Inorg. Chem. **1987**, *26*, 3487–3491

Contribution from the Dipartimento di Chimica Inorganica e Metallorganica, CNR Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, and Istituto di Chimica Strutturistica Inorganica, 20133 Milano, Italy

Chemistry of Iridium Carbonyl Cluster Complexes. Synthesis and X-ray Crystal Structure of $[PPh_4]_2[Ir_{12}(\mu\text{-}CO)_8(CO)_{18}]$, the First Example of a Medium-Size Iridium Carbonyl Cluster Complex

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Received January 25, 1987

The anionic species $[Ir_{12}(\mu\text{-}CO)_8(CO)_{18}]^{2-}$, obtained by reaction of $[Ir_6(CO)_{15}]^{2-}$ with $[Cu(CH_3CN)_4][BF_4]$, contains a Ir_{12} metallic array formed by superimposition of three face-sharing octahedral units. The compound adopts a metal framework similar to that of $[H_2Rh_{12}(CO)_{25}]$ but possesses a different number of valence electrons. $[PPh_4]_2[Ir_{12}(\mu\text{-}CO)_8(CO)_{18}]$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.968$ (3) Å, $b = 22.874$ (10) Å, $c = 26.379$ (7) Å, $\beta = 90.97$ (3)°, $V = 8427$ (8) Å^3, and $Z = 4$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least squares down to $R = 0.050$ for 3807 independent reflections with $I \geqslant 1.5\sigma(I)$.

Introduction

Dodecanuclear carbonyl clusters of different transition metals are known. These medium-size clusters, even in the absence of interstitial main-group elements, adopt drastically different geometries. Examples are provided of vertex-linked octahedra ($[Rh_{12}(CO)_{30}]^{2-}$),[2] triangular-face-sharing trigonal prisms ($[Pt_{12}(CO)_{24}]^{2-}$),[3] and raftlike structures ($[Os_3Hg(CO)_{11}]_3$).[4] Other metal arrangements may be described as fragments of close packings, such as those found in $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2–4)[5] and $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ (n = 2–4;[6] truncated ν_2 trigonal bipyramid), $[Fe_6Pd_6(CO)_{24}H]^{3-}$ (hexacapped octahedron),[7] and $[H_2Rh_{12}(CO)_{25}]$ (face-sharing trioctahedron).[8] Although several tetra- and hexanuclear neutral and anionic iridium carbonyl clusters have been reported,[9] the only structural reports of iridium clusters with nuclearity higher than 6 are the monocapped octahedron[10] $[Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})]$ and the ditetrahedral $[Ir_8(CO)_{22}]^{2-}$ dianion.[11]

We report here the synthesis, the chemical characterization, and the X-ray structural analysis of the first example of a medium-nuclearity cluster of iridium: the dodecanuclear $[PPh_4]_2[Ir_{12}(\mu\text{-}CO)_8(CO)_{18}]$, which contains a face-sharing trioctahedron of metal atoms. The metal framework of $[Ir_{12}(CO)_{26}]^{2-}$ is essentially the same found in $[H_2Rh_{12}(CO)_{25}]$, but interestingly the two clusters have different numbers of valence electrons.

Results and Discussion

Synthesis and Chemical Behavior of $[Ir_{12}(CO)_{26}]^{2-}$. $[Ir_{12}(CO)_{26}]^{2-}$ (**1**) is obtained by slow addition (under a nitrogen or carbon monoxide atmosphere) of a tetrahydrofuran (thf) solution of $[Cu(CH_3CN)_4][BF_4]$ to a stirred thf solution of $[Ir_6(CO)_{15}]^{2-}$ in a molar ratio slightly higher than 1:1. Oxidation of $[Ir_6(CO)_{15}]^{2-}$ occurs very rapidly, and the stoichiometry of the reaction is given by

$$2[Ir_6(CO)_{15}]^{2-} + 2[Cu(CH_3CN)_4]^+ \rightarrow [Ir_{12}(CO)_{26}]^{2-} + 2Cu + 4CO + 8CH_3CN$$

$[Ir_6(CO)_{15}]^{2-}$ can also be oxidized, under a nitrogen or carbon monoxide atmosphere, to $[Ir_{12}(CO)_{26}]^{2-}$ with $AgPF_6$. Complex **1** is not further oxidized when it is treated with a large excess of $[Cu(CH_3CN)_4][BF_4]$.

The red-brown thf solution of $[N(PPh_3)_2]_2[Ir_{12}(CO)_{26}]$ shows IR absorptions in the carbonyl stretching region at 2008 (vs) and 1797 (m) cm^{-1} (thf); small shifts are observed in other solvents (2010 (vs) and 1805 (m) cm^{-1} (CH_2Cl_2)) and with different cations ($[PPh_4]_2[Ir_{12}(CO)_{26}]$, 2020 (vs) and 1805 (m) cm^{-1} (thf)). The $[Ir_{12}(CO)_{26}]^{2-}$ dianion can be isolated as a salt of different bulky cations by starting from the suitable $[Ir_6(CO)_{15}]^{2-}$ salt. The salts are soluble in dry solvents such as thf, dichloromethane, and acetone; the solutions are stable for a long period of time under a nitrogen or carbon monoxide atmosphere. In wet solvents compound **1** is transformed mainly into $[Ir_6(CO)_{15}]^{2-}$ probably by reduction on nucleophilic attack of an OH^- group from water on a positively polarized carbon atom of a CO ligand. Reduction of **1** to $[Ir_6(CO)_{15}]^{2-}$ can be performed in quantitative yields when a methanolic solution of the anion is treated under carbon monoxide with KOH. Compound **1** is unstable in solvents such as acetonitrile and dimethyl sulfoxide; it is also unstable in thf if halide ions are present. In both cases ready transformation into $[Ir_6(CO)_{15}]^{2-}$ is observed without apparent IR evidence of any other product; studies are in progress to clarify this behavior. In contrast, no reaction is observed when a thf solution of **1** is treated with PPh_3 up to a molar ratio of 1:5. When a thf solution of $[Ir_{12}(CO)_{26}]^{2-}$ is refluxed for about 2 h, the IR spectrum of the original solution changes considerably and it is possible to isolate a black compound that shows IR bands at 2020 (vs), 1990 (sh), and 1830 (m) cm^{-1}; this compound is presently under investigation. $[Ir_{12}(CO)_{26}]^{2-}$ reacts with CF_3CO_2H in CH_2Cl_2 (molar ratio 1:1.5), yielding a new product with ν_{CO} bands at 2040 (vs) and 1830 (m) cm^{-1} that we formulate as the corresponding monohydride $[HIr_{12}(CO)_{26}]^-$; the reaction is reversible, and on simple dissolution of this product in more basic solvents such as thf the starting dianion is regenerated. We also have spectroscopic evidence of formation of the dihydridic species $[H_2Ir_{12}(CO)_{26}]$ when **1** is treated with a large excess of CF_3CO_2H (molar ratio 1:5; ν_{CO}

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Table I.[a] Fractional Atomic Coordinates for Complex **1** with Estimated Standard Deviations (Esd's) in Parentheses

atom	*x*	*y*	*z*
Ir(1)	0.2665 (2)	0.13539 (6)	0.67649 (7)
Ir(2)	0.2966 (2)	0.09441 (7)	0.57698 (6)
Ir(3)	0.1117 (2)	0.11598 (7)	0.61422 (7)
Ir(4)	0.1691 (2)	0.22718 (7)	0.63731 (6)
Ir(5)	0.1885 (2)	0.18604 (6)	0.53906 (6)
Ir(6)	0.3535 (2)	0.20562 (6)	0.60337 (6)
Ir(7)	0.2861 (1)	0.31926 (6)	0.61721 (6)
Ir(8)	0.3109 (1)	0.27851 (6)	0.51943 (6)
Ir(9)	0.1235 (2)	0.30038 (6)	0.55632 (6)
Ir(10)	0.1843 (2)	0.41181 (7)	0.58525 (6)
Ir(11)	0.2027 (2)	0.37270 (7)	0.48468 (6)
Ir(12)	0.3635 (2)	0.39177 (6)	0.54674 (6)
C(1)	0.286 (4)	0.182 (2)	0.735 (2)
O(1)	0.276 (3)	0.207 (1)	0.774 (1)
C(2)	0.364 (4)	0.079 (2)	0.696 (2)
O(2)	0.399 (3)	0.042 (1)	0.710 (1)
C(3)	0.339 (5)	0.079 (2)	0.515 (2)
O(3)	0.381 (3)	0.075 (1)	0.473 (1)
C(4)	0.310 (4)	0.019 (2)	0.604 (2)
O(4)	0.305 (3)	−0.030 (1)	0.612 (1)
C(5)	0.000 (4)	0.139 (2)	0.610 (2)
O(5)	−0.086 (3)	0.158 (1)	0.609 (1)
C(6)	0.074 (4)	0.042 (2)	0.596 (2)
O(6)	0.056 (3)	−0.005 (1)	0.583 (1)
C(7)	0.065 (3)	0.224 (2)	0.678 (2)
O(7)	0.004 (3)	0.228 (1)	0.708 (1)
C(8)	0.140 (3)	0.124 (1)	0.503 (1)
O(8)	0.106 (2)	0.088 (1)	0.475 (1)
C(9)	0.433 (4)	0.235 (2)	0.653 (2)
O(9)	0.488 (3)	0.248 (1)	0.685 (1)
C(10)	0.369 (4)	0.354 (2)	0.662 (2)
O(10)	0.418 (3)	0.385 (1)	0.691 (1)
C(11)	0.378 (4)	0.308 (2)	0.468 (2)
O(11)	0.434 (3)	0.313 (1)	0.431 (1)
C(12)	0.022 (5)	0.314 (2)	0.594 (2)
O(12)	−0.050 (3)	0.318 (1)	0.615 (1)
C(13)	0.092 (3)	0.462 (2)	0.566 (2)
O(13)	0.031 (3)	0.494 (1)	0.551 (1)
C(14)	0.152 (4)	0.421 (2)	0.651 (2)
O(14)	0.127 (3)	0.434 (1)	0.693 (1)
C(15)	0.186 (4)	0.447 (2)	0.464 (2)
O(15)	0.191 (3)	0.499 (1)	0.453 (1)
C(16)	0.202 (4)	0.344 (2)	0.418 (2)
O(16)	0.205 (3)	0.330 (1)	0.378 (1)
C(17)	0.404 (4)	0.436 (2)	0.496 (2)
O(17)	0.437 (3)	0.463 (1)	0.460 (1)
C(18)	0.480 (3)	0.382 (1)	0.571 (1)
O(18)	0.558 (3)	0.376 (1)	0.591 (1)
C(19)	0.151 (4)	0.098 (2)	0.686 (2)
O(19)	0.106 (3)	0.065 (1)	0.717 (1)
C(20)	0.424 (4)	0.128 (2)	0.597 (2)
O(20)	0.498 (3)	0.108 (1)	0.608 (1)
C(21)	0.267 (4)	0.209 (2)	0.475 (2)
O(21)	0.256 (2)	0.196 (1)	0.434 (1)
C(22)	0.064 (3)	0.227 (1)	0.522 (1)
O(22)	−0.006 (2)	0.218 (1)	0.499 (1)
C(23)	0.433 (4)	0.238 (2)	0.543 (2)
O(23)	0.506 (3)	0.228 (1)	0.529 (1)
C(24)	0.223 (4)	0.293 (2)	0.679 (2)
O(24)	0.201 (3)	0.314 (1)	0.721 (1)
C(25)	0.069 (3)	0.351 (2)	0.497 (1)
O(25)	−0.009 (2)	0.358 (1)	0.481 (1)
C(26)	0.296 (3)	0.459 (2)	0.585 (1)
O(26)	0.326 (3)	0.508 (1)	0.598 (1)

[a] The fractional atomic coordinates of the two cations and those of the solvent molecule are deposited as supplementary material.

Table II. Interatomic Distances (Å) within the Anion $[Ir_{12}(\mu\text{-}CO)_8(CO)_{18}]^{2-}$ with Esd's in Parentheses

Ir(1)–Ir(2)	2.826 (3)	Ir(5)–Ir(9)	2.809 (2)
Ir(1)–Ir(3)	2.729 (3)	Ir(6)–Ir(7)	2.791 (2)
Ir(1)–Ir(4)	2.698 (3)	Ir(6)–Ir(8)	2.827 (2)
Ir(1)–Ir(6)	2.803 (3)	Ir(7)–Ir(8)	2.770 (2)
Ir(2)–Ir(3)	2.822 (3)	Ir(7)–Ir(9)	2.793 (3)
Ir(2)–Ir(5)	2.761 (3)	Ir(7)–Ir(10)	2.678 (3)
Ir(2)–Ir(6)	2.751 (2)	Ir(7)–Ir(12)	2.728 (3)
Ir(3)–Ir(4)	2.733 (2)	Ir(8)–Ir(9)	2.853 (3)
Ir(3)–Ir(5)	2.779 (3)	Ir(8)–Ir(11)	2.778 (3)
Ir(4)–Ir(5)	2.775 (2)	Ir(8)–Ir(12)	2.784 (2)
Ir(4)–Ir(6)	2.785 (3)	Ir(9)–Ir(10)	2.789 (2)
Ir(4)–Ir(7)	2.723 (3)	Ir(9)–Ir(11)	2.757 (3)
Ir(4)–Ir(9)	2.780 (2)	Ir(10)–Ir(11)	2.815 (3)
Ir(5)–Ir(6)	2.873 (3)	Ir(10)–Ir(12)	2.756 (3)
Ir(5)–Ir(8)	2.774 (3)	Ir(11)–Ir(12)	2.791 (3)
Ir(1)–C(1)	1.88 (5)	C(1)–O(1)	1.21 (5)
Ir(1)–C(2)	1.94 (5)	C(2)–O(2)	1.04 (5)
Ir(2)–C(3)	1.78 (7)	C(3)–O(3)	1.26 (6)
Ir(2)–C(4)	1.87 (5)	C(4)–O(4)	1.15 (5)
Ir(3)–C(5)	1.65 (6)	C(5)–O(5)	1.28 (6)
Ir(3)–C(6)	1.83 (5)	C(6)–O(6)	1.16 (5)
Ir(4)–C(7)	1.83 (5)	C(7)–O(7)	1.17 (5)
Ir(5)–C(8)	1.83 (4)	C(8)–O(8)	1.21 (4)
Ir(6)–C(9)	1.82 (6)	C(9)–O(9)	1.17 (5)
Ir(7)–C(10)	1.82 (6)	C(10)–O(10)	1.23 (6)
Ir(8)–C(11)	1.79 (5)	C(11)–O(11)	1.25 (5)
Ir(9)–C(12)	1.78 (8)	C(12)–O(12)	1.15 (7)
Ir(10)–C(13)	1.78 (5)	C(13)–O(13)	1.20 (5)
Ir(10)–C(14)	1.80 (5)	C(14)–O(14)	1.21 (5)
Ir(11)–C(15)	1.79 (4)	C(15)–O(15)	1.24 (4)
Ir(11)–C(16)	1.88 (5)	C(16)–O(16)	1.09 (5)
Ir(12)–C(17)	1.78 (4)	C(17)–O(17)	1.22 (5)
Ir(12)–C(18)	1.76 (5)	C(18)–O(18)	1.21 (5)
Ir(1)–C(19)	1.84 (5)		
Ir(3)–C(19)	2.01 (5)	C(19)–O(19)	1.29 (5)
Ir(2)–C(20)	2.01 (5)		
Ir(6)–C(20)	2.03 (5)	C(20)–O(20)	1.16 (5)
Ir(5)–C(21)	2.09 (5)		
Ir(8)–C(21)	2.06 (5)	C(21)–O(21)	1.14 (5)
Ir(5)–C(22)	2.02 (4)		
Ir(9)–C(22)	2.08 (4)	C(22)–O(22)	1.16 (4)
Ir(6)–C(23)	2.09 (5)		
Ir(8)–C(23)	2.04 (5)	C(23)–O(23)	1.10 (5)
Ir(4)–C(24)	1.99 (5)		
Ir(7)–C(24)	1.96 (5)	C(24)–O(24)	1.26 (5)
Ir(9)–C(25)	2.08 (4)		
Ir(11)–C(25)	1.96 (5)	C(25)–O(25)	1.18 (5)
Ir(10)–C(26)	1.90 (4)		
Ir(12)–C(26)	2.07 (4)	C(26)–O(26)	1.24 (4)
$Ir\text{–}C_{term}$[a]	1.81	$C\text{–}O_{term}$[a]	1.19
$Ir\text{–}C_{brid}$[a]	2.015	$C\text{–}O_{brid}$[a]	1.19

[a] Average values.

bands at 2060 (vs) and 1840 (m) cm^{-1}); also in this case dissolution in thf causes proton dissociation to give, after 2 h, a mixture of $[Ir_{12}(CO)_{26}]^{2-}$ and $[HIr_{12}(CO)_{26}]^{-}$. The presence of hydrogen ligands in these two compounds could not be confirmed by ^{1}H NMR in CD_2Cl_2 solution, since no hydridic signals were found in the range δ −40 to +25 even at low temperature. Owing to decomposition to $Ir_6(CO)_{16}$, no crystals of the hydrido species could be obtained; nevertheless, we think that the formulation as hydrides is correct because the above-described behavior in basic solvents has been already observed in many other cluster carbonyl hydrides[8] and the absence of signals in the NMR spectra of these species is not unusual.[12]

Crystal Structure of $[PPh_4]_2[Ir(\mu\text{-}CO)_8(CO)_{18}]$. The crystal structure of $[PPh_4]_2[Ir_{12}(CO)_{26}]$ consists of the packing of discrete $[PPh_4]^+$ and $[Ir_{12}(CO)_{26}]^{2-}$ ions and clathrated thf molecules; there are no short intermolecular contacts. Positional parameters are reported in Table I and selected bond distances and angles in Tables II and III, respectively. An ORTEP drawing of the whole structure of the $[Ir_{12}(CO)_{26}]^{2-}$ dianion and the scheme used for labeling atoms are illustrated in Figure 1.

As shown in Figure 1, the geometry of the metal framework consists of a hexagonal-close-packed fragment derived from the *abab* stacking of four staggered triangles. The resulting trioctahedron would possess, if ideally regular, D_{3d} symmetry; however, an inspection of the Ir–Ir bond lengths and angles in the actual

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Table III. Angles (deg) within the Anion $[Ir_{12}(\mu\text{-}CO)_8(CO)_{18}]^{2-}$ with Esd's in Parentheses

	Terminal CO		
Ir(1)–C(1)–O(1)	164 (5)	Ir(7)–C(10)–O(10)	172 (5)
Ir(1)–C(2)–O(2)	163 (5)	Ir(8)–C(11)–O(11)	163 (3)
Ir(2)–C(3)–O(3)	169 (5)	Ir(9)–C(12)–O(12)	171 (6)
Ir(2)–C(4)–O(4)	165 (5)	Ir(10)–C(13)–O(13)	177 (4)
Ir(3)–C(5)–O(5)	177 (5)	Ir(10)–C(14)–O(14)	173 (4)
Ir(3)–C(6)–O(6)	175 (5)	Ir(11)–C(15)–O(15)	169 (4)
Ir(4)–C(7)–O(7)	171 (4)	Ir(11)–C(16)–O(16)	176 (4)
Ir(5)–C(8)–O(8)	173 (3)	Ir(12)–C(17)–O(17)	175 (4)
Ir(6)–C(9)–O(9)	173 (4)	Ir(12)–C(18)–O(18)	176 (4)
	Bridging CO		
Ir(1)–C(19)–O(19)	143 (4)	Ir(6)–C(23)–O(23)	133 (4)
Ir(3)–C(19)–O(19)	126 (4)	Ir(8)–C(23)–O(23)	139 (4)
Ir(2)–C(20)–O(20)	134 (4)	Ir(4)–C(24)–O(24)	133 (4)
Ir(6)–C(20)–O(20)	139 (4)	Ir(7)–C(24)–O(24)	137 (4)
Ir(5)–C(21)–O(21)	130 (4)	Ir(9)–C(25)–O(25)	132 (4)
Ir(8)–C(21)–O(21)	141 (4)	Ir(11)–C(25)–O(25)	142 (3)
Ir(5)–C(22)–O(22)	139 (3)	Ir(10)–C(26)–O(26)	142 (4)
Ir(9)–C(22)–O(22)	135 (3)	Ir(12)–C(26)–O(26)	130 (4)

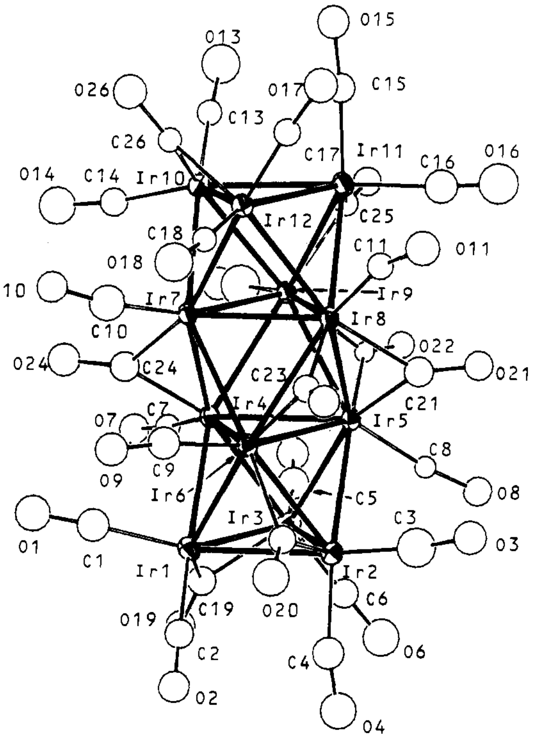

Figure 1. ORTEP drawing and numbering scheme for the $[Ir_{12}(\mu\text{-}CO)_8(CO)_{18}]^{2-}$ dianion.

polyhedron shows that its idealized symmetry is lowered to C_2, with the twofold axis bisecting the Ir(5)–Ir(8) and Ir(4)–Ir(7) edges. The CO ligands conform well to the C_2 idealized symmetry, which therefore pertains to the anion as a whole, suggesting that the deviation of the dodecametal moiety from the higher D_{3d} symmetry is chiefly due to the ligand environment.

The $[Ir_{12}(CO)_{26}]^{2-}$ cluster can be described as being derived from the condensation of two octahedral units. The close structural relationships between anion **1** and $[Ir_6(CO)_{15}]^{2-}$ are evidenced in Figure 2, which shows the structure of $[Ir_{12}(CO)_{26}]^{2-}$ and two $[Ir_6(CO)_{15}]^{2-}$ moieties[13] in a staggered orientation: it is clearly shown that the structure of **1** can be obtained by simple closure of six intertriangular Ir–Ir bonds with loss of four of the eight darkened carbonyl groups and rearrangement of the four remaining ones in bridging positions on the interlayer edges of the internal octahedron. It is noteworthy that the distribution of all the other 22 carbonyl ligands of the two external octahedra remains almost identical, from a stereochemical point of view, with that of $[Ir_6(CO)_{15}]^{2-}$.

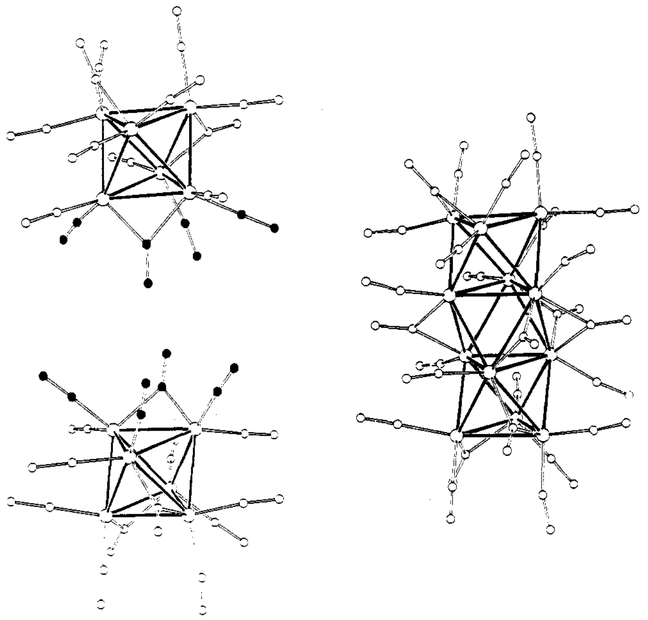

Figure 2. Scheme of condensation between two $[Ir_6(CO)_{15}]^{2-}$ units to give the $[Ir_{12}(CO)_{26}]^{2-}$ cluster dianion.

Table IV. Average Values (Å) for Ir–Ir Bond Distances

coord no.			
atom 1	atom 2	bridged	unbridged
7	7	2.743	2.813
7	8	*a*	2.709
7	9	2.754	2.771
8	8	2.723	*a*
8	9	*a*	2.781
9	9	2.820	2.863

[a] Not present.

Taking into account only the overall coordination number of each metal atom, the 12 iridium atoms of $[Ir_{12}(CO)_{26}]^{2-}$ may be divided into three sets: (i) the atoms belonging to the outer triangles, Ir(1–3) and Ir(10–12), with coordination equal to 7, (ii) the Ir(4) and Ir(7) atoms with coordination number 8, and (iii) the 9-coordinate Ir(5), Ir(6), Ir(8), and Ir(9) atoms. The Ir–Ir bond lengths are widely scattered, as often found in other anionic iridium clusters, ranging from 2.678 (3) to 2.873 (3) Å.[13-18] These interatomic separations are ordered in Table IV according to the coordination number of the linked iridium atoms and the presence of bridging CO's. An inspection of Table IV shows that no simple trend relates the length of either bridged or unbridged Ir–Ir bonds to the coordination number of the linked atoms; however, when bond distances between equally coordinated metal atoms are considered, the well-known shortening effect of bridging carbonyls on the metal–metal bond can be observed, although this effect is not always evident in the iridium clusters.[19] Of the 26 carbonyl ligands, 18 are terminal and 8 edge bridging. Ir atoms Ir(1–3,10–12), which define the two external metal triangles, bear two terminal CO's each, one in the axial and one in the equatorial

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configuration, whereas each of the remaining inner iridium atoms carries an equatorial terminal CO. The eight bridging CO's are essentially symmetric, a slight asymmetry being observable only in the Ir–C bonds involving CO(19) and CO(26), which are bound to the two external iridium triangles. Although individual Ir–C and C–O bond distances are affected by high estimated standard deviations, the average values for equivalent interactions ($Ir–C_{term}$ = 1.812 Å, $Ir–C_{brid}$ = 2.015 Å, C–O = 1.19 Å) are in agreement with the values usually observed in other anionic iridium clusters.[11,13–18]

As previously mentioned, the metal framework of the $[Ir_{12}(CO)_{26}]^{2-}$ cluster is present also in $[H_2Rh_{12}(CO)_{25}]$, the only other example of a dodecametal trioctahedral cluster known to date, but the number of ligands and their stereochemistry are different for the two compounds: thus, the $[Ir_{12}(CO)_{26}]^{2-}$ dianion contains 162 valence electrons (VE), while $[H_2Rh_{12}(CO)_{25}]$ possesses 160 VE's. Such a discrepancy in the number of valence electrons between isostructural clusters of homologous metals is unusual and provides an interesting example of how differences in both basic atomic properties of the metal and the ligand stereochemistry may alter the overall electronic requirements of a metal cluster when the energetic separations among the cluster frontier orbitals, in the naked model, are small. It confirms the view that empirical or semiempirical bonding theories based only on the geometry of a "naked" cluster can give only fair approximations to the electronic requirements of a "dressed" cluster. Thus, in a recent work on tetrahedral platinum–gold mixed clusters Mingos[20] pointed out that the substitution of a few ligands can stabilize an antibonding orbital enough, allowing the existence of two compounds with the same metal frame, but with a different number of skeletal electron pairs.

It is quite common in cluster chemistry that compounds having the same nuclearity and possessing the same number of VE's show completely different geometries for the metal frame (e.g. $[Pt_{12}(CO)_{24}]^{2-}$[3] and $[Rh_{12}(CO)_{30}]^{2-}$;[2] $[Fe_3Pt_3(CO)_{15}]^{2-}$[21] and $[Pt_6(CO)_{12}]^{2-}$;[3] $[Ni_9(CO)_{18}]^{2-}$[22] and $[Pt_9(CO)_{18}]^{2-}$[3]). Instead, only a few examples are known in which the same geometry requires different numbers of VE's (e.g. $[Rh_7(CO)_{16}]^{3-}$[23] and $[Rh_7(CO)_{16}I]^{2-}$;[24] $[Ni_8C(CO)_{16}]^{2-}$[25] and $[Co_8C(CO)_{18}]^{2-}$;[26] $[PtRh_4(CO)_{14}]^{2-}$ and $[PtRh_4(CO)_{12}]^{2-}$[27]). These differences can often be rationalized either in terms of small skeletal deformations or by the tendency of some 5d elements to adopt a 16-electron configuration.[20,28]

It may be worth mentioning, however, that, in the light of current theories, the "unexpected" compound is $[H_2Rh_{12}(CO)_{25}]$ with its 160 VE's, while the 162 VE's for $[Ir_{12}(CO)_{26}]^{2-}$ are in keeping with the number of electrons predicted by EHMO[29] calculations on high-nuclearity clusters, by topological electron counting,[28] and by the polyhedral skeletal electron pair theory,[30] which describes the metal arrangements in terms of condensed polyhedra.

Experimental Section

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under an oxygen-free nitrogen atmosphere by using the Schlenk-tube technique.

Table V. Summary of Crystal Data and Intensity Collection Parameters

formula	$C_{74}H_{40}Ir_{12}O_{26}P_2{\cdot}C_4H_8O$
fw	3875.6
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	13.968 (3)
b, Å	22.874 (10)
c, Å	26.379 (7)
β, deg	90.97 (3)
U, Å^3	8427 (8)
Z	4
calcd density, g cm^{-3}	2.984
μ(Mo Kα), cm^{-1}	189.1
min transmission factor	0.277
cryst dimens, mm	0.2 × 0.12 × 0.07
scan mode	ω
2θ range, deg	3–46
ω-scan width, deg	$1.3 + 0.35 \tan \theta$
scan rate, deg min^{-1}	3–10
octants in the reciprocal space explored	$\pm h,+k,+l$
measd reflcns	10 244
unique obsd rflns ($I \geqslant 1.5(I)$)	3807
no. of variables	547
final R, R_w[a]	0.050, 0.048
ESD[b]	1.162

[a] $R = [\sum(F_o - k|F_c|)/\sum F_o]$; $R_w = [\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}$. [b] $ESD = [\sum w(F_o - k|F_c|)^2/(N_{observns} - N_{variables})]^{1/2}$.

$[Ir_6(CO)_{15}]^{2-}$[13,31] was prepared as described in the literature. $[Cu(CH_3CN)_4][BF_4]$ was prepared by the literature method.[32]

Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer using calcium fluoride cells previously purged with N_2.

Preparation of $[PPh_4]_2[Ir_{12}(CO)_{26}]$. $[PPh_4]_2[Ir_6(CO)_{15}]$ (1.23 g, 0.56 mmol) was dissolved in thf (20.0 mL) with stirring. To the resultant brown-yellow solution was added $[Cu(CH_3CN)_4][BF_4]$ (0.19 g, 0.60 mmol) in thf (10.0 mL) by syringe. The reaction mixture was stirred at room temperature under nitrogen for 4 h when the original solution became brown-red. After the copper metal that separated off was filtered under nitrogen, the clear solution was added dropwise with stirring to 2-propanol (75 mL); this mixture was concentrated under vacuum to give a crystalline precipitate, which was filtered off, washed with 2-propanol (3 × 10 mL), and vacuum-dried: yield 0.88 g, 84%. Anal. Calcd for $C_{78}H_{48}Ir_{12}O_{27}P_2$: C, 24.75; H, 1.27; Ir, 60.92; O, 11.4; P, 1.63. Found: C, 24.2; H, 1.2; Ir, 61.7. Well-formed crystals of $[PPh_4]_2[Ir_{12}(CO)_{26}]$ were obtained in ca. 50–60% yield by slow diffusion of 2-propanol into a thf solution of the salt.

Reaction of $[N(PPh_3)_2]_2[Ir_{12}(CO)_{26}]$ with KOH. To a suspension of $[N(PPh_3)_2]_2[Ir_{12}(CO)_{26}]$ (0.62 g, 0.15 mmol) in dry methanol (20 mL) under CO was added with stirring a 0.108 M solution of KOH in MeOH (3 mL). After 30 min the reaction mixture was treated with 0.5 g of $[N(PPh_3)_2]Cl$ and then filtered. The brown solid was washed with 2-propanol (2 × 10 mL) and water (2 × 5 mL) and dried. The compound was identified as $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$: yield 0.71 g, 90%.

X-ray Analysis. Intensity Data Collection, Structure Solution, and Refinement. Crystal data and other experimental details are summarized in Table V. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer using Mo Kα radiation (λ = 0.710 73 Å) with a graphite crystal monochromator in the incident beam. Standard CAD-4 setting, indexing, and data collection programs were used. A periodic remeasurement of three standard reflections revealed a crystal decay, on X-ray exposure, which was evaluated on F_o to be about 40% at the end of data collection. Lorentz, polarization, decay, and absorption corrections were applied, the last performed with the empirical method described in ref 33. The structure solution was carried out by direct methods (MULTAN) and difference Fourier syntheses and the refinement by full-matrix least-squares, the minimized function being $\sum w(F_o - k|F_c|)^2$. Individual weights were given as $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (PI)^2]^{1/2}/Lp$ and P is the "ignorance factor" equal to 0.03. Scattering factors and anomalous dispersion corrections were taken from ref 34. Final difference Fourier maps showed

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only peaks not exceeding 0.6 e/Å^3 near the metal atoms.

All computations were done on a PDP 11/34 computer using the Enraf-Nonius structure determination package (SDP) and the physical constants therein tabulated,[35] with MULTAN[36] being used for direct methods and ORTEP[37] for drawings.

Acknowledgment. We thank the Italian CNR for financial assistance.

Registry No. 1·C_4H_8O, 110097-15-9; $[Cu(CH_3CN)_4]BF_4$, 15418-29-8; $[PPh_4]_2[Ir_6(CO)_{15}]$, 77759-20-7; $[N(PPh_3)_2]_2[Ir_{12}(CO)_{26}]$, 110097-16-0; $[H_2Ir_{12}(CO)_{26}]$, 110097-17-1; $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$, 87525-25-5; $AgPF_6$, 26042-63-7.

Supplementary Material Available: Listings of fractional atomic coordinates of the two cations and of the solvent molecule and anisotropic thermal parameters and a full listing of distances and angles (14 pages); a listing of calculated and observed structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Oxidation/Reduction Chemistry of Iron Carbonyl Clusters Containing Germanium, Tin, or Lead: Crystal and Molecular Structures of $[Et_4N]_2[Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}Ge\{Fe(CO)_4\})]$ and $Pb[Fe_2(CO)_8]_2$

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Received December 12, 1986

When $[Et_4N]_2[Fe_2(CO)_8]$ is treated with germanium(II) iodide in methylene chloride, the mixed-metal cluster $[Et_4N]_2[GeFe_4(CO)_{14}]$ ($[Et_4N]_2$[I]) is produced in approximately 25% yield along with $[Et_4N][HFe_3(CO)_{11}]$. This compound has been characterized by elemental analysis and its spectroscopic properties, as well as by single-crystal X-ray diffraction. When treated with $[Cu(NCMe)_4][BF_4]$, $[Et_4N]_2$[I] is converted into the previously reported spirocyclic complex $Ge[Fe_2(CO)_8]_2$ (II). The oxidation process is reversible by using cobaltocene as a reducing agent. Germanium tetrachloride has been found to cause oxidation of $[Et_4N]_2[Fe_2(CO)_8]$ in methylene chloride producing $[Et_4N]_2[Fe_3(CO)_{11}]$ with no evidence of formation of $[Et_4N]_2[GeFe_4(CO)_{14}]$ or other germanium-containing iron clusters. The compound $[Et_4N]_2[Sn\{Fe_2(CO)_8\}\{Fe(CO)_4\}_2]$ ($[Et_4N]_2$[III]) has been produced from $[Et_4N]_2[Fe_2(CO)_8]$ and tin(II) acetate. $[Et_4N]_2$[III] is oxidized by $[Cu(CH_3CN)_4][BF_4]$, giving spirocyclic $Sn[Fe_2(CO)_8]_2$ (IV), which is isoelectronic and isostructural with II. Similar results are obtained when $[Et_4N]_2[Pb\{Fe_2(CO)_8\}\{Fe(CO)_4\}_2]$ ($[Et_4N]_2$[V]) is treated with $[Cu(CH_3CN)_4][BF_4]$ giving $Pb[Fe_2(CO)_8]_2$ (VI). VI can be reduced to $[Et_4N]_2$[V] upon treatment with stoichiometric amounts of cobaltocene. Electrochemical studies of $[Et_4N]_2$[V] indicate an irreversible two-electron $\vec{E}C\vec{E}$ oxidation. VI is reduced to the $[V]^{2-}$ anion by treatment with cobaltocene. Single-crystal X-ray data for $[Et_4N]_2$[I] and VI were collected on a Syntex P2$_1$ diffractometer using Mo Kα radiation ($2\theta = 4.5$–$40.0°$). The complex $[Et_4N]_2$[I] crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ (No. 2) with $a = 9.229$ (3) Å, $b = 10.279$ (3) Å, $c = 20.513$ (7) Å, $\alpha = 83.926$ (27)°, $\beta = 83.147$ (26)°, $\gamma = 88.566$ (24)°, $V = 1921.2$ (11) Å^3, and $Z = 2$. The structure was refined to $R_F = 11.4\%$ and $R_{wF} = 6.2\%$ for all 3626 data ($R_F = 5.2\%$ and $R_{wF} = 5.0\%$ for those 2025 reflections with $|F_o| > 6\sigma(|F_o|)$). The $[Et_4N]^+$ ions are ordered, but the $[GeFe_4(CO)_{14}]^{2-}$ dianions are disordered. The dianions contain a tetrahedral $GeFe_3$ core in which each iron atom is linked to three terminal carbonyl ligands: a pendant $Fe(CO)_4$ group completes the tetrahedral arrangement about the germanium atom, while the 14th carbonyl ligand is bound to all three iron atoms of the $GeFe_3$ in a μ_3-mode. Disorder involves a second minor (1:3) orientation of the dianion in which the triangular Fe_3 moiety is rotated by 31.5° relative to the major orientation. Distances within the $GeFe_3$ core (major component only) are Ge–Fe = 2.389 (3)–2.400 (4) Å and Fe–Fe = 2.643 (5)–2.657 (4) Å; the Ge–$Fe(CO)_4$ bond length is 2.327 (2) Å. Compound VI crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 10.9911$ (15) Å, $b = 19.3056$ (28) Å, $c = 11.8644$ (22) Å, $\beta = 90.657$ (13)°, $V = 2517.4$ (7) Å^3, and $Z = 4$. Single-crystal X-ray diffraction data (Mo Kα, $2\theta = 4.5$–$40.0°$) were collected with a Syntex P2$_1$ diffractometer, and the structure was solved and refined to $R_F = 6.9\%$ and $R_{wF} = 6.1\%$ for all 2364 reflections ($R_F = 5.0\%$ and $R_{wF} = 5.8\%$ for those 1824 reflections with $|F_o| > 6\sigma(|F_o|)$). The molecule contains formally a central Pb(IV) atom coordinated to two chelating $[Fe_2(CO)_8]^{2-}$ dianions. The Pb(IV) atom is in a distorted tetrahedral environment, with the $Pb[Fe_2(CO)_8]_2$ molecule having approximate D_{2d} symmetry. Fe–Fe bond lengths are 2.890 (4)–2.911 (4) Å, Pb–Fe bond lengths are 2.606 (3)–2.635 (3) Å, and all CO ligands are in terminal sites. The Fe–Fe bond distances are among the longest yet reported.

Introduction

Inorganic and organic compounds of main-group elements react with low-valent transition-metal complexes, producing clusters that may adopt either "open" or "closed" geometries. The completely open structures contain no bonds between the transition metals while the closed complexes may show one or more metal–metal bonds. This effect has been correlated to size, with the smaller main-group elements showing a decided preference for closed structures.[1] Intermediate-sized atoms such as germanium can adopt either open or closed structures. Thus $PhGe[Co(CO)_4]_3$, $PhGe[Co_2(CO)_6(\mu\text{-}CO)][Co(CO)_4]$, and $PhGeCo_3(CO)_9$ are all known and possess zero, one, and three metal–metal bonds, respectively.[2] Synthesis of $Co_3(CO)_9(\mu_3\text{-}GeCo(CO)_4)$ has been reported as has work on a number of $Co_3(CO)_9(\mu_3\text{-}GeR)$ clusters including metal substitution reactions.[3,4] Clusters containing spirocyclic germanium atoms include $Ge[Fe_2(CO)_8]_2$,[5] $Ge[Co_2$-

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