J. Am. Chem. Soc. 1984, 106, 6664-6667

a chair conformation.[33] The results show that the HOMO orbital is primarily a π-type orbital centered on sulfur b and delocalized somewhat on sulfur a (Figure 3). The LUMO orbital is a mixture of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The lowest energy transition (HOMO → LUMO) is thus described as a $S(\pi) \rightarrow Ti$ charge-transfer transition. The photochemistry of the Cp_2TiS_5 complex is essentially wavelength independent. To explain this observation, we must either propose that fast internal conversion to the lowest energy excited state occurs or the absorption bands in the 300–700-nm region are all of the same type (i.e., S → Ti charge transfer). We favor the latter explanation because the Xα calculation predicts that several S → Ti CT bands will occur to lower energy than the first Cp → Ti bands. Accordingly, we qualitatively assign all three absorption bands in the region 300–700 nm as S → Ti bands.

Acknowledgment is made to the Procter and Gamble Co. for a University Exploratory Research Grant. A.E.B. thanks American Cyanamid for a fellowship. Ian Gould is thanked for his assistance with the flash photolysis experiments. Anthony Sclafani is acknowledged for experimental assistance.

Registry No. Cp_2TiS_5, 12116-82-4; $Cp_2Ti(SPh)_2$, 1292-47-3; $Cp_2Ti(SEt)_2$, 1291-79-8; Cp_2TiCl_2, 1271-19-8; Cp_2TiBr_2, 1293-73-8; $CpTiCl_3$, 1270-98-0; CCl_4, 56-23-5; $BrCCl_3$, 75-62-7; Ph_3CCl, 76-83-5; Bu_4NCl, 1112-67-0; $PhC{\equiv}CPh$, 501-65-5; $CH_3O_2CC{\equiv}CCO_2CH_3$, 762-42-5; $P(OCH_3)_3$, 121-45-9; $P(OC_2H_5)_3$, 122-52-1; CO, 630-08-0; PhSSPh, 882-33-7; EtSSEt, 110-81-6; bipyridine, 366-18-7.

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[33] The techniques used in the SCF-Xα-SW calculation have been previously described.[23]

Structures of Two Isomers of $Ir_6(CO)_{16}$

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Abstract: $Ir_6(CO)_{16}$ has been isolated in two different isomeric forms, both of which have been crystallographically characterized. The red isomer is isostructural with $Rh_6(CO)_{16}$, with four face-bridging carbonyl groups. The black isomer, in contrast, has four edge-bridging carbonyl groups, each of them being asymmetrically bonded. For both isomers, a crystallographic 2-fold rotation axis passes through two of the iridium atoms. Crystallographic details: Red isomer of $Ir_6(CO)_{16}$, space group $C2/c$ (monoclinic); a = 16.656 (2) Å, b = 9.761 (1) Å, c = 16.776 (2) Å, β = 118.09 (1)°, V = 2406 Å^3, Z = 4; R = 3.4% for 1508 reflections. Black isomer of $Ir_6(CO)_{16}$, space group $P2/c$ (monoclinic); a = 13.622 (5) Å, b = 12.807 (4) Å, c = 18.589 (5) Å, β = 132.65 (2)°, V = 2385 Å^3, Z = 4; R = 5.1% for 1973 reflections.

One of the landmark papers in organometallic chemistry is the report of the structure of $Rh_6(CO)_{16}$ by Corey, Dahl, and Beck in 1963,[1] which showed for the first time the existence of large (i.e., $n \geq 6$) metal carbonyl clusters.[2] Soon thereafter, the analogous complex $Co_6(CO)_{16}$ was synthesized[3] and shown to be isomorphous with $Rh_6(CO)_{16}$. In this paper we report that the iridium analogue, $Ir_6(CO)_{16}$, exists in two isomeric forms, one of which is isostructural with $Rh_6(CO)_{16}$, while the other one has a different (hitherto unknown) geometry.

Experimental Section

Preparation and Structure Determination of the Red Isomer of $Ir_6(CO)_{16}$. The red isomer of $Ir_6(CO)_{16}$ was originally synthesized by Malatesta and co-workers in 1970 and described as a "highly stable compound, isolable in a very pure state".[4] At that time it was already recognized that this isomer (the only one known then) was isostructural with $Rh_6(CO)_{16}$. Here we describe the results of a full structural analysis of this older compound. The sample used in the X-ray analysis was synthesized according to published procedures.[5] The red isomer of $Rh_6(CO)_{16}$ crystallizes in the monoclinic space group $C2/c$ (No. 15) with unit cell parameters and other crystallographic details listed in Table I.

Table I. Summary of Crystallographic Data and Data Collection Procedures for the Two Isomers of $Ir_6(CO)_{16}$

	red isomer	black isomer
space group	$C2/c$ (monoclinic, No. 15)	$P2/c$ (monoclinic, No. 13)
a, Å	16.656 (2)	13.622 (5)
b, Å	9.761 (1)	12.807 (4)
c, Å	16.776 (2)	18.589 (5)
β, deg	118.09 (1)	132.65 (2)
V, Å^3	2406	2385
ρ(calcd), g cm^{-3}	4.42	4.46
Z	4	4
M_r	1601.4	1601.4
cryst size, mm	0.21 × 0.14 × 0.13	0.20 × 0.25 × 0.45
radtn used	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
μ(Mo Kα), cm^{-1}	330.2	333.2
diffractometer used	Nonius CAD-4	Nicolet/Syntex P2$_1$
scan type	ω	2θ
scan width, deg	$\Delta\omega = 1.6 + 0.35 \tan\theta$	$\Delta 2\theta = 2.0 + [2\theta(K\alpha_2) - 2\theta(K\alpha_1)]$
scan speed, deg min^{-1}	2.5	2.5–15.0
data collctn range	$6° \leq 2\theta \leq 50°$	$3.5° \leq 2\theta \leq 45°$
no. unique data	2246	2954
no. data used in least-squares [$I \geq 3\sigma(I)$]	1508	1973
no. variables	173	281
R	0.034	0.051
R_w	0.039	0.056

Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer by the ω-scan technique, using Mo Kα radiation (λ = 0.7107 Å) with a graphite crystal monochromator in the incident beam. Standard CAD-4 centering, indexing, and data collection programs were used. The lattice parameters and the orientation matrix were refined by least-squares fit using 24 reflections with $7.4° < \theta < 16.1°$. Intensity data, 2325, were obtained by collecting the ($\pm h,+k,+l$) region of recip-

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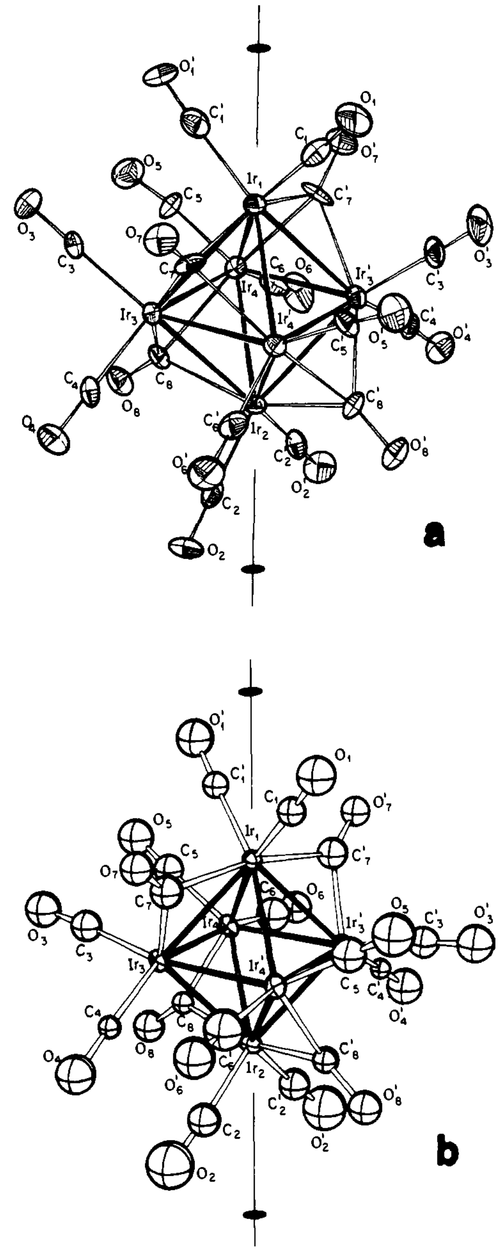

Figure 1. (a) Molecular plot of the red isomer of $Ir_6(CO)_{16}$, showing the four face-bridging carbonyl groups. A crystallographic C_2 axis passes vertically from Ir(1) to Ir(2). (b) Molecular plot of the black isomer of $Ir_6(CO)_{16}$, showing the four edge-bridging carbonyl groups (this figure displays one of the two independent molecules in the unit cell).

rocal space in the 2θ range 6–50°. The scan width for each reflection was determined as $(1.6 + 0.35 \tan \theta)°$. A periodic remeasurement of three standard reflections revealed no crystal decay. In addition, three orientation standards were checked after every 128 reflections. If the standard deviation of the (h,k,l) values for any orientation reflection exceeded 0.08, a new orientation matrix was calculated on the basis of the recentering of 21 reference reflections. Lorentz, polarization, and absorption corrections were applied. An absorption correction was made by numerical integration, sampling the crystal on a $14 \times 8 \times 8$ Gaussian grid. Transmission factors were in the range 0.046–0.111.

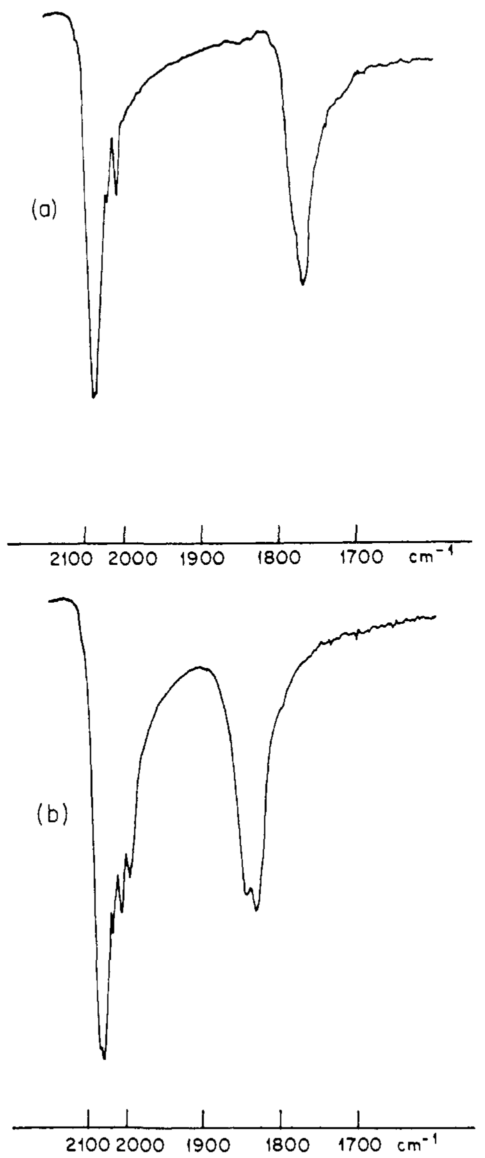

Figure 2. Infrared spectra (CO stretching region) of the red isomer (a) and the black isomer (b) of $Ir_6(CO)_{16}$.

Table II. Final Atomic Coordinates for the Red Isomer of $Ir_6(CO)_{16}$

atom	x	y	z
Ir(1)	0.00000 (0)[a]	0.56740 (9)	0.25000 (0)[a]
Ir(2)	0.00000 (0)[a]	0.16440 (9)	0.25000 (0)[a]
Ir(3)	0.09125 (4)	0.36575 (7)	0.37791 (3)
Ir(4)	0.09750 (4)	0.36593 (7)	0.21514 (3)
O(1)	−0.1504 (11)	0.778 (1)	0.1800 (11)
O(2)	−0.0015 (9)	−0.049 (1)	0.3801 (9)
O(3)	0.2542 (9)	0.546 (2)	0.4875 (10)
O(4)	0.1145 (9)	0.190 (1)	0.5349 (8)
O(5)	0.2815 (9)	0.498 (2)	0.2927 (9)
O(6)	0.1245 (1)	0.220 (2)	0.0711 (8)
O(7)	−0.0121 (8)	0.598 (1)	0.4288 (7)
O(8)	0.2128 (8)	0.139 (1)	0.3565 (8)
C(1)	−0.095 (1)	0.699 (2)	0.206 (1)
C(2)	0.000 (1)	0.031 (2)	0.331 (1)
C(3)	0.194 (1)	0.479 (2)	0.448 (1)
C(4)	0.105 (1)	0.259 (2)	0.477 (1)
C(5)	0.211 (1)	0.454 (2)	0.260 (1)
C(6)	0.115 (1)	0.273 (2)	0.126 (1)
C(7)	−0.008 (1)	0.521 (2)	0.376 (1)
C(8)	0.148 (1)	0.213 (2)	0.326 (1)

[a] Coordinate fixed by symmetry.

The structure solution was carried out by conventional Patterson and Fourier methods and the refinement was made by using 1508 independent reflections having $I > 3\sigma(I)$. The final full-matrix least-squares

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(1) Corey, E. R.; Dahl, L. F.; Beck, W. *J. Am. Chem. Soc.* **1963**, *85*, 1202.

(2) Today, the field of large ("high nuclearity") metal carbonyl clusters has expanded tremendously, with clusters ranging in size from 6 to 38 metal atoms having been isolated. For reviews, see: (a) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285. (b) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37.

(3) Albano, V.; Chini, P.; Scatturin, V. *Chem. Commun.* **1968**, 163.

(4) Malatesta, L.; Caglio, G.; Angoletta, M. *Chem. Commun.* **1970**, 532.

(5) Angoletta, M.; Malatesta, L.; Caglio, G. *J. Organomet. Chem.* **1975**, *94*, 99.

Table III. Final Atomic Coordinates for the Black Isomer of $Ir_6(CO)_{16}$

atom	x	y	z	atom	x	y	z
Ir(1)	0.5000[a]	0.8015 (2)	0.7500[a]	Ir(11)	0.0000[a]	0.3817 (2)	0.2500[a]
Ir(2)	0.5000[a]	1.1142 (2)	0.7500[a]	Ir(12)	0.0000[a]	0.6919 (2)	0.2500[a]
Ir(3)	0.3090 (1)	0.9564 (1)	0.6756 (1)	Ir(13)	−0.1014 (1)	0.5377 (1)	0.2894 (1)
Ir(4)	0.5367 (1)	0.9593 (1)	0.8713 (1)	Ir(14)	0.1664 (1)	0.5358 (1)	0.3862 (1)
C(1)	0.522 (4)	0.700 (3)	0.690 (3)	C(11)	−0.118 (4)	0.289 (3)	0.147 (3)
O(1)	0.536 (3)	0.633 (2)	0.657 (2)	O(11)	−0.177 (3)	0.225 (3)	0.088 (2)
C(2)	0.374 (5)	1.219 (3)	0.665 (3)	C(12)	−0.040 (4)	0.789 (3)	0.305 (3)
O(2)	0.290 (4)	1.281 (3)	0.614 (3)	O(12)	−0.068 (3)	0.847 (2)	0.332 (2)
C(3)	0.207 (4)	0.923 (3)	0.707 (3)	C(13)	−0.051 (4)	0.585 (3)	0.406 (3)
O(3)	0.144 (3)	0.910 (2)	0.726 (2)	O(13)	0.024 (3)	0.622 (2)	0.474 (2)
C(4)	0.172 (3)	1.032 (3)	0.569 (2)	C(14)	−0.279 (4)	0.576 (3)	0.222 (3)
O(4)	0.083 (3)	1.086 (2)	0.500 (2)	O(14)	−0.382 (3)	0.604 (2)	0.186 (2)
C(5)	0.454 (4)	0.881 (3)	0.906 (3)	C(15)	0.221 (3)	0.527 (3)	0.513 (2)
O(5)	0.409 (3)	0.835 (2)	0.928 (2)	O(15)	0.259 (3)	0.523 (2)	0.586 (2)
C(6)	0.693 (5)	0.980 (4)	1.004 (4)	C(16)	0.313 (5)	0.456 (4)	0.434 (3)
O(6)	0.783 (3)	0.992 (2)	1.084 (2)	O(16)	0.412 (4)	0.414 (3)	0.470 (3)
C(7)	0.291 (4)	0.820 (3)	0.618 (3)	C(17)	−0.121 (4)	0.383 (3)	0.295 (2)
O(7)	0.210 (3)	0.765 (2)	0.552 (2)	O(17)	−0.161 (3)	0.316 (2)	0.311 (2)
C(8)	0.433 (4)	1.091 (3)	0.828 (3)	C(18)	0.218 (4)	0.686 (3)	0.398 (3)
O(8)	0.385 (3)	1.152 (2)	0.848 (2)	O(18)	0.300 (3)	0.748 (2)	0.437 (2)

[a] Coordinate fixed by symmetry.

Table IV. Interatomic Distances in the Red Isomer of $Ir_6(CO)_{16}$

Ir(1)–Ir(3)	2.778 (1)	Ir(2)–C(8)	2.234 (15)
Ir(1)–Ir(4)	2.782 (1)	Ir(3)–C(7)	2.223 (17)
Ir(2)–Ir(3)	2.776 (1)	Ir(3)–C(8)	2.155 (15)
Ir(2)–Ir(4)	2.783 (1)	Ir(4)–C(7)	2.169 (14)
Ir(3)–Ir(4)	2.781 (1)	Ir(4)–C(8)	2.222 (14)
Ir(3)–Ir(4′)	2.775 (1)	C(1)–O(1)	1.123 (21)
Ir(1)–C(1)	1.894 (20)	C(2)–O(2)	1.144 (19)
Ir(2)–C(2)	1.884 (17)	C(3)–O(3)	1.123 (19)
Ir(3)–C(3)	1.900 (17)	C(4)–O(4)	1.127 (18)
Ir(3)–C(4)	1.889 (16)	C(5)–O(5)	1.121 (18)
Ir(4)–C(5)	1.882 (16)	C(6)–O(6)	1.135 (20)
Ir(4)–C(6)	1.883 (17)	C(7)–O(7)	1.194 (17)
Ir(1)–C(7)	2.223 (15)	C(8)–O(8)	1.193 (17)

refinement, with all the atoms treated anisotropically, led to conventional R and R_w factors of 0.034 and 0.039, respectively.[6] In the last cycles, individual weights were given as $w(hkl) = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/Lp$ and p, the "ignorance factor", = 0.04. Scattering factors and anomalous dispersion corrections were taken from ref 7a, atomic absorption coefficients from ref 7b. The final difference map showed no peaks of structural significance. A plot of the molecule is shown in Figure 1a.

Synthesis of the Black Isomer of $Ir_6(CO)_{16}$. The new black isomer was prepared according the following procedure: In a Schlenk tube and under a nitrogen atmosphere, 0.35 g (0.2 mmol) of $[Me_4N]_2^+$ $[Ir_6(CO)_{15}]^{2-}$ was dissolved in 20 mL of dichloromethane. To this solution was added 4.4 mL of a dichloromethane solution of CF_3COOH (0.05 M) (molar ratio 1.0:1.1, in slight excess over the stoichiometric amount) to obtain the $[HIr_6(CO)_{15}]^-$ anion, whose presence was verified by infrared spectroscopy. This solution was filtered and layered with 40 mL of heptane. After 5 days, a black precipitate was formed which contains crystals of $Ir_6(CO)_{16}$ together with $[HIr_6(CO)_{15}]^-$, $[Ir_6(CO)_{15}]^{2-}$, and some other uncharacterized byproducts. The black precipitate was washed with tetrahydrofuran (3 × 10 mL), leaving as a residue black crystals of $Ir_6(CO)_{16}$ (yield, ca. 10%). The compound is slightly soluble in THF and CH_2Cl_2 and insoluble in other common organic solvents. It is stable for prolonged periods of time under a nitrogen atmosphere. It reacts in wet methanol with Na_2CO_3 to give the same $[Ir_6(CO)_{15}]^{2-}$ anion obtained from the red isomer of $Ir_6(CO)_{16}$. We are in the process of studying the reactivity of the black isomer of $Ir_6(CO)_{16}$ toward nucleophiles in order to compare it with the corresponding reactions[8] of the red isomer. The IR spectra of both isomers are shown for comparison in Figure 2. Neither the black nor red isomer of $Ir_6(CO)_{16}$ is sufficiently soluble in common organic solvents to permit the collection of NMR data. Furthermore, their volatility is so low that mass spectral analysis is also excluded.

Structural Analysis of the Black Isomer of $Ir_6(CO)_{16}$. A black needle-shaped crystal measuring 0.2 × 0.25 × 0.45 mm was sealed in a glass capillary and used for the diffraction analysis. This black isomer of $Ir_6(CO)_{16}$ crystallizes in the monoclinic space group $P2/c$ (No. 13), with crystal data given in Table I. A $\theta/2\theta$ measuring mode was employed using a Nicolet/Syntex $P2_1$ automated diffractometer to collect the $(+h,+k,\pm l)$ quadrant of reciprocal space with 2θ ranging from 3.5° to 45.0°. Throughout the data collection, three check reflections were monitored at 50-reflection intervals, and they showed little or no variation in intensities. Lorentz, polarization, and empirical absorption corrections were applied to the data. A total of 3717 reciprocal points were collected, of which 2954 reflections were unique; the 1973 reflections with $I \geq 3\sigma(I)$ were used in the subsequent structural analysis.

The iridium positions were obtained from direct methods.[9] All the carbonyl positions were found from a series of difference maps. The iridium atoms were refined anisotropically, while the carbon and oxygen atoms were refined isotropically. The final agreement factors are $R = 0.051$ and $R_w = 0.056$.[6] The structure consists of two independent but structurally equivalent $Ir_6(CO)_{16}$ molecules, each situated on a crystallographic C_2 axis. One of these is shown in Figure 1b.

Description and Discussion of the Structures

As mentioned earlier, the structures of the red and black isomers of $Ir_6(CO)_{16}$ are depicted in Figure 1, parts a and b, respectively. Final atomic coordinates are listed in Tables II and III, while interatomic distances for the two structures are given in Tables IV and V (average distances are given in Table VI). Also available as supplementary material are the final thermal parameters, interatomic angles, and observed and calculated structure factors for both structure determinations.

The geometry of the red isomer (Figure 1a) is isostructural with $Rh_6(CO)_{16}$, with four face-bridging and 12 terminal carbonyl groups. The molecule is situated on a crystallographic 2-fold rotation axis. The face-bridging CO's are essentially symmetric, with Ir–C bond distances ranging from 2.16 (2) to 2.23 (2) Å.

The black isomer of $Ir_6(CO)_{16}$ (Figure 1b) has a structure that consists of 12 terminal and four *edge-bridging* CO groups. Careful

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(6) The structure of the red isomer of $Ir_6(CO)_{16}$ was solved on a PDP 11/34 computer at the University of Milan by using the Enraf-Nonius structure determination package (SDP); that of the black isomer was solved on an IBM 370–158 computer at the University of Southern California by using CRYM, an amalgamated set of crystallographic programs developed by Richard E. Marsh's group at the California Institute of Technology.

(7) (a) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. 4. (b) "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1962; Vol. 3.

(8) (a) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Sartorelli, U.; Tagliabue, F. *J. Organomet. Chem.* **1982**, *234*, C39. (b) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Raimondi, C. C.; Martinengo, S. *J. Organomet. Chem.* **1983**, *243*, C10. (c) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Malatesta, M. C.; Sartorelli, U. *J. Organomet. Chem.* **1983**, *248*, C17.

(9) MULTAN: a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368).

Table V. Interatomic Distances in the Black Isomer of $Ir_6(CO)_{16}$

molecule 1		molecule 2	
bond	distance	bond	distance
Ir(1)–Ir(3)	2.783 (2)	Ir(11)–Ir(13)	2.794 (2)
Ir(1)–Ir(4)	2.810 (2)	Ir(11)–Ir(14)	2.769 (2)
Ir(2)–Ir(3)	2.809 (2)	Ir(12)–Ir(13)	2.777 (2)
Ir(2)–Ir(4)	2.782 (2)	Ir(12)–Ir(14)	2.787 (2)
Ir(3)–Ir(4)	2.751 (2)	Ir(13)–Ir(14)	2.766 (3)
Ir(3)–Ir(4′)	2.769 (3)	Ir(13)–Ir(14′)	2.743 (2)
Ir(1)–C(1)	1.86 (5)	Ir(11)–C(11)	1.87 (3)
Ir(2)–C(2)	1.89 (5)	Ir(12)–C(12)	1.91 (5)
Ir(3)–C(3)	1.89 (7)	Ir(13)–C(13)	1.87 (4)
Ir(3)–C(4)	1.82 (3)	Ir(13)–C(14)	1.88 (6)
Ir(4)–C(5)	1.92 (6)	Ir(14)–C(15)	1.93 (4)
Ir(4)–C(6)	1.89 (5)	Ir(14)–C(16)	1.85 (7)
Ir(1)–C(7)	2.17 (5)	Ir(11)–C(17)	2.30 (6)
Ir(2)–C(8)	2.20 (5)	Ir(12)–C(18)	2.30 (5)
Ir(3)–C(7)	1.97 (4)	Ir(13)–C(17)	2.01 (4)
Ir(4)–C(8)	1.98 (4)	Ir(14)–C(18)	2.00 (4)
C(1)–O(1)	1.14 (6)	C(11)–O(11)	1.15 (5)
C(2)–O(2)	1.18 (7)	C(12)–O(12)	1.10 (6)
C(3)–O(3)	1.14 (8)	C(13)–O(13)	1.15 (5)
C(4)–O(4)	1.23 (5)	C(14)–O(14)	1.14 (7)
C(5)–O(5)	1.11 (8)	C(15)–O(15)	1.08 (5)
C(6)–O(6)	1.13 (6)	C(16)–O(16)	1.15 (8)
C(7)–O(7)	1.18 (5)	C(17)–O(17)	1.15 (6)
C(8)–O(8)	1.23 (6)	C(18)–O(18)	1.15 (6)

Table VI. Average Molecular Parameters[a] for the Two Isomers of $Ir_6(CO)_{16}$

	red isomer	black isomer
Ir–Ir	2.779 (1) Å	2.778 (6) Å
Ir–C (terminal)	1.886 (3) Å	1.882 (8) Å
Ir–C (bridging)	2.20 (1) Å	1.99 (1), 2.25 (3) Å
C–O (terminal)	1.13 (1) Å	1.14 (1) Å
C–O (bridging)	1.19 (2) Å	1.18 (2) Å
Ir–C–O (terminal)	177 (1)°	175 (1)°
Ir–C–O (bridging)	133 (1)°	132 (1)°, 145 (2)°

[a] Standard deviations of mean values are calculated as $[\sum(x_i - \bar{x})^2/n(n-1)]^{1/2}$, where n is the number of observations.

comparison of the two structures shows that the set of four face-bridging carbonyls of the red isomer (labeled C(7)O(7), C(8)O(8), C(7)′O(7)′, and C(8)′O(8)′ in Figure 1a) become edge bridging in the black isomer (Figure 1b). The net effect of the transformation can be viewed as a rotation of the $Ir(CO)_4$ units on atoms Ir(1) and Ir(2) by about 45° around the 2-fold axis.[10] Another way of visualizing the transformation is to imagine bonds Ir(4)′–C(7), Ir(4)–C(7)′, Ir(3)–C(8), and Ir(3)′–C(8)′ of Figure 1a elongating and finally breaking to reach the configuration shown in Figure 1b.

The edge-bridging carbonyl groups of the black isomer of $Ir_6(CO)_{16}$ are all asymmetric.[11] In each case, the pattern of asymmetry is such that the bridging ligand is closer to the metal atom that bears one bridging ligand (e.g., Ir(3)) than the metal atom that bears two bridging ligands (e.g., Ir(1)) (see Figure 1b). The bridging ligands span two mutually perpendicular pairs of edges (i.e., Ir(3)–Ir(1)–Ir(3)′ and Ir(4)–Ir(2)–Ir(4)′). The difference in carbonyl group arrangement appears to have no effect on the size of the Ir_6 cores; the mean Ir–Ir bond distance in the red isomer (2.779 Å) is essentially the same as that in the black isomer (2.778 Å).

Metal carbonyl compounds are classic examples of fluxional molecules,[12] and some are believed to adopt different isomeric forms in solution.[13] The existence of the two isomers of $Ir_6(CO)_{16}$ reported here may suggest that edge-bridging species could be intermediates in the interconversions of face-bridging carbonyl groups (i.e., face → edge → face) and vice versa (edge → face → edge). For $Ir_6(CO)_{16}$ itself, however, the isomers do not interconvert, either in solution or in the solid state upon heating (to 100 °C). Although isomeric forms of other metal carbonyl complexes have been crystallographically characterized (e.g., $[H_3Ru_4(CO)_{12}]^-$)[14] this work represents, to our knowledge, the first structure determination of two different isomers of a *neutral* parent metal carbonyl compound.

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Registry No. $Ir_6(CO)_{16}$ red isomer, 56801-74-2; $Ir_6(CO)_{16}$ black isomer, 92144-93-9; $[Me_4N]_2{}^+[Ir_6(CO)_{15}]^{2-}$, 56995-73-4.

Supplementary Material Available: Listings of the final temperature factors (Tables A and B), bond angles (Tables C and D), and observed and calculated structure factors (Tables E and F) for both the red and black isomers of $Ir_6(CO)_{16}$ (26 pages). Ordering information is given on any current masthead page.

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(10) For example, consider the unit Ir(1)C(1)C(1)′C(7)C(7)′ in Figure 1a: a clockwise rotation of about 45° down the two-fold axis would place C(7), formerly face-bridging, coplanar with Ir(1) and Ir(3) and hence edge-bridging (Figure 1b); note that the positions of C(1) and C(1)′ have also shifted slightly in accordance with this rotation. The same argument applies to the unit Ir(2)C(2)C(2)′C(8)C(8)′.

(11) For molecule **1** (Figure 1a), Ir(3)–C(7) = 1.97 (4), Ir(1)–C(7) = 2.17 (5), Ir(4)–C(8) = 1.98 (4), Ir(2)–C(8) = 2.20 (5) Å. For molecule **2** (not shown), Ir(13)–C(17) = 2.01 (4), Ir(11)–C(17) = 2.30 (6), Ir(14)–C(18) = 2.00 (4), Ir(12)–C(18) = 2.30 (5) Å.

(12) Cotton, F. A. *J. Organomet. Chem.* **1975**, *100*, 29.

(13) E.g., $Co_2(CO)_8$. See: Lichtenberger, D. L.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 1381 and references therein.

(14) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1978**, 920.