ir(5) 2 774(1), Ir(4)–Ir(6) 2 767(1) Å

twelve terminal and three symmetrically edge-bridging carbonyl ligands (see the Figure) All the iridium atoms are stereochemically equivalent [as previously found only in $Ir_4(CO)_{12}$[2]] each of them being bonded to one edge-bridging and two terminal carbonyl groups, so that the overall idealized symmetry of the anion is D_3 (32) The three bridging CO ligands are approximately normal to the idealized three-fold axis The twelve terminal ones can be divided into two sets, six of them being in an axial, and six in an equatorial configuration The three CO-bridged Ir–Ir edges (see Figure caption) are significantly shorter than the other unbridged nine, with mean values of 2 736 and 2 785 Å, respectively Both these values are significantly higher than those found in most of the iridium carbonyl clusters so far characterized {see for instance the unbridged Ir–Ir distance in $Ir_4(CO)_{12}$ (2 693 Å)[2b] and the symmetrically bridged one in $[Ir_4(CO)_{11}Br]^-$ (2 695 Å)[4]} Local lengthenings of the Ir–Ir interactions have been found previously in $[Ir_4(CO)_{10}H_2]^{2-}$,[5] $Ir_4(CO)_5(C_8H_{11})_2(C_8H_{10})$,[6] and $Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})$,[7] and in all cases they have been ascribed to the peculiar bonding environment of the iridium atoms involved Rationales for the lengthening observed in $[Ir_6(CO)_{15}]^{2-}$ should take into account both the higher co-ordination number of the iridium atoms, with respect to the tetranuclear clusters, and the presence of the anionic negative charge All the Ir–C and C–O bonding parameters in the present compound are normal, with average values for equivalent interactions of Ir–C(t) 1 860, Ir–C(b) 2 038, C–O(t) 1 162, C–O(b) 1 184 Å Ir–C–O(t) 176 2, and Ir–C–O(b) 137 8° Typical e s d 's on single distances are Ir–C 0 019 and C–O 0 025 Å The present structure can be usefully compared to that of the homologous $[Co_6(CO)_{15}]^{2-}$ dianion The latter has an overall C_{3v} symmetry, with three edge-bridging and three face-bridging carbonyl ligands[8] Thus, $[Ir_6(CO)_{15}]^{2-}$ provides a new example of the lower tendency of iridium with respect to cobalt and rhodium, to give carbonyl-bridged structures, a behaviour previously observed in the tetrahedral clusters

The i r spectrum of $[Ir_6(CO)_{15}]^{2-}$ in solution appears to be slightly dependent on both solvent and cation ¶ Protonation of the dianion, carried out with H_2SO_4 or CF_3CO_2H in THF or CH_2Cl_2, seems to occur without major structural changes

We are indebted to the late Prof P Chini for his encouragement of this work Financial support from the Italian CNR is also acknowledged

(*Received*, 21*st May* 1980, *Com* 549)

¶ ν_{CO} for $[NMe_3CH_2Ph]_2[Ir_6(CO)_{15}]$ in MeCN 1975vs, 1935w, and 1755m cm^{-1}

[1] L Malatesta, G Caglio, and M Angoletta, *J Chem Soc , Chem Commun* , 1970, **532**, M Angoletta, L Malatesta, and G Caglio, *J Organomet Chem* , 1975, **94**, 99
[2] (a) G R Wilkes, Ph D thesis, University of Wisconsin, 1965, (b) M R Churchill and J P Hutchinson, *Inorg Chem* , 1978, **17**, 3528
[3] L Casella, M Gullotti, A Pasini, G Ciani, M Manassero, and A Sironi, *Inorg Chim Acta*, 1978, **26**, L1
[4] P Chini, G Ciani, L Garlaschelli, M Manassero, S Martinengo, A Sironi, and F Canziani, *J Organomet Chem* , 1978 **152**, C35
[5] G Ciani, M Manassero, V G Albano, F Canziani, G Giordano, S Martinengo, and P Chini, *J Organomet Chem* , 1978, **150**, C17
[6] G F Stuntz, J R Shapley, and C G Pierpont, *Inorg Chem* , 1978, **17**, 2596
[7] C G Pierpont, G F Stuntz, and J R Shapley, *J Am Chem Soc* , 1978, **100**, 616, C G Pierpont, *Inorg Chem* , 1979, **18**, 2972
[8] V G Albano, P Chini, and V Scatturin, *J Organomet Chem* , 1968, **15**, 423