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Chemistry of Iridium Carbonyl Cluster Complexes. Synthesis and X-ray Crystal Structure Determination of the $[\text{NMe}_3(\text{CH}_2\text{Ph})_3]_3[\text{Ir}_9(\mu\text{-CO})_7(\text{CO})_{13}]$ Complex Containing a Cofacial Biocuboidal Iridium Cluster. Another Example of Different Electron Counting between Isoskeletal Rhodium and Iridium Carbonyl Clusters

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Introduction

As a part of our studies on iridium carbonyl clusters of medium nuclearity (6–12 metal atoms), we reported the syntheses and the structures of several compounds, namely, neutral² and anionic hexanuclear species,³ the octanuclear $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ complex,⁴ and the dodecanuclear derivatives $[\text{Ir}_{12}(\text{CO})_{26}]^{2-5}$ and $[\text{Ir}_{12}(\text{CO})_{24}]^{2-6}$. Preliminary X-ray data indicated also the existence of an undecanuclear species, although not fully characterized.⁶ Additionally, a heptanuclear species, $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$, has been prepared⁷ and structurally characterized⁸ by other authors. Comparison of these species with the structurally characterized rhodium compounds shows that while in the rhodium series the octanuclear species is lacking, the iridium analogues of the nonanuclear and decanuclear complexes $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ and $[\text{Rh}_{10}(\text{CO})_{21}]^{2-}$ are unknown.^{9,10} Since the two dodecanuclear species $\text{Rh}_{12}\text{H}_2(\text{CO})_{25}$ ¹¹ and $[\text{Ir}_{12}(\text{CO})_{26}]^{2-}$ possess the same metallic skeleton

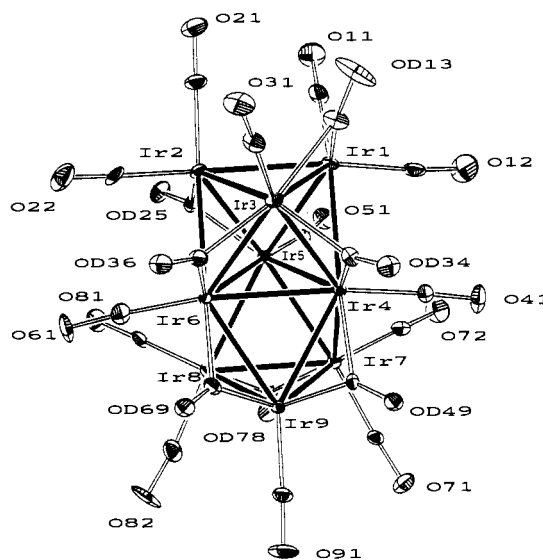


Figure 1. ORTEP drawing and atom-labeling scheme for $[\text{Ir}_9(\text{CO})_{20}]^{3-}$. Thermal ellipsoids are drawn at 30% probability. Carbonyl carbons are designated in a manner analogous to the oxygens to which they are attached.

but a different number of cluster valence electrons, we judged it worthwhile to attempt the syntheses of the Ir_9 and Ir_{10} clusters, in order to ascertain whether this discrepancy was limited to the above mentioned case or if it was of wider occurrence. Unfortunately, it was impossible to apply the synthetic methods developed for the preparation of Rh_9 and Rh_{10} clusters to the iridium case owing to the lack of suitable starting materials for rational syntheses. Thus, we decided to search for the missing species among the byproducts of the syntheses of known iridium compounds having a similar charge to metal atom ratio and to adopt, in order to separate different products, the technique of fractional precipitation of the alkali-metal cation salts from water.

We report here the first results of these studies, i.e., the isolation of the nonanuclear $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ complex from the mother liquor of the synthesis of $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ and the complete account of the structure determination of its benzyltrimethylammonium salt $[\text{NMe}_3(\text{CH}_2\text{Ph})_3]_3[\text{Ir}_9(\text{CO})_{20}]$. The metal framework of $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ is the same found in $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ but also in this case the two clusters possess a different number of valence electrons.

Results

Isolation of $[\text{Ir}_9(\text{CO})_{20}]^{3-}$. The anion $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ is isolated as a byproduct of the synthesis of $[\text{Ir}_6(\text{CO})_{15}]^{2-}$, which is prepared by reacting a tetrahydrofuran (THF) solution of $\text{Na}[\text{Ir}(\text{CO})_4]$ with a slight excess, over the stoichiometric amount, of $\text{Ir}_4(\text{CO})_{12}$. The resulting brown solution contains, as the main product, $\text{Na}_2[\text{Ir}_6(\text{CO})_{15}]$ and a small amount of $\text{Na}_3[\text{Ir}_9(\text{CO})_{20}]$ as a byproduct. After evaporation to dryness and redissolution in water, the pure hexanuclear dianion is quantitatively precipitated as the potassium salt by saturation with KBr . After filtration of $\text{K}_2[\text{Ir}_6(\text{CO})_{15}]$, the mother liquor is treated with CsCl , which causes the precipitation of pure $\text{Cs}_3[\text{Ir}_9(\text{CO})_{20}]$. The yields are rather low (5–8%), reaching the higher value when the $\text{Ir}_4(\text{CO})_{12}$, instead of being added as a whole to the $\text{Na}[\text{Ir}(\text{CO})_4]$ solution, is added in a few portions, waiting for its consumption between each addition. $\text{Cs}_3[\text{Ir}_9(\text{CO})_{20}]$ is very soluble in MeOH , THF , and MeCN . Metathesis with $[\text{PPh}_4]^+$, $[\text{N}(\text{PPh}_3)_2]^+$, $[\text{NET}_4]^+$, and

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Table I. Selected Bond Distances (Å) for the Anion $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ with Estimated Standard Deviations (Esd's) in Parentheses

Metal-Metal			
Ir(1)-Ir(2)	2.797 (1)	Ir(4)-Ir(7)	2.838 (1)
Ir(1)-Ir(3)	2.786 (1)	Ir(4)-Ir(9)	2.764 (1)
Ir(1)-Ir(4)	2.816 (1)	Ir(5)-Ir(6)	2.794 (1)
Ir(1)-Ir(5)	2.726 (1)	Ir(5)-Ir(7)	2.704 (1)
Ir(2)-Ir(3)	2.792 (1)	Ir(5)-Ir(8)	2.720 (1)
Ir(2)-Ir(5)	2.717 (1)	Ir(6)-Ir(8)	2.879 (1)
Ir(2)-Ir(6)	2.805 (1)	Ir(6)-Ir(9)	2.740 (1)
Ir(3)-Ir(4)	2.759 (1)	Ir(7)-Ir(8)	2.719 (1)
Ir(3)-Ir(6)	2.814 (1)	Ir(7)-Ir(9)	2.821 (1)
Ir(4)-Ir(5)	2.772 (1)	Ir(8)-Ir(9)	2.796 (1)
Ir(4)-Ir(6)	2.820 (1)		
Metal-Terminal Carbon			
Ir(1)-C(11)	1.86 (1)	Ir(6)-C(61)	1.82 (1)
Ir(1)-C(12)	1.85 (2)	Ir(7)-C(71)	1.85 (1)
Ir(2)-C(21)	1.87 (1)	Ir(7)-C(72)	1.94 (1)
Ir(2)-C(22)	1.84 (1)	Ir(8)-C(81)	1.83 (1)
Ir(3)-C(31)	1.84 (1)	Ir(8)-C(82)	1.88 (1)
Ir(4)-C(41)	1.85 (1)	Ir(9)-C(91)	1.83 (1)
Ir(5)-C(51)	1.82 (1)		
Metal-Bridging Carbon			
Ir(1)-CD(13)	1.94 (1)	Ir(5)-CD(25)	2.00 (1)
Ir(2)-CD(25)	2.08 (1)	Ir(6)-CD(36)	2.02 (1)
Ir(3)-CD(13)	2.19 (1)	Ir(6)-CD(69)	2.15 (1)
Ir(3)-CD(34)	2.01 (1)	Ir(7)-CD(78)	2.04 (1)
Ir(3)-CD(36)	2.04 (1)	Ir(8)-CD(78)	2.02 (1)
Ir(4)-CD(34)	2.08 (1)	Ir(9)-CD(49)	1.92 (1)
Ir(4)-CD(49)	2.16 (1)	Ir(9)-CD(69)	1.95 (1)
C-O ^a _{terminal}	1.15		
C-O ^a _{bridging}	1.19		

^a Average value.

$[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ cation salts affords the corresponding crystalline salts. Crystals of $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ were found suitable for the X-ray structural analysis.

The salts of the above mentioned bulky cations are quite soluble in MeCN and acetone while they are sparingly soluble in THF. The IR spectrum of selected crystals of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_3[\text{Ir}_9(\text{CO})_{20}]^{3-}$ shows bands at 2030 vw, 1985 vs, 1965 sh, and 1769 m (cm^{-1} , MeCN solution).

$[\text{Ir}_9(\text{CO})_{20}]^{3-}$ is stable in MeCN solution and under nitrogen atmosphere for a long time; both the $[\text{N}(\text{PPh}_3)_2]^+$ and the cesium salts of $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ do not give $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ when submitted to 1 atm of carbon monoxide; on the contrary, $[\text{Rh}_9(\text{CO})_{19}]^{2-}$ gives quantitatively $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ under these conditions.⁹

Since $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ and $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ have the same charge to metal atoms ratio, we tried to produce the nonanuclear species by thermal decarbonylation of the hexanuclear cluster. Thus, we refluxed $[\text{N}(\text{PPh}_3)_2]_2[\text{Ir}_6(\text{CO})_{15}]$ in high boiling solvents (up to 125 °C) but we found that the hexanuclear carbonyl cluster is stable in these conditions. Also $\text{K}_2[\text{Ir}_6(\text{CO})_{15}]$ is stable in similar conditions, and only the formation of a small amount of iridium metal was observed after refluxing this salt for 12 h in 2-methoxyethanol. These evidences seem to exclude that $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ is an intermediate species for the formation of $[\text{Ir}_9(\text{CO})_{20}]^{3-}$.

Crystal Structure of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_3[\text{Ir}_9(\text{CO})_{20}]^{3-}$. The crystal structure of $[\text{NMe}_3(\text{CH}_2\text{Ph})]_3[\text{Ir}_9(\text{CO})_{20}]^{3-}$ was determined by single-crystal X-ray diffraction. The molecular geometry of the anion and the atomic numbering scheme are shown in the Figure 1. The most significant bond distances and angles for the $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ trianion are reported in Tables I and II, respectively; all bonding parameters for the $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ cations fall within the normal range and have been included in supplementary Table 2S. The crystal contains discrete cluster anions and tetrasubstituted ammonium cations; no short interionic contacts between different fragments are observed. The metal atom polyhedron may be described in terms of two condensed octahedra sharing a triangular face, representing an hexagonal close-packed fragment formed by the stack of three triangles with a sequence *aba*. This metallic array, of idealized D_{3d} symmetry, has been

Table II. Selected Bond Angles (deg) for the Anion $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ with Esd's in Parentheses

Ir-C-O _{terminal}			
Ir(1)-C(11)-O(11)	177 (2)	Ir(6)-C(61)-O(61)	176 (1)
Ir(1)-C(12)-O(12)	174 (1)	Ir(7)-C(71)-O(71)	177 (1)
Ir(2)-C(21)-O(21)	175 (2)	Ir(7)-C(72)-O(72)	179 (1)
Ir(2)-C(22)-O(22)	174 (2)	Ir(8)-C(81)-O(81)	178 (1)
Ir(3)-C(31)-O(31)	176 (1)	Ir(8)-C(82)-O(82)	173 (1)
Ir(4)-C(41)-O(41)	177 (1)	Ir(9)-C(91)-O(91)	178 (1)
Ir(5)-C(51)-O(51)	175 (1)		
Ir-C _{bridging} -Ir			
Ir(1)-CD(13)-Ir(3)	85 (1)	Ir(4)-CD(49)-Ir(9)	85 (1)
Ir(2)-CD(25)-Ir(5)	83 (1)	Ir(6)-CD(69)-Ir(9)	84 (1)
Ir(3)-CD(34)-Ir(4)	85 (1)	Ir(7)-CD(78)-Ir(8)	84 (1)
Ir(3)-CD(36)-Ir(6)	88 (1)		
Ir-C-O _{bridging}			
Ir(1)-CD(13)-OD(13)	143 (1)	Ir(5)-CD(25)-OD(25)	142 (1)
Ir(2)-CD(25)-OD(25)	134 (1)	Ir(6)-CD(36)-OD(36)	134 (1)
Ir(3)-CD(13)-OD(13)	132 (1)	Ir(6)-CD(69)-OD(69)	134 (1)
Ir(3)-CD(34)-OD(34)	140 (1)	Ir(7)-CD(78)-OD(78)	135 (1)
Ir(3)-CD(36)-OD(36)	138 (1)	Ir(8)-CD(78)-OD(78)	140 (1)
Ir(4)-CD(34)-OD(34)	135 (1)	Ir(9)-CD(49)-OD(49)	143 (1)
Ir(4)-CD(49)-OD(49)	132 (1)	Ir(9)-CD(69)-OD(69)	143 (1)

Table III. Crystallographic Data for the Compound $[\text{NMe}_3(\text{CH}_2\text{Ph})]_3[\text{Ir}_9(\text{CO})_{20}]^{3-}$

chem formula:	$\text{C}_{50}\text{H}_{48}\text{Ir}_9\text{N}_3\text{O}_{20}$	fw = 2740.75
<i>a</i>	= 12.906 (7) Å	space group: $P\bar{1}$ (No. 2)
<i>b</i>	= 12.861 (6) Å	<i>T</i> = 25 °C
<i>c</i>	= 9.495 (2) Å	<i>d</i> _{calc} = 2.998 g/cm ³
α	= 83.60 (3)°	λ = 0.710 73 Å
β	= 85.13 (3)°	μ (Mo K α) = 196.4 cm ⁻¹
γ	= 80.91 (3)°	min transm factor = 0.59
<i>V</i>	= 3036 (3) Å ³	<i>R</i> (<i>F</i> _o) = 0.032
<i>Z</i>	= 2	<i>R</i> _w (<i>F</i> _o) = 0.039

found previously in $[\text{Ni}_9(\text{PEt}_3)_6\text{S}_9]^{2+}$,¹² $[\text{PtRh}_8(\text{CO})_{19}]^{2-}$,¹³ $[\text{Rh}_9(\text{CO})_{19}]^{3-}$,⁹ $\text{Rh}_9(\text{CO})_{19}(\text{NCMe})[\text{Cu}(\text{NCMe})_2]$,¹⁴ and $[\text{Ni}_6\text{Ir}_3(\text{CO})_{17}]^{3-}$.¹⁵

The Ir-Ir distances are scattered in the range 2.704 (1)–2.879 (1) Å, with an average value of 2.780 Å; as often observed in other anionic iridium clusters,³ it is not easy to find a simple correlation between bond lengths, the metal-to-metal connectivity, and/or the presence of bridging ligands, although the average Ir-Ir bond distances for unbridged and bridged edges (2.791 and 2.757 Å, respectively) seem to suggest a small shortening effect in the presence of μ -carbonyls. Thirteen of the twenty carbonyl groups are terminally bonded (average values: Ir-C, 1.85 Å; C-O, 1.15 Å; Ir-C-O, 176°). Ir(1), Ir(2), Ir(7), and Ir(8) possess two terminal CO groups, as often found in structurally characterized octahedral iridium carbonyl clusters.^{2,3} All the other metal atoms are bound to one terminal carbon monoxide group. Seven carbonyls are more or less symmetrically edge bridging: two span one edge of the outer triangles, while the remaining five connect two different triangular layers (average values: Ir-C, 2.05 Å; C-O, 1.19 Å; Ir-C-O, 137°).

Discussion

In the vast family of medium and high nuclearity carbonyl clusters, there are few strictly isostructural species containing different metal atoms and/or ligands.¹⁶ Several cores of nine

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Table IV. Fractional Atomic Coordinates for $[\text{NMe}_3(\text{CH}_2\text{Ph})_3][\text{Ir}_9(\text{CO})_{20}]$ with Esd's in Parentheses

atom	x	y	z	atom	x	y	z
Ir(1)	0.25818 (4)	0.06466 (4)	-0.26775 (3)	C(91)	0.434 (1)	-0.487 (1)	-0.2618 (9)
Ir(2)	0.14686 (4)	-0.01595 (4)	-0.14448 (3)	CD(13)	0.347 (1)	0.122 (1)	-0.2084 (9)
Ir(3)	0.36595 (4)	-0.03641 (4)	-0.15017 (3)	CD(25)	0.037 (1)	-0.059 (1)	-0.2059 (7)
Ir(4)	0.38107 (4)	-0.13584 (4)	-0.27488 (2)	CD(34)	0.492 (1)	-0.090 (1)	-0.2145 (7)
Ir(5)	0.16325 (4)	-0.10997 (4)	-0.26900 (3)	CD(36)	0.353 (1)	-0.167 (1)	-0.0794 (7)
Ir(6)	0.26764 (4)	-0.21660 (4)	-0.15097 (3)	CD(49)	0.496 (1)	-0.277 (1)	-0.2732 (7)
Ir(7)	0.27036 (4)	-0.24242 (4)	-0.36161 (3)	CD(69)	0.386 (1)	-0.355 (1)	-0.1399 (8)
Ir(8)	0.15942 (4)	-0.32177 (4)	-0.24335 (3)	CD(78)	0.143 (1)	-0.321 (1)	-0.3499 (8)
Ir(9)	0.37880 (4)	-0.35070 (4)	-0.24387 (3)	N(1)	0.692 (1)	0.640 (1)	0.9704 (7)
O(11)	0.079 (1)	0.242 (1)	-0.2849 (8)	N(2)	0.1783 (9)	0.1832 (9)	0.3959 (6)
O(12)	0.343 (2)	0.131 (1)	-0.4169 (7)	N(3)	0.7133 (9)	0.1501 (9)	0.8269 (6)
O(21)	0.079 (1)	0.209 (1)	-0.1077 (8)	C(111)	0.690 (1)	0.527 (1)	0.9468 (8)
O(22)	0.083 (1)	-0.099 (1)	0.0065 (7)	C(112)	0.757 (1)	0.502 (1)	0.8793 (8)
O(31)	0.420 (1)	0.0786 (9)	-0.0321 (6)	C(113)	0.710 (1)	0.516 (1)	0.8124 (8)
O(41)	0.4830 (9)	-0.077 (1)	-0.4212 (6)	C(114)	0.764 (1)	0.494 (2)	0.748 (1)
O(51)	0.0488 (8)	-0.0024 (8)	-0.3959 (5)	C(115)	0.869 (2)	0.455 (2)	0.749 (1)
O(61)	0.1271 (9)	-0.3320 (9)	-0.0441 (6)	C(116)	0.919 (1)	0.439 (1)	0.8118 (9)
O(71)	0.4267 (9)	-0.4022 (9)	-0.4348 (6)	C(117)	0.865 (1)	0.464 (1)	0.8766 (8)
O(72)	0.249 (1)	-0.098 (1)	-0.5009 (6)	C(118)	0.657 (2)	0.720 (2)	0.908 (1)
O(81)	-0.0606 (8)	-0.292 (1)	-0.1748 (7)	C(119)	0.614 (2)	0.651 (2)	1.036 (1)
O(82)	0.201 (1)	-0.5551 (8)	-0.1938 (9)	C(120)	0.801 (2)	0.650 (2)	0.990 (1)
O(91)	0.468 (1)	-0.5745 (9)	-0.2708 (8)	C(211)	0.178 (1)	0.301 (1)	0.3883 (8)
OD(13)	0.377 (1)	0.2023 (9)	-0.1982 (8)	C(212)	0.201 (1)	0.347 (1)	0.4570 (8)
OD(25)	-0.0552 (7)	-0.0510 (9)	-0.2016 (6)	C(213)	0.124 (1)	0.380 (1)	0.5053 (9)
OD(34)	0.5846 (8)	-0.0912 (8)	-0.2205 (6)	C(214)	0.146 (2)	0.414 (2)	0.567 (1)
OD(36)	0.3781 (9)	-0.1992 (8)	-0.0190 (5)	C(215)	0.248 (2)	0.418 (2)	0.582 (1)
OD(49)	0.5881 (7)	-0.2913 (8)	-0.2892 (6)	C(216)	0.325 (2)	0.387 (2)	0.533 (1)
OD(69)	0.4264 (8)	-0.4042 (8)	-0.0904 (5)	C(217)	0.306 (2)	0.351 (2)	0.469 (1)
OD(78)	0.0872 (7)	-0.3449 (9)	-0.3895 (6)	C(218)	0.290 (1)	0.124 (1)	0.4041 (8)
C(11)	0.148 (1)	0.177 (1)	-0.2769 (9)	C(219)	0.105 (1)	0.148 (1)	0.4589 (9)
C(12)	0.314 (2)	0.100 (1)	-0.3602 (9)	C(220)	0.139 (1)	0.155 (1)	0.3281 (9)
C(21)	0.101 (1)	0.123 (1)	-0.124 (1)	C(311)	0.717 (1)	0.114 (1)	0.7508 (9)
C(22)	0.103 (1)	-0.069 (1)	-0.0533 (8)	C(312)	0.739 (1)	0.194 (1)	0.6889 (7)
C(31)	0.404 (1)	0.033 (1)	-0.0774 (8)	C(313)	0.660 (1)	0.262 (1)	0.6583 (9)
C(41)	0.443 (1)	-0.097 (1)	-0.3647 (7)	C(314)	0.679 (2)	0.339 (2)	0.602 (1)
C(51)	0.097 (1)	-0.0469 (9)	-0.3481 (7)	C(315)	0.781 (2)	0.337 (2)	0.577 (1)
C(61)	0.181 (1)	-0.283 (1)	-0.0857 (9)	C(316)	0.863 (1)	0.270 (2)	0.603 (1)
C(71)	0.365 (1)	-0.343 (1)	-0.4057 (8)	C(317)	0.841 (1)	0.198 (1)	0.6619 (9)
C(72)	0.256 (1)	-0.149 (1)	-0.4503 (9)	C(318)	0.811 (1)	0.192 (1)	0.8405 (9)
C(81)	0.024 (1)	-0.303 (1)	-0.2027 (8)	C(319)	0.700 (1)	0.057 (1)	0.8820 (9)
C(82)	0.190 (1)	-0.468 (1)	-0.215 (1)	C(320)	0.619 (1)	0.235 (1)	0.8364 (9)

metal atoms formed by stacked triangles were observed, and beside the above mentioned compounds of approximate D_{3d} symmetry, other arrangements of triangles have been found in $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ (C_{3v})¹⁷ and $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ (C_3).¹⁸ Large metal clusters often exhibit multiple electron counts for the same geometry (with or without structural distortions); this was previously observed, for example, in $[\text{Ir}_{12}(\text{CO})_{26}]^{2-}$ [162 cluster valence electrons (CVE)]⁵ and $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$ (160 CVE),¹¹ analogously, $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ (124 CVE) contains two electrons more than the rhodium derivative $[\text{Rh}_9(\text{CO})_{19}]^{3-}$. This is somewhat in contrast with the common belief that the late third transition metals may require a lower number of CVE than their lighter analogues.

As already pointed out,⁵ all the extensions of borane-type rules to transition-metal clusters have been made by considering regular metal skeletons;¹⁹ however, the presence of ligands can induce small deformations from the idealized symmetry, leading to structures that require different numbers of electrons. The observed value of 124 CVE in $[\text{Ir}_9(\text{CO})_{20}]^{3-}$ is in agreement with those predicted by all current electron-counting theories, i.e., topological electron counting,^{19a} polyhedral skeleton electron pair theory,^{19b} and EHMO computations,^{19c} where an "anomalous" number of cluster valence molecular orbitals (CVMO), $6N + 8$, is predicted, whereas hexagonal close-packed clusters usually contain only $6N + 7$ CVMO like $[\text{Rh}_9(\text{CO})_{19}]^{3-}$. Moreover, the value of 124 CVE for

$[\text{Ir}_9(\text{CO})_{20}]^{3-}$ is also in agreement with the stoichiometry and the topology of $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ (128 CVE), where the face-sharing polyhedra are an octahedron and a trigonal prism; an increase of four electrons is indeed required in transforming an octahedron (86 electrons) into a more open prismatic unit (90 electrons).

Experimental Section

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 by using the Schlenk-tube technique.²⁰ $\text{Ir}_4(\text{CO})_{12}$ and the solution of $\text{Na}[\text{Ir}(\text{CO})_4]$ were prepared as already described.^{21,22} Infrared spectra (IR) were recorded on a Perkin-Elmer 781 grating spectrophotometer using calcium fluoride cells previously purged with N_2 .

Isolation of $[\text{NMe}_3(\text{CH}_2\text{Ph})_3][\text{Ir}_9(\text{CO})_{20}]$. A THF solution of $\text{Na}[\text{Ir}(\text{CO})_4]$ (about 2.3–2.5 mmol in 30 mL) was added to a first portion of $\text{Ir}_4(\text{CO})_{12}$ (0.55 g, 0.5 mmol) suspended in THF (30 mL) under nitrogen. The stirred suspension was refluxed for 2 h with the consumption of all the $\text{Ir}_4(\text{CO})_{12}$. At this stage, a second portion of $\text{Ir}_4(\text{CO})_{12}$ (1.1 g, 1 mmol) was added and the suspension refluxed until the IR band of $[\text{Ir}(\text{CO})_4]^-$ at 1895 cm^{-1} disappeared (about 3 h). After cooling, the brown solution was filtered, leaving behind some unreacted $\text{Ir}_4(\text{CO})_{12}$ and some decomposition products; the solution was evaporated to dryness and the residue dissolved in water (50 mL). The filtered solution was saturated with solid KBr (ca. 15 g), causing the precipitation of the brown-red $\text{K}_2[\text{Ir}_6(\text{CO})_8]$ salt, which was filtered off, washed apart with an aqueous saturated KBr solution, and vacuum-dried. The clear brownish mother liquor was treated with CsCl (ca. 5 g), and the brown precipitate of

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$\text{Cs}_3[\text{Ir}_9(\text{CO})_{20}]$ was filtered off, washed with a 10% solution of CsCl ($3 \times 5 \text{ mL}$), and vacuum-dried. The cesium salt was dissolved in methanol, and the brown solution was cautiously layered with a 0.5% solution of benzyltrimethylammonium chloride in 2-propanol; the slow diffusion of the two solvents produced prismatic dark brown crystals of $[\text{NMe}_3(\text{CH}_2\text{Ph})_3][\text{Ir}_9(\text{CO})_{20}]$. The yields are rather low and variable (5–8% based on starting $\text{Ir}_4(\text{CO})_{12}$), depending on the experimental conditions. Salts of other bulky cations can be obtained in a similar way.

X-ray Analysis. Intensity Data Collection, Structure Solution, and Refinement. Crystal data and other experimental details are summarized in Table III. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite crystal monochromator in the incident beam. Standard CAD-4 setting, indexing, and data collection programs were used. Periodic measurements of three standard reflections revealed a crystal decay, on X-ray exposure, which was evaluated as about 17% on F_0 at the end of data collection. Intensities were corrected for Lorentz, polarization, and decay effects. An empirical absorption correction was applied to the intensities, based on ψ scans ($\psi = 0\text{--}360^\circ$) of suitable reflections with χ values close to 90° as described in ref 23. The structure was solved by direct methods (MULTAN) and difference Fourier syntheses and refined by full-matrix least-squares methods, the minimized function being $\sum w(F_0 - k|F_c|)^2$. Individual weights were given as $w = 1/\sigma^2(F_0)$ where $\sigma(F_0) = \sigma(F_0^2)/2F_0$, $\sigma(F_0^2) = [\sigma^2(I) + (pI)^2]^{1/2}/Lp$, and p , the "ignorance factor", was equal to 0.03. Scattering factors and anomalous dispersion corrections were taken from ref 24.

The final difference Fourier map showed peaks not exceeding 1.2 e/\AA^3 near the metal atoms.

Fractional atomic coordinates of non-hydrogen atoms are listed in Table IV. All computations were done on a PDP 11/73 computer using the Enraf-Nonius structure determination package (SDP) and the physical constants tabulated therein,²⁵ MULTAN²⁶ for direct methods, and ORTEP for drawings.²⁷

Supplementary Material Available: Listings of thermal parameters (Table 1S), complete distances and angles (Table 2S), calculated cation hydrogen atom positions (Table 3S), isotropic thermal parameters for cation non-hydrogen atoms (Table 4S), and crystal data (Table 5S) (11 pages); a listing of observed and calculated structure factors (Table 6S) (47 pages). Ordering information is given on any current masthead page.

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X-ray Powder Diffraction Studies of Alkalides and Electrides That Contain 15-Crown-5

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Introduction

Crystalline alkalides and electrides were first synthesized in 1974 and 1983, respectively.^{1,2} Alkalides contain alkali metals in both the cationic and anionic forms, while in electrides, charge compensation is made, not by conventional anions but by trapped electrons. Single-crystal X-ray structures have been determined and published for 10 alkalides and 2 electrides,^{3–9} and the

structures of an additional 14 alkalides and 2 electrides have been determined.¹⁰

Due to the thermal instability and reactivity of these compounds, it is often difficult to grow single crystals. Some show evidence of phase transitions. X-ray powder diffraction studies of alkalides and electrides can provide information about structures, thermal stabilities, and thermally induced phase transitions. In addition, the homogeneity of a polycrystalline sample can be assessed.

We chose for this study the alkalides and electrides formed with the crown ether 15-crown-5 (15C5, 1,4,7,10,13-pentaoxacyclopentadecane) because of the wide variety of compounds that can be made. Because they are reasonably stable, easy to prepare, relatively inexpensive, and soluble in aprotic solvents such as dimethyl ether, such compounds are promising candidates for use as reductants.

Compounds of this type were first synthesized in 1985,¹¹ and five single-crystal structures have been determined by X-ray diffraction. The alkalides $\text{Rb}^+(\text{15C5})_2\text{Na}^-$, $\text{Rb}^+(\text{15C5})_2\text{Rb}^-$, and $\text{Cs}^+(\text{15C5})_2\text{K}^-$ are monoclinic ($C2/m$),^{8,10} while $\text{Cs}^+(\text{15C5})_2\text{Na}^-$ and $\text{Cs}^+(\text{15C5})_2\text{e}^-$ belong to the triclinic system ($P\bar{1}$).¹⁰ Others have been prepared as polycrystalline samples, but so far it has not been possible to grow single crystals. X-ray powder diffraction provides a way to determine the crystallographic system and cell parameters and to see whether complications such as phase transitions interfere with crystal growth.

Experimental Section

The compounds $\text{M}_a^+(\text{15C5})_2\text{M}_b^-$ and $\text{M}^+(\text{15C5})_2\text{e}^-$ were synthesized in a vacuum-tight apparatus called a K-cell by using previously reported techniques.^{6,12,13} In all the experimental steps, low temperatures and inert atmosphere conditions must be used due to the air and thermal sensitivities of these compounds.

A Rigaku D/max-RBX rotating-anode diffractometer equipped with a scintillation counter detector and a graphite monochromator to yield $\text{Cu K}\alpha$ (wavelength 1.54184 Å) radiation was used under the control of a DEC Microvax computer. All data were recorded by scans at 45 kV and 80 mA. The low-temperature attachment permitted evacuation to about 35 mTorr and the temperature could be varied from 80 to 300 K.

Results and Discussion

The X-ray powder diffraction patterns were recorded at several temperatures for the nine compounds synthesized so far with the crown ether 15C5. Two copper peaks at $2\theta = 43.28$ and 50.41° (wavelength 1.54184 Å) from the sample holder provided calibration points. All attempts to obtain a well-defined powder pattern for $\text{K}^+(\text{15C5})_2\text{e}^-$ were unsuccessful, as even the best diffractogram was poorly resolved.

The temperature dependence of the diffractograms showed two kinds of behavior: (1) For the compounds $\text{Rb}^+(\text{15C5})_2\text{Na}^-$, $\text{Cs}^+(\text{15C5})_2\text{Na}^-$, $\text{Rb}^+(\text{15C5})_2\text{Rb}^-$, $\text{Cs}^+(\text{15C5})_2\text{K}^-$, $\text{Cs}^+(\text{15C5})_2\text{e}^-$, and $\text{Rb}^+(\text{15C5})_2\text{e}^-$, the pattern difference from 80 to 200 K consisted of a shift to lower angles of nearly all the peaks. Above 200 K the peak positions did not shift appreciably but there was an increasing amorphous background relative to the significantly lower peak intensities. (2) For the compounds $\text{K}^+(\text{15C5})_2\text{Na}^-$ and $\text{K}^+(\text{15C5})_2\text{K}^-$, some peaks disappeared and new ones appeared

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