the solids afforded pure 9 as colorless solids in 90% yield (0.409 g, 0.45 mmol): mp 197 °C dec; ^{1}H NMR (CD$_3$CN) 7.38 (dd, $J_{\rm TlH}$ = 903 Hz, $J_{\rm HH}$ = 7.5 Hz, 2 H, H$_2$), 7.52 (dt, $J_{\rm TlH}$ = 335 Hz, $J_{\rm HH}$ = 7.5 Hz, 2 H, H$_3$), 7.47 (dt, $J_{\rm TlH}$ = 116 Hz, $J_{\rm HH}$ = 7.5 Hz, 1 H, H$_4$), 3.73 (s, 15 H, CH$_3$), 7.60 (s, 5 H, H$_{2'}$), 7.18 (s, 5 H, H$_{4'}$), 6.86 (s, 5H, H$_{5'}$); IR (Nujol) ν(C–O–C and ClO$_4$) 1097 (s) cm^{-1}. Anal. Calcd for (C$_{26}$H$_{35}$Cl$_2$N$_{10}$O$_8$Tl)H$_2$O: C, 34.36; H, 4.10; N, 15.41. Found: C, 34.31; H, 3.88; N, 15.39.

Reaction of 1 with Aniline. Into an acetonitrile-d_3 (0.6 mL) solution of 1 (0.074 g, 0.1 mmol) was added aniline (0.037 g, 0.4 mmol). ^{1}H NMR spectra of the reaction mixture were measured after 20 min at room temperature. The complex 1 completely changed to [Ph(OH)Tl$^{\rm III}$(18-crown-6)](ClO$_4$).[9]

Reaction of 8 with NaCl in CD$_3$CN/D$_2$O Mixed Solvent. Into an acetonitrile-d_3 (0.5 mL) solution of 8 (0.0816 g, 0.1 mmol) was added a D$_2$O (0.2 mL) solution of NaCl (0.0040 g, 0.1 mmol). An ^{1}H NMR spectrum of the reaction mixture measured after 20 min at room temperature showed that complex 8 completely changed to [Ph(Cl)Tl$^{\rm III}$(18-crown-6)](ClO$_4$)[13] and free imidazole.

Reaction of 8 with Triethylamine. Into an acetonitrile-d_3 (0.6 mL) solution of 8 (0.0816 g, 0.1 mmol) was added triethylamine (0.0010 g, 0.1 mmol). An ^{1}H NMR spectrum of the reaction mixture measured after 20 min at room temperature showed that complex 8 completely changed to [Ph(OH)Tl$^{\rm III}$(18-crown-6)](ClO$_4$)[9] and free imidazole.

Reaction of 8 with Pyridine. Into an acetonitrile-d_3 (0.6 mL) solution of 8 (0.0816 g, 0.1 mmol) was added pyridine (0.079 g, 1.0 mmol). An ^{1}H NMR spectrum of the reaction mixture measured after heating at 60 °C for 1 day showed no ligand-exchange reaction.

Acknowledgment. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for the use of the facilities. This work has been supported in part by a Grant-in-Aid for Scientific Research (No. 0364051) from Ministry of Science, Culture, and Education.

Alkyne-Substituted Carbonyl Clusters of Iridium: Synthesis, Characterization, and Solid-State Structures of Ir$_6$(CO)$_{13}$(μ-CO)(μ_3-η^2-PhCCPh) and Ir$_6$(CO)$_{12}$(μ_3-η^2-PhCCPh)$_2$·CH$_2$Cl$_2$

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The carbonyl cluster Ir$_6$(CO)$_{14}$(μ_3-η^2-PhCCPh) (1) is obtained by oxidation of [Ir$_6$(CO)$_{15}$]$^{2-}$ with the [Fe(C$_5$H$_5$)$_2$]$^+$ cation, in the presence of diphenylacetylene. Complex 1 crystallizes in the triclinic space group (No. 2) $P\bar{1}$ with a = 9.443 (1) Å, b = 16.622 (1) Å, c = 21.560 (3) Å, α = 89.87 (1)°, β = 96.45 (1)°, γ = 101.78 (1)°, V = 3291 (1) Å^3, and Z = 4; R = 0.034 for 6236 observed reflections having $I \geq 3\sigma(I)$. When complex 1 is heated with excess of PhC≡CPh, a further substitution occurs, yielding the carbonyl cluster Ir$_6$(CO)$_{12}$(μ_3-η^2-PhCCPh)$_2$ (2). Crystals of 2 are monoclinic, space group $C2/c$ (No. 15) with a = 10.751 (6) Å, b = 17.393 (7) Å, c = 23.240 (7) Å, β = 85.42 (4)°, V = 4332 (5) Å^3, and Z = 4; R = 0.028 for 1645 observed reflections having $I \geq 3\sigma(I)$. Both compounds contain an octahedron of iridium atoms, with the alkynyl units interacting with the faces of the metallic cores, in a μ_3-η^2 fashion.

Introduction

Many efforts are devoted in these days to the preparation of metal carbonyl clusters substituted with small organic fragments, in order to mimic the interactions of such molecules with metallic surfaces.[2] The most intense research is focused on alkyne-substituted clusters, mainly for the metals of group 8 of the periodic table.[3] In contrast, relatively few compounds are known for the metals of the Co subgroup, and these few examples are restricted to clusters of three and four metal atoms.[3] The main reason is probably due to the thermal or photochemical activation methods employed for the synthesis of the alkyne-substituted compounds, with consequent cluster fragmentation or reorganization. For example, when the tetrahedral cluster Ir$_4$(CO)$_{12}$ is irradiated in the presence of C$_2$(CO$_2$Me)$_2$, the rectangular cluster Ir$_4$(CO)$_8$(Me$_2$CO$_2$C$_2$)$_4$ is formed.[4]

When studying the chemistry of iridium clusters, we observed that [Ir$_6$(CO)$_{15}$]$^{2-}$ typically adds 2e-donor ligands (such as halides or CO), when oxidized.[5] Therefore, we exploited the same synthetic approach, which requires very mild conditions, using ligands with different donor capability.[6] We report here the preparation and the solid-state characterization of two new hexanuclear iridium carbonyl clusters containing one and two molecules of diphenylacetylene, respectively.

Results

Synthesis of Ir$_6$(CO)$_{14}$(μ_3-η^2-PhCCPh) (1) and Ir$_6$(CO)$_{12}$(μ_3-η^2-PhCCPh)$_2$ (2). When [Ir$_6$(CO)$_{15}$]$^{2-}$ is oxi-

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Table I. Summary of Crystal Data for Compounds 1 and 2 with Estimated Standard Deviations (Esd's) on the Last Figure in Parentheses

formula	$C_{28}H_{10}O_{14}Ir_6$	$C_{41}H_{22}Cl_2O_{12}Ir_6$
fw	1723.6	1930.7
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	9.443 (1)	10.751 (6)
b, Å	16.622 (1)	17.393 (7)
c, Å	21.560 (1)	23.240 (7)
α, deg	89.87 (1)	
β, deg	96.45 (1)	85.42 (4)
γ, deg	101.78 (1)	
V, Å^3	3291 (1)	4332 (5)
D_c	3.478	2.957
Z	4	4
$F(000)$	3008	3432
λ(Mo Kα radiation), Å	0.71073	0.71073
μ(Mo Kα), cm^{-1}	241.5	184.8
min transm factor	0.32	0.30
cryst decay		4%
scan mode	ω	ω
θ scan width	0.8 + 0.35 tan θ	2.2 + 0.35 tan θ
θ range	3–25	3–22
octants	$+h,\pm k,\pm l$	$+h,+k,\pm l$
no. of measd reflns	11548	2816
no. of unique reflns having $I \geq 3\sigma(I)$	6236	1645
refined params	445	274
R^a	0.033	0.028
$R_w{}^a$	0.038	0.032
GOF^b	1.357	1.048

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

dized with ferrocenium ions (1:2 molar ratio), the short-lived unsaturated cluster "$Ir_6(CO)_{15}$" is generated, and rapid addition of available ligands occurs.[7] When the reaction is carried out in the presence of diphenylacetylene (PhC≡CPh), the alkyne-substituted cluster $Ir_6(CO)_{14}$(PhCCPh) (1) is produced within a few minutes. The main byproduct of this reaction is $Ir_6(CO)_{16}$, since 1 mol of CO is also formed according to reaction 1. When 1 is heated

$$[Ir_6(CO)_{15}]^{2-} + 2[Fe(C_5H_5)_2]^+ + PhC{\equiv}CPh \rightarrow Ir_6(CO)_{14}(PhCCPh) + CO + 2Fe(C_5H_5)_2 \quad (1)$$

in toluene at 75 °C, in the presence of excess PhC≡CPh, two carbonyl groups are substituted by a second molecule of alkyne, yielding the polysubstituted carbonyl cluster $Ir_6(CO)_{12}(PhCCPh)_2$ (2).

The method of synthesis of 1, reported here, represents a definite advantage over the hypothetical direct reaction of $Ir_6(CO)_{16}$ and alkyne, since (i) the neutral carbonyl $Ir_6(CO)_{16}$ can only be prepared via oxidation of $[Ir_6(CO)_{15}]^{2-}$ under a CO atmosphere[8] (thus the one-step oxidation and ligand substitution process is more straightforward) (ii) the direct reaction would require more forcing conditions, as those used for the preparation of 2, and probably the intermediate formation of 1 would not have been detected, (iii) the reaction is extremely selective, and the following workup does not require any tedious separation procedure, such as thin-layer chromatography or fractional crystallizations.

Crystal Structures of $Ir_6(CO)_{13}(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PhCCPh)$ (1) and $Ir_6(CO)_{12}(\mu_3\text{-}\eta^2\text{-}PhCCPh)_2{\cdot}CH_2Cl_2$ (2).

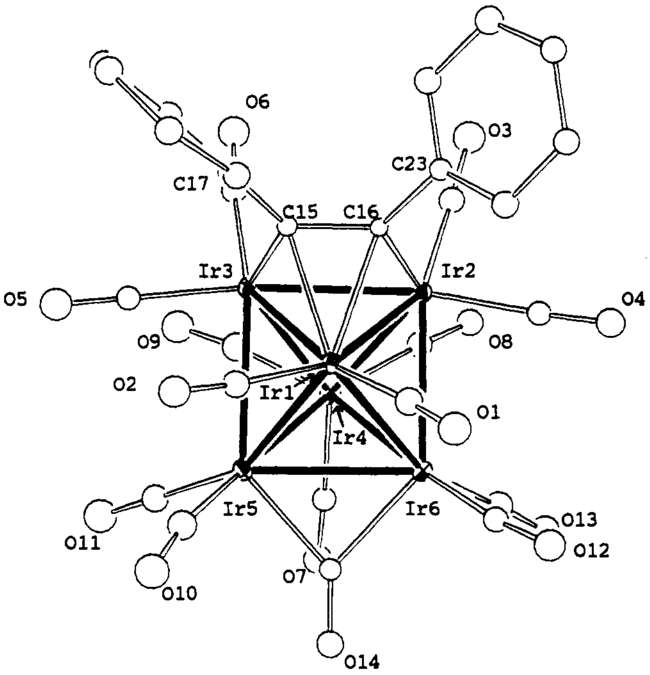

Figure 1. ORTEP drawing of $Ir_6(CO)_{14}$(PhCCPh) (1), with partial labeling scheme. Thermal ellipsoids are drawn at 30% probability.

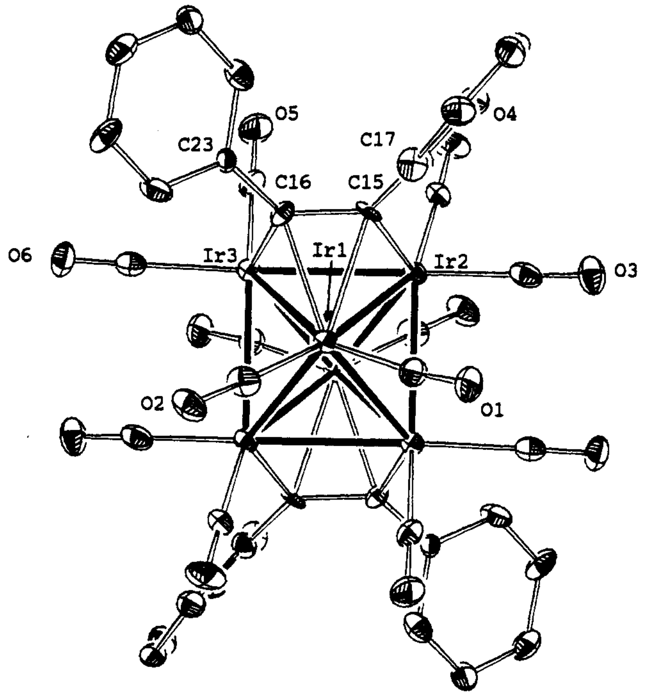

Figure 2. ORTEP drawing of $Ir_6(CO)_{12}(PhCCPh)_2$ (2), with partial labeling scheme. Thermal ellipsoids are drawn at 30% probability.

Crystal data for compounds 1 and 2 are collected in Table I; selected bond distances and angles are collected in Table II. Crystals of 1 contain two crystallographically independent molecules with negligible discrepancies between their distances and angles; all the molecular parameters were therefore averaged for discussion and the tables. In 2 the $Ir_6(CO)_{12}(C_2Ph_2)_2$ molecule lies on a crystallographic center and the two faces capped by the organic ligands are identical because of symmetry. The molecular structures of 1 and 2 are shown in Figures 1 and 2, respectively: these molecules possess slightly distorted octahedral cores of metal atoms. All the alkyne ligands interact with three metal atoms in the most common μ_3-η^2-binding mode, with the C≡C unit (conventionally denoted C(15) and C(16)

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Table II. Synoptic Table of Relevant Parameters in Compounds 1 and 2 with Esd's on the Last Figure in Parentheses

	1 molecule A	1 molecule B	2
	Ir–Ir Intralayer[a]		
Ir(1)–Ir(2)	2.689 (1)	2.688 (1)	2.671 (1)
Ir(2)–Ir(3)	2.686 (1)	2.681 (1)	2.710 (1)
Ir(1)–Ir(3)	2.682 (1)	2.679 (1)	2.695 (1)
⟨Ir–Ir⟩	2.686	2.683	2.692
Ir(4)–Ir(5)	2.754 (1)	2.756 (1)	
Ir(5)–Ir(6)	2.756 (1)	2.764 (1)	
Ir(4)–Ir(6)	2.745 (1)	2.752 (1)	
⟨Ir–Ir⟩	2.752	2.757	
	Ir–Ir Interlayer[a]		
Ir(1)–Ir(5)	2.787 (1)	2.773 (1)	
Ir(1)–Ir(6)	2.784 (1)	2.851 (1)	
Ir(2)–Ir(4)	2.847 (1)	2.842 (1)	
Ir(2)–Ir(6)	2.761 (1)	2.766 (1)	
Ir(3)–Ir(4)	2.793 (1)	2.805 (1)	
Ir(3)–Ir(5)	2.821 (1)	2.849 (1)	
Ir(1)–Ir(2)			2.828 (1)
Ir(1)–Ir(3)			2.804 (1)
Ir(2)–Ir(3)			2.775 (1)
⟨Ir–Ir⟩	2.813	2.814	2.802
⟨Ir–Ir⟩$_{\text{overall}}$	2.766	2.767	2.747
% Q^b	3.9	3.2	2.9
	Ir–PhCCPh		
Ir(1)–C(15)	2.22 (2)	2.24 (2)	2.20 (2)
Ir(1)–C(16)	2.22 (2)	2.19 (2)	2.23 (2)
⟨Ir(1)–C⟩	2.22	2.22	2.22
Ir(2)–C(16)	2.07 (2)	2.07 (2)	2.07 (1)
Ir(3)–C(15)	2.06 (2)	2.08 (2)	2.07 (2)
⟨Ir(2,3)–C⟩	2.07	2.08	2.07
C(15)–C(16)	1.39 (2)	1.41 (2)	1.39 (2)
C(15)–C(16)–C(23)	126 (2)	127 (2)	125 (2)
C(16)–C(15)–C(17)	127 (2)	125 (2)	126 (2)
⟨C≡C–C⟩	127	126	126
	Ir–CO		
⟨C–O⟩$_{\text{term.}}$	1.17	1.16	1.14
⟨Ir–CO⟩$_{\text{term.}}$	1.87	1.86	1.88
⟨Ir–C–O⟩$_{\text{term.}}$	175	175	177
C(14)–O(14)$_{\text{bridg}}$	1.17 (2)	1.22 (2)	
⟨Ir–CO⟩$_{\text{bridg}}$	2.06	2.03	
⟨Ir–C–O⟩$_{\text{bridg}}$	136	137	

[a] We define "layers" as the two faces of the metal octahedron almost parallel to the C≡C coordinated bond. [b] $Q = 100\max_{i,j}|(\mathrm{Ir}_i–\mathrm{Ir}_j) - \langle \mathrm{Ir–Ir}\rangle| / \langle \mathrm{Ir–Ir}\rangle$.

in both complexes) parallel to one Ir–Ir edge; therefore each organic ligand donates 4 electrons to the cluster, through two σ and one π bond. Of the 14 carbonyls in **1**, 13 are terminal and only one is edge-bridging. In **2**, only 12 terminal carbonyl groups are present, two on each metal atom. Compounds **1** and **2** have C_s and $C2/m$ idealized symmetry, respectively, the mirror planes bisect the PhCCPh units in both cases, and the plane of **1** includes the unique bridging carbonyl also. Notably, in **1**, Ir(4) possesses three terminal carbonyl ligands, a feature which was never observed before in octahedral iridium carbonyl clusters; moreover in **2** only terminal carbonyl groups are found while in hexanuclear or in larger iridium carbonyl clusters bridging carbonyls are always present.[5] The structural parameters of the Ir_3C_2 units are schematized in Figure 3a for **1** and Figure 3b for **2** and are strikingly similar. The C(15)–C(16) bond distances, statistically identical in both compounds (1.40 Å for **1** and 1.39 Å for **2**), indicate a carbon–carbon bond order lower than 2; the average C(ipso)–C≡C angles are also identical.

In both clusters, the edges of the faces bridged by the organic fragment are slightly shorter (averages 2.692 Å for **1** and 2.684 Å for **2**) than the remaining Ir–Ir distances (2.814 Å and 2.802 Å, for **1** and **2** respectively). The degree of distortion from ideality of the two metal cages, measured by the parameter Q (defined in Table II), is mainly due to the difference between inter- and intralayer bonding parameters; in the highly symmetric neutral $Ir_6(CO)_{16}$ (red and black isomers) Q values of 0.1 and 1.2 are calculated.[8]

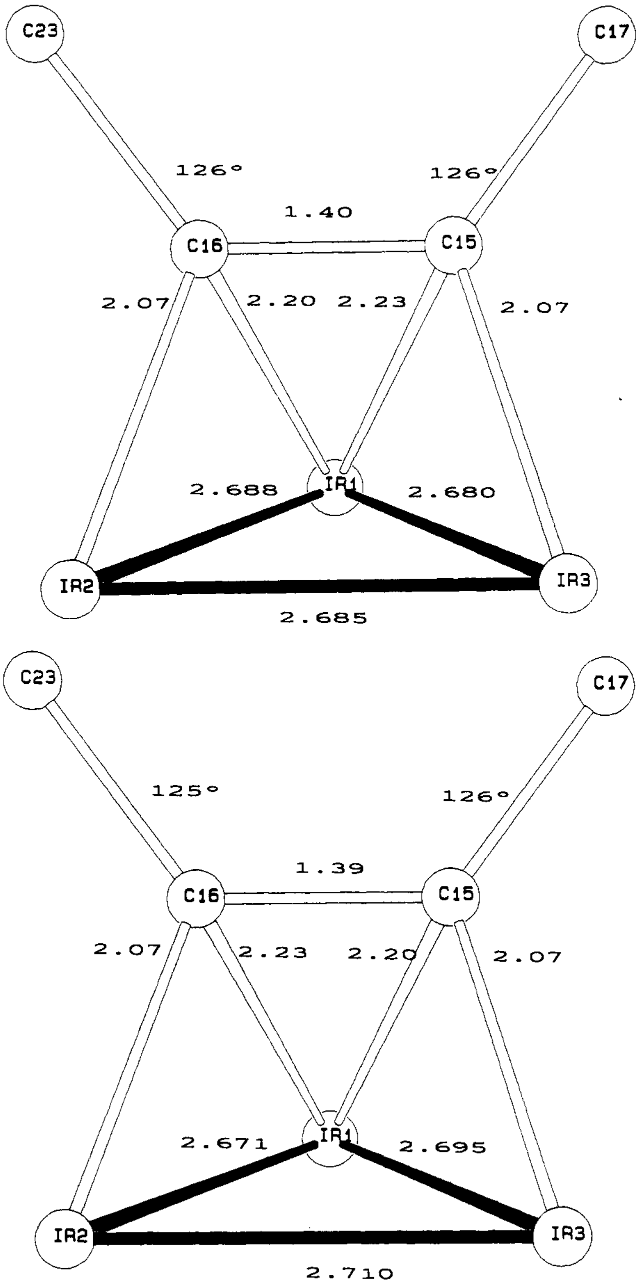

Figure 3. Schematic representation of the Ir_3C_2 units (a) in compound **1** (b) in compound **2**.

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 using Schlenk-tube techniques.[9] $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$[10] and $[Fe(C_5H_5)_2]PF_6$[11] were prepared by using literature methods. Infrared (IR) spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer using

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Table III. Fractional Atomic Coordinates for the Two Independent Units A and B of $Ir_6(CO)_{14}(C_2Ph_2)$ (1) with Esd's on the Last Figure in Parentheses

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ir(1A)	0.49315 (8)	0.19830 (4)	0.58941 (4)	C(9A)	0.494 (3)	0.086 (1)	0.809 (1)
Ir(2A)	0.32721 (8)	0.23174 (4)	0.67560 (4)	C(10A)	0.620 (3)	0.025 (1)	0.584 (1)
Ir(3A)	0.59320 (8)	0.20195 (4)	0.71103 (4)	C(11A)	0.597 (2)	−0.018 (1)	0.701 (1)
Ir(4A)	0.35375 (8)	0.08350 (4)	0.73803 (4)	C(12A)	0.153 (2)	0.085 (1)	0.532 (1)
Ir(5A)	0.51401 (8)	0.04953 (4)	0.64589 (4)	C(13A)	0.062 (3)	0.035 (1)	0.642 (1)
Ir(6A)	0.23927 (8)	0.08060 (4)	0.61509 (4)	C(14A)	0.325 (2)	−0.024 (1)	0.606 (1)
Ir(1B)	1.19614 (8)	0.19470 (4)	0.13263 (4)	C(15A)	0.619 (2)	0.300 (1)	0.6523 (9)
Ir(2B)	1.04161 (8)	0.31382 (4)	0.11763 (4)	C(16A)	0.480 (2)	0.3157 (9)	0.6346 (9)
Ir(3B)	1.31117 (8)	0.33808 (4)	0.08345 (4)	C(17A)	0.757 (2)	0.353 (1)	0.644 (1)
Ir(4B)	1.07745 (8)	0.31951 (5)	−0.01154 (4)	C(18A)	0.789 (2)	0.382 (1)	0.586 (1)
Ir(5B)	1.22660 (8)	0.19352 (5)	0.00624 (4)	C(19A)	0.932 (2)	0.425 (1)	0.577 (1)
Ir(6B)	0.94894 (8)	0.17570 (4)	0.04084 (4)	C(20A)	1.030 (3)	0.450 (1)	0.631 (1)
O(1A)	0.351 (2)	0.217 (1)	0.4575 (9)	C(21A)	1.002 (2)	0.426 (1)	0.688 (1)
O(2A)	0.769 (2)	0.1890 (9)	0.5331 (8)	C(22A)	0.862 (2)	0.378 (1)	0.695 (1)
O(3A)	0.284 (2)	0.342 (1)	0.7805 (9)	C(23A)	0.446 (2)	0.394 (1)	0.607 (1)
O(4A)	0.062 (2)	0.2616 (9)	0.5921 (8)	C(24A)	0.365 (2)	0.397 (1)	0.549 (1)
O(5A)	0.897 (2)	0.171 (1)	0.7071 (9)	C(25A)	0.329 (2)	0.473 (1)	0.531 (1)
O(6A)	0.643 (2)	0.297 (1)	0.8337 (9)	C(26A)	0.386 (2)	0.542 (1)	0.566 (1)
O(7A)	0.237 (2)	−0.0988 (9)	0.7473 (8)	C(27A)	0.465 (2)	0.538 (1)	0.620 (1)
O(8A)	0.117 (2)	0.1337 (8)	0.8044 (7)	C(28A)	0.503 (2)	0.464 (1)	0.641 (1)
O(9A)	0.577 (2)	0.079 (1)	0.8499 (9)	C(1B)	1.089 (2)	0.107 (1)	0.173 (1)
O(10A)	0.666 (2)	−0.000 (1)	0.5434 (9)	C(2B)	1.360 (2)	0.147 (1)	0.142 (1)
O(11A)	0.651 (2)	−0.060 (1)	0.7330 (9)	C(3B)	0.866 (2)	0.267 (1)	0.148 (1)
O(12A)	0.085 (2)	0.0904 (9)	0.4849 (8)	C(4B)	1.023 (3)	0.422 (1)	0.130 (1)
O(13A)	−0.051 (2)	0.0033 (9)	0.6569 (8)	C(5B)	1.497 (3)	0.329 (1)	0.066 (1)
O(14A)	0.280 (2)	−0.0919 (8)	0.5898 (8)	C(6B)	1.347 (3)	0.454 (1)	0.090 (1)
O(1B)	1.033 (2)	0.0489 (9)	0.1989 (8)	C(7B)	1.008 (3)	0.283 (1)	−0.093 (1)
O(2B)	1.472 (2)	0.1233 (8)	0.1518 (7)	C(8B)	0.941 (2)	0.384 (1)	−0.003 (1)
O(3B)	0.761 (2)	0.2372 (8)	0.1706 (8)	C(9B)	1.227 (3)	0.399 (1)	−0.035 (1)
O(4B)	1.023 (2)	0.490 (1)	0.141 (1)	C(10B)	1.322 (2)	0.110 (1)	0.015 (1)
O(5B)	1.616 (2)	0.3241 (9)	0.0585 (9)	C(11B)	1.303 (2)	0.223 (1)	−0.066 (1)
O(6B)	1.369 (2)	0.524 (1)	0.1006 (9)	C(12B)	0.846 (2)	0.084 (1)	0.080 (1)
O(7B)	0.960 (2)	0.257 (1)	−0.143 (1)	C(13B)	0.778 (2)	0.190 (1)	−0.003 (1)
O(8B)	0.854 (2)	0.4260 (9)	−0.0042 (8)	C(14B)	1.028 (2)	0.116 (1)	−0.022 (1)
O(9B)	1.316 (2)	0.449 (1)	−0.057 (1)	C(15B)	1.326 (2)	0.312 (1)	0.1781 (9)
O(10B)	1.387 (2)	0.054 (1)	0.0204 (9)	C(16B)	1.184 (2)	0.297 (1)	0.1947 (9)
O(11B)	1.364 (2)	0.244 (1)	−0.111 (1)	C(17B)	1.459 (2)	0.319 (1)	0.220 (1)
O(12B)	0.774 (2)	0.0327 (9)	0.1035 (8)	C(18B)	1.476 (3)	0.265 (1)	0.269 (1)
O(13B)	0.674 (2)	0.197 (1)	−0.0345 (9)	C(19B)	1.604 (3)	0.273 (1)	0.312 (1)
O(14B)	0.987 (2)	0.0637 (9)	−0.0629 (8)	C(20B)	1.719 (3)	0.336 (2)	0.298 (1)
C(1A)	0.401 (2)	0.210 (1)	0.511 (1)	C(21B)	1.710 (3)	0.387 (1)	0.257 (1)
C(2A)	0.661 (2)	0.191 (1)	0.552 (1)	C(22B)	1.579 (2)	0.383 (1)	0.214 (1)
C(3A)	0.299 (2)	0.296 (1)	0.739 (1)	C(23B)	1.145 (2)	0.297 (1)	0.260 (1)
C(4A)	0.159 (2)	0.247 (1)	0.626 (1)	C(24B)	1.076 (3)	0.232 (1)	0.291 (1)
C(5A)	0.782 (2)	0.181 (1)	0.710 (1)	C(25B)	1.049 (3)	0.239 (1)	0.352 (1)
C(6A)	0.631 (2)	0.259 (1)	0.790 (1)	C(26B)	1.088 (2)	0.314 (1)	0.384 (1)
C(7A)	0.277 (2)	−0.031 (1)	0.742 (1)	C(27B)	1.147 (3)	0.379 (1)	0.355 (1)
C(8A)	0.208 (2)	0.121 (1)	0.778 (1)	C(28B)	1.178 (2)	0.375 (1)	0.292 (1)

calcium fluoride cells previously purged with N_2.

NMR spectra were recorded at 200 MHz on a Bruker AC200 spectrometer and are reported in ppm downfield from the internal standard Me_4Si. Elemental analyses were obtained by the staff of the Laboratorio Analisi Università di Milano. Mass spectra were recorded with a VG Micromass machine; mass weights are referred to the most abundant isotopomers; isotopic patterns were calculated with the aid of the ISO computer program provided by the manufacturer.

Preparation of $Ir_6(CO)_{14}(PhCCPh)$ (1). A 100-mL, two-necked round-bottomed flask is equipped with a gas inlet. The flask is purged with nitrogen, then filled with CH_2Cl_2 (15 mL), $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ (1.1 g, 0.41 mmol), and PhC≡CPh (0.15 g, 0.85 mmol). The mixture is stirred and cooled in an ice bath. Under a light stream of nitrogen, $[Fe(C_5H_5)_2]PF_6$ (0.282 g, 0.85 mmol) is added in two portions. After about 30 min, the completeness of the reaction is checked by IR spectrophotometry, the solution is warmed to room temperature, the gas inlet is quickly substituted by a stopcock, and the solvent is dried in vacuum. The dark residue is then extracted with toluene (3 × 20 mL). The three fractions are filtered and collected in the same Schlenk tube and then dried under vacuum. The residue is dissolved in tetrahydrofuran (THF) (6 mL) and layered with 2-propanol. Yield: 0.212 g (30%). A second crop of product can be recovered from the dark mother liquor, drying it under vacuum and crystallizing the residue from smaller volumes of the same solvents. Anal. Calcd for $C_{28}H_{10}Ir_6O_{14}$: C, 19.51; H, 0.58. Found: C, 19.87; H, 0.51.

Compound 1 is almost insoluble in 2-propanol, very soluble in THF and CH_2Cl_2, and sparingly soluble in hexane and toluene. ν_{CO} IR bands at 2093 (m), 2051 (s), 2003 (w), 1838 (m) cm^{-1}, toluene solution. ^1H NMR (thf-d_8 solution): multiplet centered at δ 7.2. Electron impact mass spectrum: m/z^+ 1724, $Ir_6(CO)_{14}(PhCCPh)$; fragmentation process m/z^+ 1724 − 28 x (x = 2–14), $Ir_6(CO)_{14-x}(PhCCPh)$.

Preparation of $Ir_6(CO)_{12}(PhCCPh)_2$ (2). In a 100-mL round-bottomed flask are placed $Ir_6(CO)_{14}(PhCCPh)$ (0.145 g, 0.08 mmol), diphenylacetylene (0.050 g, 0.28 mmol), and toluene (25 mL). The mixture is heated to 75 °C in an oil bath for 10 h, and then the solution is cooled at room temperature and dried under vacuum. The deep red residue is repeatedly extracted with portions of hot CH_2Cl_2 (5 × 15 mL). The fractions are collected, concentrated to 20 mL, and layered with 2-propanol. Yield: 0.068 g (46 %). Anal. Calcd for $C_{40}H_{20}Ir_6O_{12}$: C, 26.03; H, 1.08. Found: C, 26.31; H, 1.01.

Compound 2 is only slightly soluble in toluene, thf, and CH_2Cl_2; crystalline samples of 2 show an extreme inertness to be redissolved. ν_{CO} IR bands at 2082 (vw), 2057 (sh), 2042 (s), 1992 (w), 1830 (vw, br) cm^{-1}, CH_2Cl_2 solution. ^1H NMR (thf-d_8 solution): multiplet centered at δ 7.2. FAB-MS (positive ions): m/z^+ 1846, $Ir_6(CO)_{12}(PhCCPh)_2$; fragmentation process m/z^+ 1846 − 28 x (x = 1–12), $Ir_6(CO)_{12-x}(PhCCPh)_2$

Table IV. Fractional Atomic Coordinates for $Ir_6(CO)_{12}(C_2Ph_2)_2 \bullet CH_2Cl_2$ (2) with Esd's on the Last Figure in Parentheses[a]

atom	*x*	*y*	*z*
Ir(1)	−0.38138 (6)	0.17335 (3)	−0.00410 (3)
Ir(2)	−0.33901 (6)	0.31046 (3)	−0.05360 (3)
Ir(3)	−0.33788 (6)	0.30069 (3)	0.06553 (3)
O(1)	−0.649 (1)	0.1992 (8)	0.0390 (7)
O(2)	−0.377 (1)	0.0085 (6)	0.0373 (6)
O(3)	−0.592 (1)	0.3903 (7)	−0.0374 (7)
O(4)	−0.245 (1)	0.4142 (9)	−0.1498 (6)
O(5)	−0.456 (1)	0.2234 (8)	0.1727 (6)
O(6)	−0.491 (1)	0.4476 (6)	0.0823 (6)
C(1)	−0.548 (2)	0.1878 (9)	0.0254 (9)
C(2)	−0.381 (2)	0.0718 (9)	0.0221 (9)
C(3)	−0.494 (2)	0.3628 (9)	−0.0431 (8)
C(4)	−0.280 (2)	0.376 (1)	−0.1121 (8)
C(5)	−0.413 (2)	0.253 (1)	0.1311 (8)
C(6)	−0.438 (2)	0.3934 (9)	0.0759 (8)
C(15)	−0.411 (1)	0.2154 (8)	−0.0927 (7)
C(16)	−0.323 (1)	0.1562 (8)	−0.0962 (8)
C(17)	−0.531 (2)	0.2142 (9)	−0.1209 (8)
C(18)	−0.618 (2)	0.156 (1)	−0.1125 (9)
C(19)	−0.722 (2)	0.156 (1)	−0.1422 (9)
C(20)	−0.738 (2)	0.213 (1)	−0.1814 (9)
C(21)	−0.653 (2)	0.269 (1)	−0.1930 (8)
C(22)	−0.556 (2)	0.270 (1)	−0.1605 (9)
C(23)	−0.328 (1)	0.0877 (8)	−0.1325 (7)
C(24)	−0.350 (2)	0.0947 (9)	−0.1900 (9)
C(25)	−0.357 (2)	0.033 (1)	−0.2265 (9)
C(26)	−0.341 (2)	−0.040 (1)	−0.2067 (9)
C(27)	−0.321 (2)	−0.0512 (9)	−0.1495 (9)
C(28)	−0.310 (2)	0.012 (1)	−0.1134 (9)
Cl(S1)	−0.010 (2)	0.1089 (5)	−0.2357 (6)
Cl(S2)	0.004 (2)	−0.0499 (8)	−0.2234 (7)
C(S)	0.000 (6)	0.019 (3)	−0.213 (3)

[a] Cl(S) = chlorine atoms of clathrated solvent molecule; C(S) = carbon atom of clathrated solvent molecule.

X-ray Analysis. Crystal samples of 1 and 2, of 0.30 × 0.10 × 0.05 and 0.12 × 0.10 × 0.10 mm dimensions, respectively, were mounted, on a glass fiber in air and at room temperature, on an Enraf-Nonius CAD4 diffractometer; graphite-monochromatized Mo $K\alpha$ radiation was used with the generator operated at 55 KV and 25 mA. The cell parameters and the orientation matrix were obtained from a least-squares refinement of the setting angles of 25 randomly distributed intense reflections having $16 \leq 2\theta \leq 25°$. The intensity data were collected using the ω-scan technique within the limits $6 \leq 2\theta \leq 50°$, in the $+h,\pm k,\pm l$ and $+h,+k,\pm l$ octants, for 1 and 2, respectively. A variable scan speed (from 2 to 16°/min) and variable scan ranges were used, with a 25% extension at each side of the peaks for background determination. The monitoring of the intensities of three intense reflections allowed correction for crystal decay, which was estimated at about 4%, for 2, at the end of the data collection. Lorentz, polarization, and absorption corrections were applied. The latter was applied to the reduced intensities on the basis of ψ-scans (ψ = 0–360°, every 10°) of three reflections having χ values close to 90°; the minimum relative transmission factors were 0.32 and 0.30 for 1 and 2, respectively.

The structures were solved by direct methods (MULTAN)[12] (compound 1) and three-dimensional Patterson (compound 2) and Fourier techniques and refined with full-matrix least-squares methods on the basis of 6236 (compund 1) and 1645 (compound 2) independent reflections having $I \geq 3\sigma(I)$; individual weights were assigned 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, the "ignorance factor", equal to 0.04. The crystals of 2 contain clathrated CH_2Cl_2 molecules, disordered in proximity of a crystallographic inversion center, which have been modeled using occupancy numbers of 0.50. Anisotropic temperature factors were assigned to all the non-hydrogen atoms, except those of the solvent molecule, in compound 2. For compound 1 only the iridium atoms were refined anisotropically; anisotropic refinement of the carbonyl atoms was tried but gave imaginary ellipsoids for some carbon atoms and so was therefore rejected. The hydrogen atoms of the alkyne units were included in the last stages of the refinements in ideal positions (C–H = 0.95 Å, B_{iso} = 6.0 Å^2) but not refined. Scattering factors for neutral atoms were taken from the SDP[13] package database; anomalous scattering factors were taken from ref 14. The final Fourier maps difference showed maximum peaks of 1.57 (1) and 1.07 (2) e/Å^3 in proximity of the metal atoms. All the computations were performed on a PDP 11/73 computer. The positional parameters for compounds 1 and 2 are listed in Tables III and IV, respectively.

Registry No. 1, 138261-04-8; 2, 138285-62-8; 2·CH_2Cl_2, 138285-63-9; $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$, 87525-25-5; $[Fe(C_4H_5)_2]PF_6$, 11077-24-0; PhC≡CPh, 501-65-5.

Supplementary Material Available: Table 1, listing anisotropic (metals) and isotropic (non-hydrogen atoms) thermal parameters for 1, Table 2, listing anisotropic thermal parameters for 2, Table 3, giving calculated fractional coordinates of the hydrogen atoms for 1, Table 4, giving calculated fractional coordinates of the hydrogen atoms for 2, and Tables 5 and 6, listing distances and angles for 1 and 2 (18 pages); Tables 7 and 8, listing structure factors for 1 and 2 (55 pages). Ordering information is given on any current masthead page.

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