Synthesis and Derivatization of Iridium(I) and Iridium(III) Pentamethyl[60]fullerene Complexes

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An iridium(I) pentamethyl[60]fullerene complex, Ir(η^5-$C_{60}Me_5$)$(CO)_2$ (**1**), was prepared by the reaction of K($C_{60}Me_5$) with $[IrCl(CO)_2]_2$ in an acetonitrile/THF solution. Oxidation of the iridium atom of **1** by I_2 successfully proceeded to afford an iridium(III) complex, Ir(η^5-$C_{60}Me_5$)I_2(CO) (**2**), in 80% yield. Ligand exchange reactions of **1** took place to give phosphine complexes, Ir(η^5-$C_{60}Me_5$)(CO)(PEt_3) (**3b**) and Ir(η^5-$C_{60}Me_5$)(CO)(PPh_3) (**3c**), in 60% and 35% yields, respectively. Similarly, the Ir(I) phosphine complex Ir(η^5-$C_{60}Me_5$)(CO)(PMe_3) (**3a**) was also obtained by the reaction of **2** with PMe_3 in 92% yield via reduction of the complex, while treatment of **2** with XylNC (Xyl = 2,6-dimethylphenyl isocyanide) gave another Ir(III) complex, Ir(η^5-$C_{60}Me_5$)I_2(XylNC) (**4**), in 93% yield. MeMgBr and PhCCMgBr reacted with **2** to give alkyl and alkynyl complexes, Ir(η^5-$C_{60}Me_5$)Me_2(CO) (**5**) and Ir(η^5-$C_{60}Me_5$)$(CCPh)_2$(CO) (**6**), in 60% and 81% yields, respectively. The molecular structures of **1**, **2**, and **3a** were determined by X-ray crystallographic analysis. Cyclic voltammetric investigation of **1** and **2** revealed the electrochemical properties of the Ir(I) and Ir(III) complexes. Complex **1** showed three reversible one-electron-reduction waves in the cathodic scan, and one reversible two-electron-oxidation wave in the anodic scan, while the complex **2** exhibited two-electron reduction of the metal center and one-electron reduction of the fullerene part. The isolated diiodide complex **2** will be a useful starting material for the synthesis of various metal fullerene complexes.

Introduction

Incorporation of transition metals into the carbon network of fullerene and carbon nanotubes[1] creates a rich world of chemistry through synergy of the metallic and carbonaceous components. Immediately after the start of the mass production of [60]fullerene,[2] efforts to synthesize transition-metal η^2-fullerene complexes and to examine their reactivities started.[3] However, the chemistry of exohedral metal η^2-fullerene complexes has suffered from the difficulty of chemical derivatization of the complexes. In particular, the electron-deficient nature of the fullerene has limited the possibility of making higher-valent organometallics, since back-donation of the metal d-electron density to the low-lying antibonding orbitals[4] of the fullerene is weakened in these complexes. Thus, upon oxidation of the metal center, the η^2-bonded transition metal tends to dissociate from the fullerene core.[5,6] Another general problem is the radial orientation of the fullerene π-orbitals, which is fundamentally unsuitable for bonding with a metal atom on the surface of the spherical molecules.[7] The η^2-fullerene ligand tends to be displaced in the course of ligand exchange reactions.[3]

We previously reported that a pentamethylated [60]-fullerene anion ($=C_{60}Me_5$)[8] forms stable transition-metal η^5-complexes, such as Fe(η^5-$C_{60}Me_5$)Cp,[9] Ru(η^5-$C_{60}Me_5$)Cp,[10] Ru(η^5-$C_{60}Me_5$)Cl$(CO)_2$,[11] Rh(η^5-$C_{60}Me_5$)$(CO)_2$,[12] and Pd(η^5-$C_{60}Me_5$)(π-allyl).[13] Ru(η^5-$C_{60}Me_5$)Cl$(CO)_2$ has been shown to undergo exchange of the carbonyl ligand and the chlorine atom to afford a variety of alkyl and alkynyl complexes without loss of the $C_{60}Me_5$ ligand.[11] In the present study, we examined whether the metal $C_{60}Me_5$ complex can be chemically oxidized to give a higher-valent metal complex without cleavage of the metal−fullerene bond. To this end, we focused on the iridium fullerene complex,[14−20] since iridium complexes are known to give stable high-valent complexes.[21] Successful oxidation of the metal center of metal fullerene complexes has not been reported so far,

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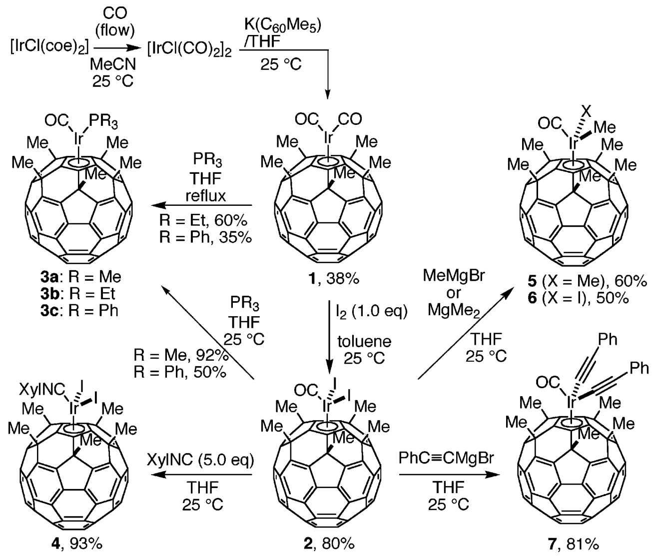
except for a rare example of oxidation of the iridium complex by molecular oxygen.[17d] We herein report the synthesis of the Ir(I) $C_{60}Me_5$ complex **1** and oxidation reaction of this Ir(I) complex **2** by iodine into an Ir(III) complex bearing two iodo ligands. We also describe the structures and the electrochemical properties of the Ir(I) and Ir(III) complexes and report on the carbonyl ligand exchange and alkylation and alkynylation of the iodo complex.

Results and Discussion

Synthesis and Characterization of Iridium Dicarbonyl Complex. We found that the success of complexation of an iridium metal to the $C_{60}Me_5$ ligand strongly depends on the choice of the starting iridium compound. Synthesis of the first iridium−$C_{60}Me_5$ complex was achieved by the use of the rather uncommon iridium dicarbonyl chloro dimer $[IrCl(CO)_2]_2$,[22] which can be prepared by treatment of $[IrCl(coe)_2]_2$ (coe = cyclooctene) with carbon monoxide gas (1 atm) in acetonitrile. A yellow acetonitrile solution of $[IrCl(CO)_2]_2$ was mixed with a THF solution of $K(C_{60}Me_5)$, affording the iridium $C_{60}Me_5$ dicarbonyl complex $Ir(C_{60}Me_5)(CO)_2$ (**1**) as orange microcrystals (Scheme 1). Several attempts to obtain iridium $C_{60}Me_5$ complexes by the reaction of $K(C_{60}Me_5)$ with other starting materials, $[IrCl(coe)_2]_2$, $[IrCl(1,5\text{-cod})_2]_2$ (cod = cyclooctadiene), $IrCl(py)(CO)_2$ (py = pyridine), $Ir(acac)(CO)_2$ (acac = acetylacetonato), and $IrCl(CO)(PPh_3)_2$, resulted in recovery of $C_{60}Me_5H$. The η^5 complex **1** is quite stable toward molecular oxygen, water, and heat (100 °C) both in a solution and as a solid. This property stands in contrast to that of most of the known iridium η^2-fullerene complexes;[3] for instance, a complex of the Vaska-type iridium complex[23] and C_{60}, $Ir(\eta^2\text{-}C_{60})Cl(CO)(PPh_3)_2$, is fluxional in solution.[14a,19]

Scheme 1. Synthesis and Derivatization of the Ir(η^5-$C_{60}Me_5$) Complexes



Complex **1** was characterized by IR, ^1H and ^{13}C NMR, and UV measurements and combustion analysis. The IR spectrum of **1** showed two bands for symmetric and asymmetric stretching vibrations of the two carbonyl ligands at 2031 and 1968 cm^{-1}, which are nearly identical with those of the similar dicarbonyl complex $IrCp(CO)_2$ (ν_{CO} 2037 and 1957 cm^{-1}; Cp = C_5H_5),[24] and higher than those of $IrCp^*(CO)_2$ (ν_{CO} 2000 and 1925 cm^{-1}; Cp* = C_5Me_5).[25] The increase of the ν_{CO} value observed in **1** is probably caused by stronger back-donation to the $C_{60}Me_5$ ligand than to the C_5Me_5 ligand. The ^1H NMR spectrum of **1** exhibited only one singlet at δ 2.43 for the five magnetically equivalent methyl groups on the C_{60} skeleton. The ^{13}C NMR spectrum displayed only a small number of signals due to the C_{5v}-symmetric fullerene skeleton: the cyclopentadienyl moiety (δ 109.73), the sp^3 fullerene carbon atom (δ 51.99), and five other types of fullerene sp^2 carbon atoms (δ 143.09, 144.32, 147.30, 148.54, 148.82, and 151.36), together with five methyl groups on the fullerene moiety (δ 30.59) and a carbonyl signal on the iridium (δ 193.14). The UV spectrum of **1** showed a broad absorption extended to ca. 550 nm with the maximum wavelengths (λ_{max}/nm) 261 ($\epsilon = 6.7 \times 10^4$), 349 ($\epsilon = 1.6 \times 10^4$), and 400 ($\epsilon = 8.7 \times 10^3$).

An unambiguous structure determination of **1** was achieved by single-crystal X-ray diffraction analysis. Recrystallization of **1** by slow diffusion of methanol into a toluene solution of **1** gave single crystals suitable for X-ray crystallography. Figure 1 shows the molecular structure of **1**, and selected geometrical parameters are summarized in Table 1. The iridium atom is bonded to the fullerene cyclopentadienide carbon atoms in an η^5

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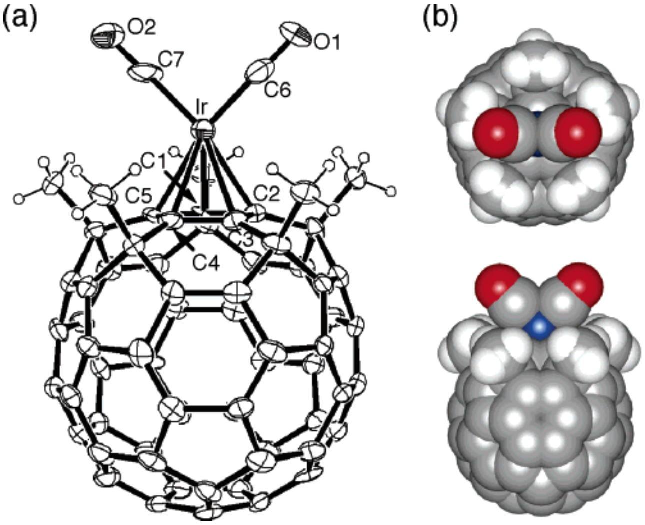

Figure 1. Crystal structure of **1**: (a) ORTEP drawing with 30% probability level ellipsoids; (b) space-filling models.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1, 2, and 3a

	$Ir(\eta^5\text{-}C_{60}Me_5)(CO)_2$ (**1**)		
Ir−C1	2.310(10)	Ir−centroid(Cp)	1.95
Ir−C2	2.276(11)	Ir−C6	1.84(2)
Ir−C3	2.322(11)	Ir−C7	1.815(19)
Ir−C4	2.326(10)	C6−O1	1.16(2)
Ir−C5	2.286(11)	C7−O2	1.19(2)
Ir−C(Cp)[a]	2.30		
C6−Ir−C7	89.3(7)		
	$Ir(\eta^5\text{-}C_{60}Me_5)I_2(CO)$ (**2**)		
Ir−C1	2.225(9)	Ir−C(Cp)[a]	2.28
Ir−C2	2.243(9)	Ir−centroid(Cp)	1.93
Ir−C3	2.350(9)	Ir−C16	1.881(19)
Ir−C4	2.340(9)	C16−O1	1.14(2)
Ir−C5	2.239(10)		
C1−C6−C11	120.9(10)	C4−C9−C14	117.2(9)
C2−C7−C12	115.0(9)	C5−C10−C15	112.6(9)
C3−C8−C13	115.9(10)		
	$Ir(\eta^5\text{-}C_{60}Me_5)(PMe_3)(CO)$ (**3a**)		
Ir−C1	2.370(16)	Ir−C16	1.83(2)
Ir−C2	2.359(16)	Ir−P	2.261(6)
Ir−C3	2.305(15)	P−C17	1.81(2)
Ir−C4	2.285(16)	P−C18	1.79(2)
Ir−C5	2.323(16)	P−C19	1.80(2)
Ir−C(Cp)[a]	2.33	C16−O1	1.09(2)
Ir−centroid(Cp)	1.99		
C1−C6−C11	120.9(10)	C4−C9−C14	117.2(9)
C2−C7−C12	115.0(9)	C5−C10−C15	112.6(9)
C3−C8−C13	115.9(10)	P−Ir−C16	87.0(7)

[a] Averaged bond distances of the five Ir−C(Cp) bonds.

fashion with an average Ir−C distance of 2.30 Å, which is slightly longer than that of the Cp* analogue (2.26 Å for IrCp*(CO)$_2$).[26] The iridium−carbon bond length for the η^5-complex **1** is substantially longer than those for η^2-complexes (2.155(8)−2.194(10) Å)[14] and for the μ^2,η^2:η^2-complex $C_{60}\{Ir_2Cl_2(1,5\text{-cod})_2\}_2$ (2.201(7)−2.231(6) Å).[16]

In the electrochemical analysis, **1** showed reversible three-electron-reduction events ($E_{1/2}{}^{red1} = -1.39$, $E_{1/2}{}^{red2} = -2.01$, and $E_{1/2}{}^{red3} = -2.66$ V vs Fc/Fc$^+$) within the solvent cutoff window of THF, as shown in Figure 2. The lower two reduction potentials of **1** are comparable to those of Rh(η^5-C$_{60}$Me$_5$)(CO)$_2$ ($E_{1/2}{}^{red1} = -1.46$ V and $E_{1/2}{}^{red2} = -1.94$ V) and Ru(η^5-C$_{60}$Me$_5$)Cl(CO)$_2$ ($E_{1/2}{}^{red1} = -1.34$ V and $E_{1/2}{}^{red2} = -1.94$ V) and, thus, are assigned to the reduction of fullerene moieties. Note that the iridium complex **1** shows the third reversible reduction peak of the fullerene moiety at −2.66 V, which has not so far been observed for the previously reported C$_{60}$Me$_5$ and C$_{60}$Ph$_5$ metal complexes.[9a,11,12,13,27] The compound **1** is thus robust even under the harsh reduction conditions. In the anodic scan, complex **1** exhibited a one-step two-electron irreversible oxidation (0.71 V vs Fc/Fc$^+$), which is due to Ir(I)/Ir(III) oxidation. We next examined chemical oxidation to prepare the Ir(III) complexes, as described in the following section.

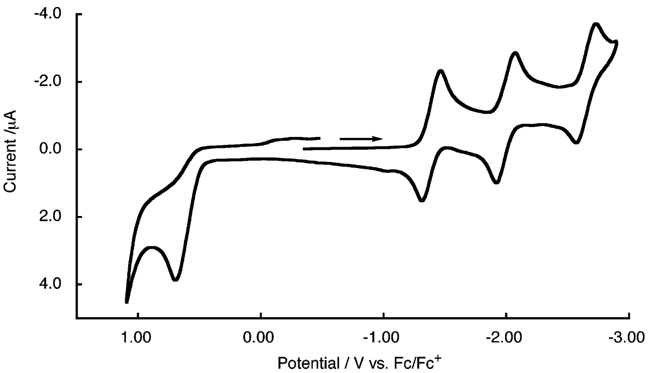

Figure 2. Cyclic voltammogram of **1** at 25 °C in a THF solution containing n-Bu$_4$NClO$_4$ as a supporting electrolyte (scan rate 100 mV/s).

Oxidation of 1: Synthesis of the Ir(III) C$_{60}$Me$_5$ Complexes. Oxidation of the metal center of the Ir(I) complex **1** by I$_2$ smoothly proceeded to afford the expected Ir(III) complex. Treatment of **1** with 1.0 equiv of I$_2$ in toluene at 25 °C afforded an air-stable iridium diiodo complex, Ir(η^5-C$_{60}$Me$_5$)I$_2$(CO) (**2**), in 80% yield (Scheme 1). This clean conversion from Ir(I) to Ir(III) and stability of the Ir(III) complex can be attributed to the electronic properties of the C$_{60}$R$_5$ ligand, whose occupied highest molecular orbital (HOMO) is delocalized at the top pentagon.[27b] This cyclopentadienyl moiety stabilizes the d^6 metal center of the octahedral geometry by facial coordination. In the IR spectrum of **2**, absorption due to the carbonyl ligand was observed at 2051 cm^{-1}. The ^{1}H NMR measurement gave a very simple spectrum consisting of only one singlet signal due to the methyl groups on the fullerene moiety at δ 2.42. The ^{13}C NMR spectrum exhibited 10 signals: two signals in the sp^3 region (δ 30.16 and 51.74), one (δ 109.79) due to the Cp carbons, six in the sp^2 region (δ 142.70, 143.90, 147.01, 148.25, 148.50, and 150.93), and one (δ 186.28) due to the carbonyl carbon. These observations indicate time-averaged pseudo C_{5v} symmetry of the C$_{60}$Me$_5$ ligand in solution.

The molecular structure of **2** was determined by the single-crystal X-ray diffraction study. The ORTEP drawing and space-filling models are shown in Figure 3, and selected bond distances and angles are listed in Table 1. The d^6 iridium metal center adopts a three-

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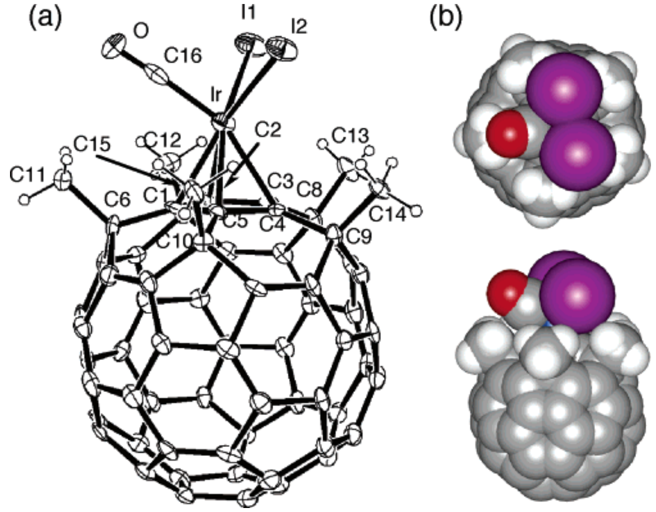

Figure 3. Crystal structure of $2 \cdot C_6H_6$: (a) ORTEP drawing with 30% probability level ellipsoids (a benzene molecule found in the unit cell is omitted for clarity); (b) space-filling models.

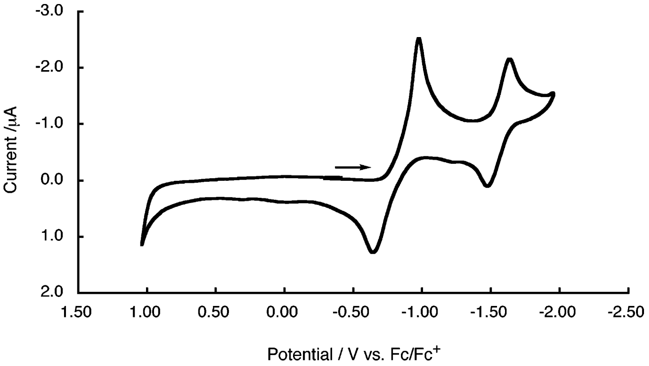

Figure 4. Cyclic voltammogram of **2** at 25 °C in a THF solution containing *n*-Bu_4NClO_4 as a supporting electrolyte (scan rate 100 mV/s).

legged piano-stool geometry surrounded by two iodine atoms and one carbon monoxide ligand. The average distance between iridium and fullerene cyclopentadienide carbon atoms (2.28 Å) is comparable to that of **1**, but the steric bulkiness of the iodo ligand induces dissymmetric coordination of the $C_{60}Me_5$ ligand (Ir−C1 = 2.225(9) Å, Ir−C2 = 2.243(9) Å, Ir−C3 = 2.350(9) Å, Ir−C4 = 2.340(9) Å, and Ir−C5 = 2.239(10) Å). Steric repulsion between the carbonyl ligand and the methyl groups on the fullerene also affects the structure of the fullerene ligand. The methyl group of C11, which is situated under the carbonyl group, is pushed outward. The C1−C6−C11 angle (120.9(10)°) is 3.7−7.3° larger than the other four angles.

The electrochemical behavior of the Ir(III) complex **2** in THF at 25 °C was investigated (Figure 4). A one-step two-electron reduction (−0.81 V) and a one-electron reduction (−1.56 V) were observed in the cathodic scan. The first large reduction wave is due to the reduction of the metal center (Ir(III)/Ir(I)), while the second reduction wave must be due to the reduction of the fullerene moiety, as judged by a comparison with the reported reduction potentials of the $C_{60}Me_5$ ligand and the transition metal-$C_{60}Me_5$ complexes.[8−13,27] It is noteworthy that neither the $C_{60}Me_5^-$ nor the I^- anion dissociates from the three-electron-reduced species $\mathbf{2}^{3-}$. The reversible reduction of **2** suggests that conversion between the Ir(III) and the reduced complexes occurs without structural changes. This stability of the complex **2** to the reduction is probably due to the ability of the $C_{60}Me_5$ ligand to conjugatively[27b] stabilize the negative charges that would otherwise localize on the metal atom. Complex **2** could not be oxidized within the solvent cutoff window.

Carbonyl Ligand Exchange of 1 and 2. The carbonyl ligand of the Ir−$C_{60}Me_5$ complexes could be readily replaced by phosphine and isonitrile ligands. Note that such ligand exchange reactions of the carbonyl ligand have not been observed for the iridium η^2-fullerene mononuclear complexes.[3,15a] The reaction of **1** with an excess amount (15 equiv) of PEt_3 and PPh_3 in THF proceeded under reflux conditions to afford the phosphine complexes Ir(η^5-$C_{60}Me_5$)(PEt_3)(CO) (**3b**) and Ir(η^5-$C_{60}Me_5$)(PPh_3)(CO) (**3c**) in 60% and 35% yields, respectively. Neither prolonged reaction time nor addition of phosphines promoted the exchange reaction of the second carbonyl group, likely because of both steric and electronic effects of the $C_{60}Me_5$ ligand. We next attempted to replace the carbonyl ligand of **2** by the phosphine ligand: we found that addition of phosphines to **2** reduces the complex, giving back an Ir(I) complex. Treatment of **2** with 5 equiv of PMe_3 or PPh_3 proceeded in THF at 25 °C to afford Ir(η^5-$C_{60}Me_5$)(PR_3)(CO) (**3a** (R = Me), **3c** (R = Ph)) in 92% and 50% yields, respectively. When an isonitrile was used, the ligand exchange reaction of **2** with XylNC (Xyl = 2,6-dimethylphenyl) cleanly took place without changing the valence of the metal center and afforded the Ir(III) isonitrile complex Ir($C_{60}Me_5$)I_2(XylNC) (**4**) in 93% yield.

The ^1H and ^{13}C NMR spectra of **3a**−**c** and **4** exhibited signals due to the pseudo C_{5v} symmetric structure, and the ^{31}P NMR signals were observed for the phosphine complexes (δ −48.32 for **3a**, δ 3.27 for **3b**, and δ 11.22 for **3c**). The vibration stretching values (1932−1933 cm^{-1}) of the carbonyl ligand in the IR spectra of the Ir(I) trialkylphosphine complexes **3a**,**b** are lower than those of **1** and **2**, being in good accordance with the more electron-rich nature of the Ir atoms in **3a**,**b**. The molecular structure of the phosphine complex was determined by the X-ray analysis of a crystal of **3a**, which was obtained by slow evaporation of the toluene solution. The crystal structure of **3a** is shown in Figure 5, and selected bond lengths and angles are listed in Table 1. The P−Ir−C16 angle is 87.0(7)°, smaller than the C6−Ir−C7 angle of **1** (89.3(7)°), probably because of the steric hindrance between $C_{60}Me_5$ and the phosphine ligand.

Alkylation and Alkynylation of 2. Since **2** has two halogen atoms on the iridium center, we anticipated that **2** serves as a useful starting material for the synthesis of various iridium $C_{60}Me_5$ complexes. Complex **2** was converted to the air-stable dimethyl complex Ir(η^5-$C_{60}Me_5$)Me_2(CO) (**5**) in 60% yield by reaction with excess MeMgBr in THF at room temperature (Scheme 1). In the ^1H and ^{13}C NMR spectra of **5**, characteristic proton and carbon signals due to the methyl group directly bonded to the iridium center were observed at δ 1.57 and −30.73, respectively. These chemical shift values are comparable to those of the Cp* complex

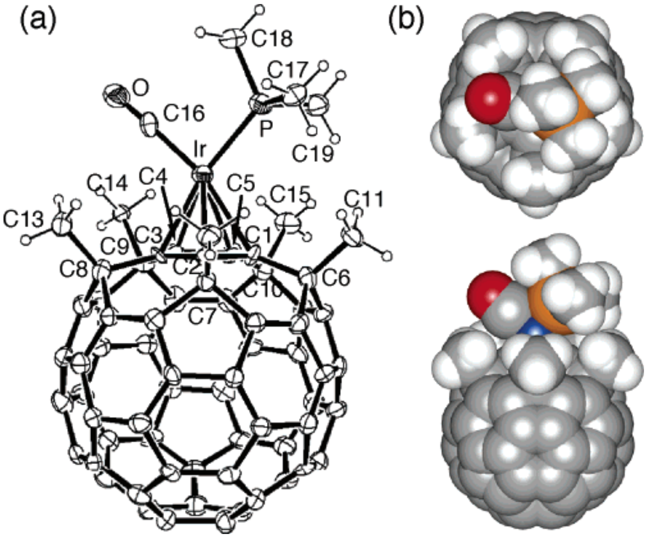

Figure 5. Molecular structure of **3a**·$C_6H_5CH_3$: (a) ORTEP drawing with 30% probability level ellipsoids (a toluene molecule found in the unit cell is omitted for clarity); (b) space-filling models.

Ir(Cp*)Me_2(CO) (δ_H 0.32, δ_C −24.3).[28] The monomethylated complex Ir(η^5-$C_{60}Me_5$)MeI(CO) (**6**) was also obtained by the reaction of **2** with equimolar $MgMe_2$ in THF at 25 °C in 50% yield. An alkynyl complex was synthesized in a similar manner. The reaction of **2** with a phenylalkynyl Grignard reagent at 25 °C proceeded smoothly to give the air-stable dialkynyl complex Ir(η^5-$C_{60}Me_5$)$(CCPh)_2$(CO) (**7**) in 81% yield.

Conclusion

We synthesized the iridium(I) $C_{60}Me_5$ complex **1** as a new member of the transition-metal $C_{60}Me_5$ complexes (transition metals = Fe, Ru, Rh, group 10 triad) and demonstrated that **1** tolerates oxidation of the metal center and can be converted to the Ir(III) complex **2** by treatment with iodine in good yield. The iodo and carbonyl ligands of **2** are easily replaced by alkyl, alkynyl, phosphine, and isonitrile ligands. Complex **2** will therefore be a useful starting material for the construction of various metal fullerene hybrid molecules. Hereupon, the difunctional nature of **2** (i.e., the two metal−halogen bonds of **2**) is complementary to the monofunctional nature of the reported ruthenium $C_{60}Me_5$ monochloro complexes.[11] Transition-metal dihalides bearing a suitable ancillary ligand are generally useful catalyst precursors for various synthetic reactions, and in particular, d^6 iridium(III) cyclopentadienyl complexes are useful for C−H bond activation[29] and catalytic transfer hydrogenation reactions.[30] Therefore, we anticipate that the Ir(III) $C_{60}Me_5$ complexes will serve as catalysts for organic synthesis. The light-sensitizing and electron-accepting nature[31] of the fullerene are the properties of interest when we consider utilization in catalysis.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen or argon atmosphere with standard Schlenk techniques. The water content of solvents was determined with a Karl Fischer moisture titrator (MK-210, Kyoto Electronics Co.) to be less than 30 ppm. All reactions were monitored by HPLC (column, Cosmosil-Buckyprep, 4.6 × 250 mm, Nacalai Tesque; flow rate, 1.0 mL/min; eluent, toluene/2-propanol (7/3); detector, Shimadzu SPD-M10Avp). Preparative HPLC was performed on a Buckyprep column (20 × 250 mm) using toluene/2-propanol (9/1 or 7/3) as eluent (flow rate 20 mL/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Isolated yields were calculated on the basis of the starting fullerene compounds. All NMR spectra were measured with JEOL EX-400 (400 MHz), JEOL ECA-500 (500 MHz), or Bruker AM500 (500 MHz) instruments. Spectra are reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ^{1}H NMR, from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ^{13}C NMR, and from external H_3PO_4 (δ 0.00 ppm) for ^{31}P NMR. Other spectra were recorded by the use of the following instruments: IR spectra, Applied Systems Inc. React-IR 1000; UV/vis spectra, Hitachi U3500; mass spectra, Shimadzu LCMS-QP8000, Waters ZQ2000, and JEOL JMS-T100LC. Elemental analyses were performed at the organic elemental analysis laboratory in this department.

Materials. THF and toluene were distilled from Na/K alloy, and acetonitrile and hexane were distilled from CaH_2 before use. All solvents were thoroughly degassed by trap-to-trap distillation and stored under argon. A THF solution of *t*-BuOK was purchased from Sigma-Aldrich Co. and used as received. $C_{60}Me_5H$ was prepared according to our previous report.[8] $[IrCl(coe)_2]_2$ was prepared according to literature methods.[32]

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]dicarbonyliridium, Ir(η^5-$C_{60}Me_5$)$(CO)_2$ (1). To a suspension of $C_{60}Me_5H$ (500 mg, 0.628 mmol) in THF (50 mL) was added a solution of *t*-BuOK (1.0 M, 0.75 mL, 0.75 mmol) in THF under argon. The reaction mixture was stirred for 30 min at room temperature. After removal of the solvent under reduced pressure, the resulting solid was dissolved in THF again. In another Schlenk tube, $[IrCl(coe)_2]_2$ (703 mg, 0.785 mmol) was suspended in CH_3CN (50 mL) under argon, and the suspension was vigorously stirred. Replacement of argon with carbon monoxide followed by stirring for ca. 10 min afforded a yellow solution of $[IrCl(CO)_2]_2$. The solution of K($C_{60}Me_5$) was added to the solution of $[IrCl(CO)_2]_2$ through a cannula, and the mixture was stirred for 5 min. After the solvent was evaporated in vacuo, the residue was dissolved in toluene (50 mL) and insoluble products were removed by filtration through a pad of silica

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gel. Purification with repeated preparative HPLC separation (Buckyprep 20 mm × 250 mm, toluene/*i*-PrOH (7/3), flow rate 20 mL/min, retention time 8 min) gave **1** (248 mg, 38% yield) as brown crystals. IR (KBr, cm^{-1}): 2031 (s), 1968 (s) (ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 15H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 30.59 (5C, CH_3), 51.99 (5C, CH_3C), 109.73 (5C, C(Cp)), 143.09 (10C, C_{60}), 144.32 (10C, C_{60}), 147.30 (5C, C_{60}), 148.54 (10C, C_{60}), 148.82 (5C, C_{60}), 151.36 (10C, C_{60}), 193.14 (2C, CO). APCI-MS (−): *m/z* 1043 (M^-). UV−vis (1.0 × 10^{-5} M in CH_2Cl_2; λ_{max}/nm (ϵ)): 261 (6.7 × 10^4), 349 (1.6 × 10^4), 400 (8.7 × 10^3). Anal. Calcd for $C_{67}H_{15}O_2Ir$: C, 77.08; H, 1.45. Found: C, 76.89; H, 1.72.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]carbonyldiiodoiridium, Ir(η^5-$C_{60}Me_5$)I_2(CO) (2). To a solution of Ir(η^5-$C_{60}Me_5$)$(CO)_2$ (**1**; 100 mg, 0.0957 mmol) in THF (100 mL) was added I_2 (24.5 mg, 0.0957 mmol). After the mixture was stirred for 5 min, the solvent was evaporated under reduced pressure. Repeated preparative HPLC separation (Buckyprep 20 mm × 250 mm, toluene/*i*-PrOH (9/1), flow rate 20 mL/min, retention time 12 min) afforded reddish brown crystals of **2** (97.3 mg, 80% yield). IR (powder, cm^{-1}): 2051 (s) (ν_{CO}), 2964 (m), 2921 (m), 2854 (m) (ν_{C-H}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 15H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 30.16 (5C, CH_3), 51.74 (5C, CH_3C), 109.79 (5C, Cp), 142.70 (10C, C_{60}), 143.90 (10C, C_{60}), 147.01 (5C, C_{60}), 148.25 (10C, C_{60}), 148.50 (5C, C_{60}), 150.93 (10C, C_{60}), 186.28 (1C, CO). UV−vis (1.0 × 10^{-5} M in CH_2Cl_2; λ_{max}/nm (ϵ)): 260 (7.67 × 10^4), 354 (2.06 × 10^4), 393 (1.31 × 10^4). APCI-MS (−): *m/z* 1269 (M^-). APCI-HRMS (−): *m/z* calcd for $C_{65}H_{15}I_2Ir$ (M^- − CO), 1241.8890; found, 1241.8860.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]carbonyl(trimethylphosphine)iridium, Ir(η^5-$C_{60}Me_5$)(CO)(PMe_3) (3a). To a solution of **2** (5.00 mg, 0.003 91 mmol) in THF (5.0 mL) was added a solution of PMe_3 in THF (1.0 M, 20 μL, 0.0200 mmol), and the mixture was stirred for 10 min. After the solvent was evaporated in vacuo, the residue was dissolved in toluene (10 mL). The resulting suspension was filtrated through a pad of silica gel, and the filtrate was concentrated to 2 mL under reduced pressure. Addition of hexane (10 mL) to the solution precipitated a solid, which was collected by filtration, washed with hexane (10 mL), and dried under vacuum to afford **3a** (3.93 mg, 92%) as dark red crystals. IR (powder, cm^{-1}): 2962 (m), 2910 (m), 2854 (m) (ν_{C-H}), 1933 (s) (ν_{CO}). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.11 (d, $^2J_{P-H}$ = 10.5 Hz, 9H, PCH_3), 2.41 (s, 15H, $C_{60}CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 26.71 (d, $^1J_{P-C}$ = 38.8 Hz, 9C, PMe_3), δ 31.98 (5C, CH_3), 50.09 (5C, CH_3C), 106.70 (5C, C(Cp)), 143.57 (10C, C_{60}), 144.65 (10C, C_{60}), 146.71 (5C, C_{60}), 147.73 (10C, C_{60}), 148.41 (5C, C_{60}), 153.51 (10C, C_{60}), 178.75 (1C, CO). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ -48.32 (PMe_3). APCI-HRMS (+): *m/z* calcd for $C_{69}H_{25}IrOP$ (M + H^+), 1091.1249; found, 1091.1240.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]carbonyl(triethylphosphine)iridium, Ir(η^5-$C_{60}Me_5$)(CO)(PEt_3) (3b). To a solution of **1** (8.70 mg, 0.008 33 mmol) in THF (5 mL) was added a solution of triethylphosphine (14.5 mg, 0.125 mmol) in THF (1.7 M, 0.74 mL) under nitrogen in a Schlenk tube, and the solution was stirred and heated under reflux for 15 h. The solvent was evaporated in vacuo, and the residue was diluted in toluene (50 mL). The resulting suspension was passed through a pad of silica gel. Repeated preparative HPLC separation (Buckyprep 20 mm × 250 mm, toluene/*i*-PrOH (7/3), flow rate 20 mL/min, retention time 10 min) afforded reddish brown crystals of **3b** (5.70 mg, 60% yield). IR (powder, cm^{-1}): 2960 (m), 2920 (m), 2851 (m) (ν_{C-H}), 1932 (s) (ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (td, $^3J_{H-H}$ = 7.6 Hz, $^3J_{P-H}$ = 16.8 Hz, 9H, PCH_2CH_3), 2.14 (qd, $^3J_{H-H}$ = 7.6 Hz, $^2J_{P-H}$ = 7.6 Hz, 6H, PCH_2), 2.42 (s, 15H, $C_{60}CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 8.83 (d, $^2J_{P-C}$ = 2.37 Hz, 3C, PCH_2), 23.38 (d, $^2J_{P-C}$ = 36.4 Hz, 3C, PCH_2CH_3), 32.17 (s, 5C, CH_3), 50.23 (5C, CH_3C), 106.92 (5C, C(Cp)), 143.54 (10C, C(C_{60})), 144.63 (10C, C(C_{60})), 146.71 (5C, C(C_{60})), 147.73 (10C, C(C_{60})), 148.40 (5C, C(C_{60})), 153.52 (10C, C(C_{60})), 177.35 (d, $^2J_{P-C}$ = 19.9 Hz, 1C, CO). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 3.27. APCI-HRMS (−): *m/z* calcd for $C_{72}H_{30}IrOP$ (M^-), 1132.1640; found, 1132.1600.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]carbonyl(triphenylphosphine)iridium, Ir(η^5-$C_{60}Me_5$)(CO)(PPh_3) (3c). This compound was prepared in a manner similar to that for **3b**. Complex **3c** was isolated (35% yield) as reddish brown crystals by repeated preparative HPLC separation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 15H, CH_3), 7.44−7.70 (m, 15H, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3/CS_2$): δ 30.83 (s, 5C, CH_3), 50.20 (s, 5C, CH_3C), 107.36 (s, 5C, C(Cp)), 127.78 (d, $^3J_{C-P}$ = 10.8 Hz, 6C, *m*-C_6H_5), 130.19 (s, 3C, *p*-C_6H_5), 134.96 (d, $^2J_{C-P}$ = 12.0 Hz, 6C, *o*-C_6H_5), 136.99 (d, $^1J_{C-P}$ = 56.38 Hz, 3C, *ipso*-C_6H_5), 143.39 (s, 10C, C(C_{60})), 144.23 (s, 10C, C(C_{60})), 146.40 (s, 5C, C(C_{60})), 147.47 (s, 10C, C(C_{60})), 148.13 (s, 5C, C(C_{60})), 153.01 (s, 10C, C(C_{60})), 174.08 (s, 1C, CO). $^{31}P\{^1H\}$ NMR (200 MHz, CD_2Cl_3): δ 11.22 (br, 1P, PPh_3). APCI−HRMS (−): *m/z* calcd for $C_{84}H_{30}IrOP$ (M^-), 1276.1640; found, 1276.1665.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]carbonyl(2,6-dimethylphenyl isocyanide)iridium, Ir(η^5-$C_{60}Me_5$)I_2(XylNC) (4). To a solution of **2** (4.50 mg, 0.00354 mmol) in THF (5 mL) was added a solution of 2,6-dimethylphenyl isocyanide (2.31 mg, 0.0177 mmol) under argon. After stirring for 15 h at 25 °C, the solvent was removed under reduced pressure. The residue was dissolved in toluene and this solution passed through a pad of silica gel. The filtrate was concentrated under reduced pressure, and addition of ethanol to the solution afforded **4** (4.10 mg, 93% yield) as reddish brown crystals. IR (powder, cm^{-1}): 2964 (m), 2917 (m), 2858 (m) (ν_{C-H}), 2167 (s) (ν_{NC}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (s, 15H, $C_{60}CH_3$), 2.79 (s, 6H, CCH_3), 7.24 (br, 3H, CH(Xyl)). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 19.27 (2C, CH_3(Xyl)), 29.89 (5C, CH_3), 51.68 (5C, CH_3C), 105.46 (5C, Cp), 124.91 (1C, *ipso*-C_6H_3), 128.20 (2C, *m*-C_6H_3), 129.74 *p*-C_6H_3), 136.81 (*m*-C_6H_3), 143.08 (10C, C(C_{60})), 143.90 (10C, C(C_{60})), 147.18 (5C, C(C_{60})), 148.35 (10C, C(C_{60})), 148.55 (5C, C(C_{60})), 151.72 (10C, C(C_{60})), 177.57 (1C, CO), 209.90 (1C, NC). APCI-HRMS (+): *m/z* calcd for $C_{74}H_{24}IIrN$ (M − I^+), 1244.0585; found, 1244.0559.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]dimethyliridium, Ir(η^5-$C_{60}Me_5$)-Me_2(CO) (5). To a solution of **2** (10.0 mg, 0.00788 mmol) in THF (5 mL) was added a solution of MeMgBr in THF (1.0 M, 95 μL, 0.095 mmol). After the mixture was stirred for 5 min at room temperature, the solvent was evaporated in vacuo, and the residue was diluted in toluene. The resulting suspension was passed through a pad of silica gel. Repeated preparative HPLC separation (Buckyprep 20 mm × 250 mm, toluene/*i*-PrOH (7/3), flow rate 16 mL/min, retention time 10 min) afforded reddish brown crystals of **5** (4.9 mg, 60% yield). IR (powder, cm^{-1}): 1994 (s) (ν_{CO}), 2962 (m), 2920 (m), 2851 (m) (ν_{CH}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57 (s, 6H, Ir−CH_3), 2.44 (s, 15H, $C_{60}CH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ −30.73 (2C, Ir−CH_3), 27.91 (5C, $C_{60}CH_3$), 51.39 (5C, CH_3C), 110.74 (5C, Cp), 143.69 (10C, C_{60}), 144.03 (10C, C_{60}), 146.90 (5C, C_{60}), 147.93 (10C, C_{60}), 148.52 (5C, C_{60}), 152.97 (10C, C_{60}), 169.67 (1C, CO). APCI−HRMS (−): *m/z* calcd for $C_{68}H_{21}IrO$ (M^-), 1046.1222; found, 1046.1246.

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]methyliodoiridium, Ir(η^5-$C_{60}Me_5$)MeI(CO) (6). To a solution of **2** (6.68 mg, 0.005 25 mmol) in THF (5 mL) was added a solution of $MgMe_2$ in THF (0.020 M, 0.53 mL, 0.011 mmol). After the mixture was stirred for 5 min at room temperature, the solvent was evaporated under reduced pressure, and the residue was dissolved in toluene. After the solution was passed through a pad of silica gel, repeated preparative HPLC separation (Buckyprep 20 mm × 250 mm, toluene/ *i*-PrOH (7/3), flow rate 16 mL/min, retention time 15 min) afforded reddish brown crystals of **6** (3.0 mg, 50% yield). IR (powder, cm^{-1}): 2023 (s) (ν_{CO}), 2968 (m), 2920 (m), 2851 (m) (ν_{CH}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (s, 3H, Ir−CH_3), 2.57 (s, 15H, $C_{60}CH_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ −30.73 (1C, Ir−CH$_3$), 29.08 (5C, $C_{60}CH_3$), 51.48 (5C, MeC), 110.55 (5C, Cp), 143.35 (10C, C_{60}), 143.78 (10C, C_{60}), 146.92 (5C, C_{60}), 148.08 (10C, C_{60}), 148.50 (5C, C_{60}), 151.79 (10C, C_{60}), 179.50 (1C, CO). APCI-MS (−): *m/z* 1157 (M^-).

[(1,2,3,4,5-η)-6,9,12,15,18-Pentamethyl-1,6,9,12,15,18-hexahydro[60]fulleren-1-yl]carbonyldi(phenylethynyl)-iridium, Ir(η^5-$C_{60}Me_5$)$(CCPh)_2$(CO) (7). To a suspension of **2** (10.0 mg, 0.00788 mmol) in THF (5.0 mL) was added a solution of (phenylethynyl)magnesium bromide (63.0 mL, 0.0320 mmol) in THF (0.50 M) at 25 °C. After the mixture was stirred for 5 min at 25 °C, the solvent was removed in vacuo. The residue was diluted in toluene, and the resulting suspension was passed through a pad of silica gel. The purification of the product was carried out by preparative HPLC (Buckyprep 20 mm × 250 mm, toluene/*i*-PrOH (7/3), flow rate 20 mL/min, retention time 13 min). The title compound **7** (7.76 mg, 81%) was obtained as a reddish powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.64 (s, 15H, CH_3), 7.21 (tt, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 2H, *p*-C_6H_5), 7.33 (dd, ^3J = 7.6 Hz, ^3J = 8.4 Hz, 4H, *m*-C_6H_5), 7.50 (dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 4H, *o*-C_6H_5). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 28.71 (5C, CH_3), 46.44 (2C, Ir−C), 51.16 (5C, CCH$_3$), 102.82 (2C, PhC), 112.02 (5C, C(Cp)), 126.26 (2C, *p*-C_6H_5), 127.23 (2C, *ipso*-C_6H_5), 127.96 (4C *m*-C_6H_5), 132.04 (4C, *o*-C_6H_5), 143.59 (10C, C_{60}), 143.94 (10C, C_{60}), 146.97 (5C, C_{60}), 148.15 (10C, C_{60}), 148.65 (5C, C_{60}), 151.94 (10C, C_{60}), 159.92 (1C, CO). APCI-HRMS (−): *m/z* calcd for $C_{82}H_{25}IrO$ (M^-), 1216.1511; found, 1216.1554.

X-ray Crystallographic Analysis. Crystals of **1**, **2**, and **3a** suitable for X-ray diffraction study were mounted on a MacScience DIP2030 imaging plate diffractometer for data collection using Mo Kα (graphite monochromated, λ = 0.710 69) radiation. Crystal data and data statistics are summarized in Table 2. The structures of complexes **1**, **2**, and **3a** were solved by direct methods (SHELXS-97)[33] and expanded using Fourier techniques (DIRDIF-94).[34] The positional and thermal parameters of non-hydrogen atoms of **1**, **2**, and **3a** were refined using a full-matrix least-squares method. Hydrogen atoms were placed at calculated positions (C−H = 0.95 Å) and kept fixed. All non-hydrogen atoms of **1**, **2**, and **3a** were anisotropically refined. In the subsequent refinement, the function $\sum w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$.

Table 2. Crystal Data Collection Parameters for 1, 2, and 3a

	1	**2**·C_6H_6	**3a**·$C_6H_5CH_3$
formula	$C_{67}H_{15}IrO_2$	$C_{72}H_{21}I_2IrO$	$C_{76}H_{32}IrOP$
formula wt	1043.99	1347.98	1184.28
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	9.9750(10)	9.9950(8)	21.462(2)
b (Å)	23.1470(16)	13.5060(13)	20.660(2)
c (Å)	16.0130(15)	17.1450(16)	10.0920(8)
α (deg)	90	73.171(5)	90
β (deg)	93.525(4)	87.823(6)	90.906(6)
γ (deg)	90	79.239(5)	90
V (Å^3)	3690.3(6)	2176.1(3)	4474.3(8)
Z	4	2	4
D_{calcd} (g/cm^3)	1.879	2.057	1.758
T (K)	153(2)	153(2)	153(2)
cryst size (mm)	0.15 × 0.02 × 0.02	0.20 × 0.20 × 0.05	0.40 × 0.20 × 0.01
$2\theta_{min}$, $2\theta_{max}$ (deg)	4.68, 51.5	4.14, 51.6	4.38, 51.5
no. of rflns (unique)	7012	7686	7693
no. of rflns ($I > 2\sigma(I)$)	3562	5748	5512
no. of params	632	686	707
R1, wR2 (all data)	0.1523, 0.2921	0.1033, 0.2646	0.1317, 0.2932
R, R_w ($I > 2.0\sigma(I)$)	0.0913, 0.2306	0.0821, 0.2226	0.1043, 0.2772
GOF on F^2	0.933	1.136	1.116

Electrochemical Measurements. Electrochemical measurements were performed using a Hokuto HZ-5000 voltammetric analyzer. A glassy-carbon electrode was used as the working electrode. The counter electrode was a platinum coil, and the reference electrode was a Ag/Ag$^+$ electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s. All half-wave potentials are given as $E_{1/2} = (E_{p,c} + E_{p,a})/2$, where $E_{p,c}$ and $E_{p,a}$ are the cathodic and anodic peak potentials, respectively. The potential was corrected against Fc/Fc$^+$.

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Supporting Information Available: Lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles and figures giving labeling schemes for **1**, **2**, and **3a**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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