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Synthesis and Solid State Characterization of a Meridional Triphos Iridium Metallacycle−Carbene Complex: $[\{PhP(CH_2CH_2PPh_2)_2\}$ $\overline{Ir(CR{=}CRCR{=}C}R)\{{=}\overline{C(CH_2)_3}O\}][BF_4]$ (R = Co_2Me)

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Summary: The five-coordinate iridium metallacycle $[(PPh_3)_2Ir(CR{=}CRCR{=}CR)(Cl)]$ *(**5**, R =* CO_2CH_3*) and trisphosphine* $[PhP(CH_2CH_2PPh_2)_2]$ *are readily converted in refluxing toluene to the fac- and mer-triphos metallacyclopentadiene complexes* $[\{PhP(CH_2CH_2PPh_2)_2\}Ir(CR{=}CRCR{=}CR)Cl]$ *(**6**-fac and **6**-mer). Halide abstraction from the facial isomer **6**-fac gives the isolable cationic solvate* $[\{PhP(CH_2CH_2PPh_2)_2\}Ir(CR{=}CR{-}CR{=}CR)(ClCH_2Cl)]BF_4$ *(**7**, R =* CO_2CH_3*) which adopts a mer-geometry. Reaction of **7** with carbon monoxide generates the mer isomer of* $[\{PhP(CH_2CH_2PPh_2)_2\}Ir(CR{=}CRCR{=}CR)(CO)]\ BF_4$ *(**8**, R =* CO_2CH_3*); whereas, reaction of **7** with 3-butyn-1-ol gives the mer-carbene complex* $[\{PPh(CH_2CH_2PPh_2)_2\}Ir(CR{=}CRCR{=}CR)({=}COCH_2CH_2CH_2)]BF_4$ *(**9**, R =* CO_2CH_3*). A single-crystal X-ray crystallographic analysis of **9** represents the first solid-state characterization of a meridional* $[PhP(CH_2CH_2PPh_2)_2]$ *iridium complex.*

Iridium metallacyclopentadiene complexes exhibit a rich reactivity toward terminal alkynes.[1,2] For example, $[(PPh_3)_2\overline{Ir(CR{=}CRCR{=}C}R)(CO)(NCMe)][BF_4]$ (**1**, R = CO_2CH_3) undergoes reaction with 3-butyn-1-ol to give metallacyclopentadiene−carbene complex **2**;[2a] whereas, the triphos metallacycle $[\{CH_3C(CH_2PPh_2)_3\}\overline{Ir(CR{=}CRCR{=}C}R)(NCMe)]BF_4$ (**3**, R = CO_2CH_3) undergoes reaction with 3-butyn-1-ol to give the π-allyl complex **4** (Scheme 1).[2j] The oxacyclopentylidene ligand in **2** presumably arises via formation of a vinylidene ligand (**I**), which is trapped by attack of the pendant hydroxyl substituent at the vinylidene α-carbon, followed by proton transfer to the β-carbon. Complex **4** may arise via the fulvene intermediate **II**, which in turn *may* have resulted from insertion of a vinylidene ligand into the metallacycle ring.

The results shown in Scheme 1 for the reactions of iridacyclopentadiene complexes **1** and **3** with 3-butyn-1-ol demonstrate a dramatic effect on reaction outcome upon going from the bis(phosphine)/CO coordination environment to a tris(phosphine) ligation. In addition to a more electron rich metal center in **3**, the labile coordination site is trans to a phosphine ligand in **3**; whereas, in **1** the alkyne substrate coordinates trans to one of the metallacycle carbons. In an effort to prepare a *fac*-triphos analogue of **3** for which the reactive coordination site would be trans to a better donor (dialkyl-substituted phosphine) ligand, we set out to prepare bis(2-diphenylphosphinoethyl)phenylphosphine analogues of **3**. Complexes of $[PPh(CH_2CH_2PPh_2)_2]$ are known to adopt either *fac*- or *mer*-coordination geometries, as compared to $[MeC(CH_2PPh_2)_3]$ for which only a *fac* tridentate coordination geometry is possible.[3] Although $[PPh(CH_2CH_2PPh_2)_2]$ complexes of iridium are rare,[4] both five coordinate *fac* iridium(I) and six-coordinate *fac* iridium(III) complexes have been previously characterized by X-ray crystallography.[4a,b]

When the iridium(III) metallacycle chloride **5**[1a] (1.8 mmol, 15.0 mM) and bis(2-diphenylphosphinoethyl)phenylphosphine (2.3 mmol, 19.2 mM) were heated in toluene at reflux for 24 h a light-colored precipitate of $[\{PhP(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CRCR{=}C}R)Cl]$ (**6**-*fac*) was formed and isolated in 65% yield (Scheme 2). Slow evaporation of the filtrate led to isolation of a small amount of orange crystalline $[\{PhP(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CRCR{=}C}R)Cl]$ (**6**-*mer*, 5% yield, Scheme 2). The structural assignments for **6** are based primarily on NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) exhibited two $^{31}P\{^1H\}$ NMR signals for each isomer: δ 56.06 (t, $J = 7$ Hz), -0.63 (d, $J = 7$ Hz) for **6**-*fac*, and δ 58.27 (t, $J = 8$ Hz), 1.60 (d, $J = 8$ Hz) for **6**-*mer*. A second (unobserved) *fac* arrangement of the triphos ligand

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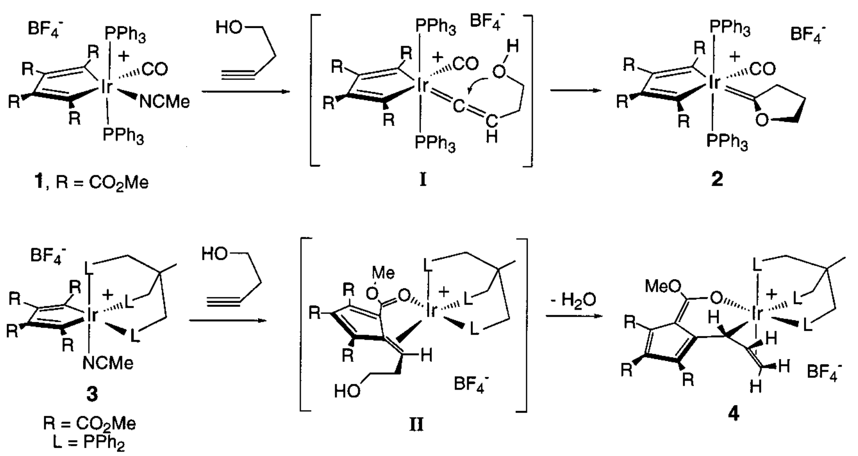
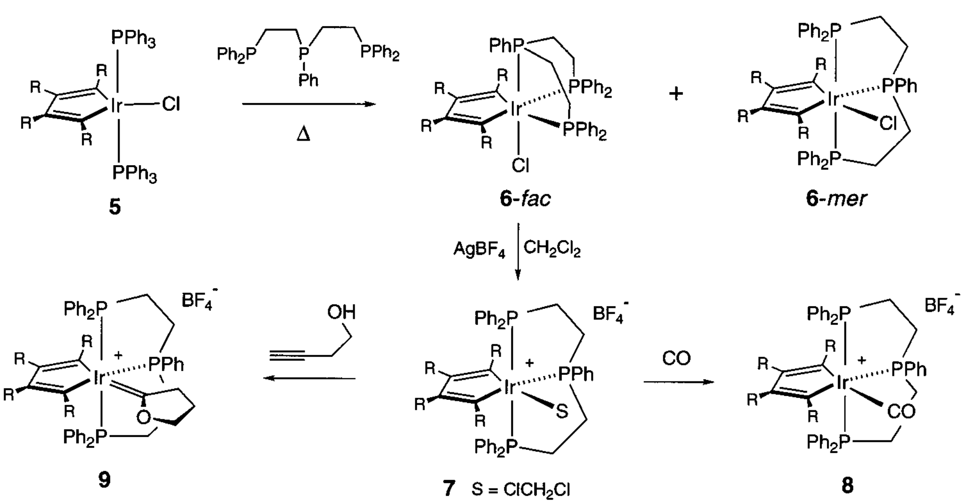
Scheme 1



Scheme 2



would have exhibited three phosphorus signals in the $^{31}P\{^1H\}$ NMR spectrum.

Complex **6**-*fac* has a vertical plane of symmetry bisecting the two PPh_2 groups and the metallacycle, resulting in two resonances for the methyl ester hydrogens in the ^1H NMR spectrum ($CDCl_3$) at δ 3.31 (s, 6H) and 2.52 (s, 6H). The minor isomer, **6**-*mer*, has a horizontal symmetry plane equating the two PPh_2 groups but leaving the metallacycle with nonequivalent methyl esters, as indicated by four methyl ester resonances in the ^1H NMR spectrum ($CDCl_3$) at δ 3.76, 3.50, 3.31, and 3.19.

The formation of both the *fac*- and *mer*-isomers of **6** held out hope that halide abstraction would give *fac*- and *mer*-isomers of the corresponding Ir(III) cations. However, treatment of either **6**-*mer* or **6**-*fac* (0.60 mmol, 12.0 mM) with $AgBF_4$ (0.66 mmol, 13.2 mM) gave $[\{PhP(CH_2CH_2PPh_2)_2\}Ir(CR{=}CRCR{=}CR)(ClCH_2Cl)]BF_4$ (**7**) in 87% isolated yield. The $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) exhibited phosphorus signals at δ 62.87 (t, J = 8.4 Hz, 1P) and 12.97 (br s, 2P), and the ^1H NMR spectra ($CDCl_3$) of **7** exhibited four methyl singlets at δ 3.89, 3.47, 3.34, and 2.41. The presence of the methylene dichloride ligand was supported by a two-proton singlet in the ^1H NMR spectrum ($CDCl_3$) at δ 5.47, as well as by combustion analysis. The hydrogen chemical shift for the hydrogens of noncoordinated CH_2Cl_2 is observed at δ 5.30 in $CDCl_3$ solvent.[5] In the IR spectrum (Nujol) of **7** a band at 1062 cm^{-1} is consistent with a noncoordinated BF_4 counterion.[6]

A priori it is difficult to predict the relative electronic effect at the substitutionally labile coordination sites in **3** and **7**. The $[PhP(CH_2CH_2PPh_2)_2]$ ligand in **7** is expected to be a better donor than the $[CH_3C(CH_2PPh_2)_3]$ ligand in **3**; however, the labile site is trans to phosphorus in **3** and trans to a metallacycle carbon in **7**. We therefore prepared the corresponding carbon monoxide complexes from **3** and **7**. Exposure of methylene dichloride solutions of cation **7** to one atmosphere of carbon monoxide at room temperature led to formation of the *mer* carbon monoxide complex **8**, which was isolated as an off-white solid in 78% yield. The *mer* formulation for **8** is consistent with the observation of four 3H methyl ester singlets in the ^1H NMR spectrum; and a triplet at δ 75.24 (J = 11 Hz, 1P) and a doublet at δ 19.45 (J = 11 Hz, 2P) in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$). In the IR spectrum of **8**, $\nu(C{\equiv}O)$ is observed at 2069 cm^{-1}. For comparison, the *fac* triphos carbonyl complex $[\{MeC(CH_2PPh_2)_3\}Ir(CR{=}CRCR{=}CR)(CO)]BF_4$ (**11**) exhibits $\nu(C{\equiv}O)$ in the IR spectrum (KBr) at 2094 cm^{-1}.[7] The 25 cm^{-1} lower wavenumber stretch for

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(5) For an iridium(III) methylene dichloride complex, see: Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

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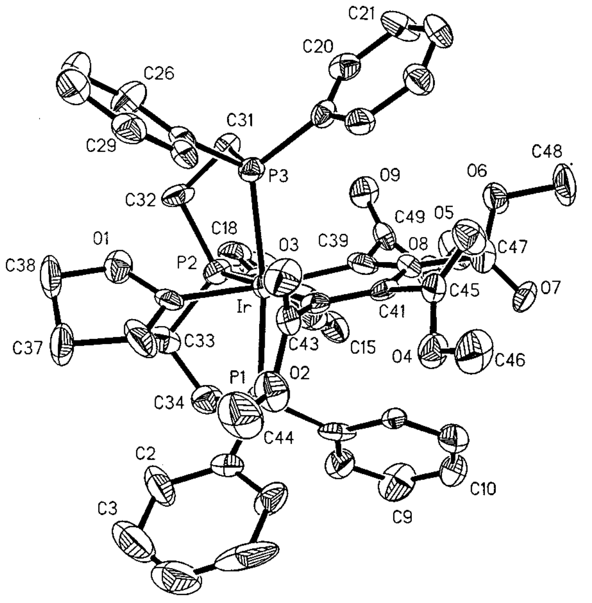

Figure 1. Ortep drawing for (**9**), $C_{50}H_{51}IrO_9P_3BF_4$.

$\nu(C{\equiv}O)$ in **8** relative to **11** is indicative of greater back-bonding to CO in the *mer* complex **8** relative to that in *fac*-**11**.

Whereas the cationic $[MeC(CH_2PPh_2)_3]$ complex **3** undergoes reaction with 3-butyn-1-ol to give the allyl complex **4** (Scheme 1), the $[PhP(CH_2CH_2PPh_2)_2]$ cation **7** undergoes reaction with 3-butyn-1-ol to give the oxacyclopentylidene complex $[\{PhP(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CRCR{=}CR})({=}\overline{C(CH_2)_3O})]BF_4$ (**9**, R = CO_2CH_3) (Scheme 2). Thus, addition of 3-butyn-1-ol (28 mM) to a chloroform solution of **7** (20 mM) at room temperature gave carbene **9** as an analytically pure peach-colored solid in 67% yield. Two $^{31}P\{^1H\}$ NMR signals are observed for **9** at δ 79.27 (br s, 1P) and 10.57 (br s, 2P), and in the ^1H NMR spectrum ($CDCl_3$) four methyl singlets at δ 3.79, 3.46, 3.38, and 2.36. These data supports a formulation with a plane of symmetry through the metallacycle, but with no symmetry plane perpendicular to the metallacycle. The sp^2-carbene carbon was observed in the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) as a broad singlet at δ 282.7. For comparison, the carbene carbon of **2** gave rise to a broad singlet at δ 278.3 in the $^{13}C\{^1H\}$ NMR spectrum.

X-ray data was acquired on a pale yellow obelisk-shaped crystal of **9**, obtained by slow diffusion from CH_2Cl_2/Et_2O. The structure, as shown in Figure 1, is consistent with that deduced from the NMR spectroscopy data. Selected bond distances and bond angles are summarized in Table 1. The complex deviates from ideal octahedral geometry with the C(39)–Ir–C(42) angle constrained by the metallacycle ring to 78.1(7)°. The 2-oxacyclopentylidene ligand mean plane bisects the metallacycle plane at an angle of 33.8°, which compares with a 24° angle in **2**. Presumably the carbene ligand rotates more in **9** than in **2** in order to relieve steric congestion arising from the *cis*-phosphine ligand of **9**. The Ir–C(35) distance of 2.045(14) Å (compared to 2.025(7) Å for **2**) is consistent with a metal–carbon double bond. The metallacycle iridium–carbon distances of 2.131(12) and 2.097(17) Å are similar to the corresponding 2.108(7) and 2.101(7) Å distances in **2**. The carbon–carbon bond distances of the metallacycle in **9** are consistent with the presence of a conjugated 1,3-diene: C(39)–C(40), 1.343 Å, C(40)–C(41), 1.482 Å, and 1.367 Å. The iridium–phosphorus distances in **9** are 2.368(5) Å and 2.359(5) Å for the trans phosphines, and 2.324(6) Å for the central phosphorus which is trans to a metallacycle carbon.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 9

Bond Distances, Å

A	B	distance	A	B	distance
Ir	P(1)	2.368(5)	Ir	P(2)	2.324(6)
Ir	P(3)	2.359(5)	Ir	C(35)	2.045(14)
Ir	C(39)	2.131(12)	Ir	C(42)	2.097(17)
C(35)	C(36)	1.422(28)	C(35)	O(1)	1.343(17)
C(36)	C(37)	1.519(17)	C(37)	C(38)	1.541(28)
C(38)	O(1)	1.493(19)	C(39)	C(40)	1.367(23)
C(40)	C(41)	1.482(25)	C(41)	C(42)	1.343(14)

Bond Angles (deg)

A	B	C	angle	A	B	C	angle
P(1)	Ir	P(2)	82.1(2)	P(2)	Ir	P(3)	83.7(2)
P(1)	Ir	P(3)	165.7(2)	P(2)	Ir	C(35)	90.3(5)
P(1)	Ir	C(35)	88.0(4)	P(1)	Ir	C(39)	99.4(4)
P(3)	Ir	C(35)	90.2(4)	P(3)	Ir	C(39)	84.6(4)
P(2)	Ir	C(39)	98.6(6)	P(1)	Ir	C(42)	96.2(3)
P(2)	Ir	C(42)	176.0(4)	P(3)	Ir	C(42)	98.1(3)
C(35)	Ir	C(42)	93.2(6)	C(39)	Ir	C(42)	78.1(7)
C(35)	Ir	C(39)	169.2(7)	Ir	P(1)	C(1)	121.4(4)
Ir	C(35)	C(36)	134.4(10)	Ir	C(35)	O(1)	117.4(12)
C(36)	C(35)	O(1)	108.2(11)	C(35)	C(36)	C(37)	108.4(16)
C(36)	C(37)	C(38)	99.2(12)	C(37)	C(38)	O(1)	102.4(12)
C(35)	O(1)	C(38)	111.3(14)	Ir	C(39)	C(40)	113.7(13)
C(39)	C(40)	C(41)	116.3(11)	C(40)	C(41)	C(42)	115.4(14)
Ir	C(42)	C(41)	116.3(13)				

Conclusion

Reaction of the bis(triphenylphosphine)iridacyclopentadiene complex **5** with $[PhP(CH_2CH_2PPh_2)_2]$ gives predominantly the *fac*-metallacycle complex, **6**-*fac*, along with a minor amount of the *mer*-isomer. Halide abstraction from **6**-*fac*, however, leads only to the *mer* isomer of the cationic iridacyclopentadiene **7**. Whereas the cationic $[MeC(CH_2PPh_2)_3]$ triphos complex **3** undergoes reaction with 3-butyn-1-ol to give a π-allyl complex **4**, the $[PhP(CH_2CH_2PPh_2)_2]$ triphos complex **7** forms the oxacyclopentylidene complex **9** upon reaction with 3-butyn-1-ol. We conclude that the differing reactivity toward alkynol previously observed for **1** and **3** (Scheme 1) is primarily the result of the geometric factors and not the greater electron density at the metal center in intermediates derived from **3** relative to those derived from **1**. The solid-state structure of **9** is the first such structure to be reported for a *mer* iridium complex of $[PhP(CH_2CH_2PPh_2)_2]$.

Experimental Section

General. The iridium starting complex **5** was prepared as described in the literature.[1a] Bis(2-diphenylphosphinoethyl)-phenylphosphine and 3-butyn-1-ol were obtained from Aldrich Chemical Co. IR spectra were recorded on a Matteson Instruments Galaxy Series 2020 FT-IR spectrometer. ^1H and ^{31}P NMR spectra were obtained on a GE QE 300, Varian Hg 300, or Varian Hg 400 (^1H 300 MHz, ^{31}P, 122 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Varian UNITY 500 (126 MHz) spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to residual protio-solvent signal, and ^{31}P NMR chemical shifts were referenced to external 85% H_3PO_4. Melting point determinations were performed on an Electrothermal melting point apparatus and were determined in an open capillary. FAB mass spectra were performed at the University of California, Riverside Mass Spectroscopy Facility. Elemental analyses were performed by Desert Analytics, NuMega Resonance Labs, or Galbraith Laboratories, Inc.

$[\{PPh(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CR{-}CR{=}C}R)Cl]$ (6-*fac*, R = CO_2CH_3). A 250 mL round-bottom flask was charged under a nitrogen atmosphere with $[(C\overline{R{=}CRCR{=}CR)Ir}\ (PPh_3)_2(Cl)]$ (**5**; R = CO_2Me; 1.88 g, 1.8 mmol) and bis(2-diphenylphosphinoethyl)phenylphosphine (1.23 g, 2.3 mmol). Dry toluene (120 mL) was vacuum distilled into the flask, and the solution was heated under nitrogen at reflux for 24 h. The reaction mixture was cooled to room temperature and filtered to remove a precipitate which was then washed sequentially with benzene and hexanes and dried in vacuo to give **6**-*fac* as a pink/tan powder (1.24 g, 65% yield). An analytically pure sample of **6**-*fac* was obtained by recrystallization by slow diffusion from CH_2Cl_2/Et_2O. mp: 289 °C (dec); IR(KBr): 1692(vs), 1486(s), 1434(s), 1331(s) cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.76−6.67 (m, 25 H), 3.44 (m, 4H), 3.31 (s, 6H), 2.52 (s, 6H), 2.33 (m, 4H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): A_2B, $\delta(P_A) = -0.63$, $\delta(P_B) = 56.03$; $^2J(P_AP_B) = 7.1$ Hz). Anal. Calcd for $C_{46}H_{45}O_8P_3ClIr$: 52.80% C, 4.33% H. Found: 52.64% C, 4.11% H.

$[\{PPh(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CR{-}CR{=}C}R)Cl]$ (6-*mer*, R = CO_2CH_3). The supernatant from the filtration of **6**-*fac* (above) was slowly evaporated in the hood yielding analytically pure square orange crystals of **6**-*mer* (10 mg, 5.3% yield). mp: 274−279 °C; IR(KBr): 1696(vs), 1434(s), 1333(s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.77−7.07 (m, 25 H), 3.76 (s, 3H), 3.50 (s, 3H), 3.31 (s, 3H), 3.19 (s, 3H), 2.85 (m, 4H), 2.55 (m, 2H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 58.27 (t, J = 8.0 Hz), 1.6 (d, J = 8.0 Hz). Anal. Calcd for $C_{46}H_{45}O_8P_3ClIr$: 52.80% C, 4.33% H. Found: 52.56% C, 4.02% H.

$[\{PPh(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CR{-}CR{=}C}R)(ClCH_2Cl)]BF_4$ (7, R = CO_2CH_3). A 100 mL round-bottom flask was charged under a nitrogen atmosphere with **6**-*fac* (628 mg, 0.60 mmol), $AgBF_4$ (129 mg, 0.66 mmol), and dry CH_2Cl_2 (50 mL). After 60 h at room temperature, the solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (50 mL, wet) and the solution stirred in the air for 1 h. The mixture was filtered through Celite and concentrated in vacuo, and hexanes were added to give **7** as a bright yellow powder (616 mg, 87% yield). mp: 195 °C (dec); IR(KBr): 1707(vs), 1435(s), 1062 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.59−7.18 (m, 25 H), 5.47 (s, 2H), 3.89 (s, 3H), 3.55−3.78 (m, 2H), 3.47 (s, 3H), 3.34 (s, 3H), 3.18−2.86 (m, 6 H), 2.41 (s, 3H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 62.87 (t, 1P, J = 8.4 Hz), 12.97 (br s, 2P). Anal. Calcd for $C_{47}H_{47}O_8P_3Cl_2IrBF_4$: 47.73% C, 4.01% H. Found: 47.78% C, 4.25% H.

$[\{PPh(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CRCR{=}C}R)(CO)]BF_4$ (8, R = CO_2CH_3). Carbon monoxide gas was bubbled through a wet CH_2Cl_2 (30 mL) solution of **7** (102.1 mg, 0.08 mmol) for 1 h at room temperature. The CO-saturated solution was then stirred at room temperature for 24 h, followed by evaporation of the volatiles in vacuo. The residue was dissolved in CH_2Cl_2, and addition of Et_2O led to precipitatation of **8** as an off-white powder (73 mg, 75% yield). Recrystallization from THF/MeOH/Et_2O afforded 45.2 mg (46% yield) of analytically pure white crystals. mp: 270−272 °C. IR(KBr): 2069 (s), 1702 (s) 1062 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.66 (m, 4 H), 7.47 (m, 10 H), 7.36 (m, 2 H), 7.29 (m, 4 H), 7.24 (t, 1 H, J = 8.5 Hz), 7.11 (t, 2 H, J = 9.5 Hz), 6.88 (dd, 2 H, J = 13.5, 2 Hz), 3.92 (br s, 2 H), 3.86 (s, 3H), 3.54 (s, 3 H), 3.48 (s, 3 H), 3.45 (br s, 1 H), 3.32 (s, 3 H), 3.09 (sept, 5 H, J = 11 Hz). Anal. Calcd for $C_{47}H_{45}P_3O_9IrBF_4$: 50.14% C, 4.03% H. Found: 50.18% C, 4.17% H.

$[\{PPh(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CRCR{=}C}R)({=}\overline{COCH_2CH_2C}H_2)]BF_4$ (9, R = CO_2CH_3). The cationic metallacycle **7** (607 mg, 0.513 mmol) was placed in a 50 mL round-bottom flask, and dry degassed $CHCl_3$ (25 mL) was transferred to the flask under vacuum. 3-Butyn-1-ol (52 mL, 0.692 mmol) was added at −78 °C, and the solution was degassed several times. After stirring at room temperature for 5 h, the solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ (20 mL) and filtered. The filtrate was then concentrated, and Et_2O was added to precipitate **9** as peach-colored powder (400 mg, 67% yield). mp: 238−240 °C; IR(KBr): 1718(vs), 1699(vs) cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.55−7.33 (m, 26 H), 7.18 (m, 4H), 4.23 (t, 2H, J = 8.06 Hz), 3.79 (s, 3H), 3.58 (m, 2H), 3.46 (s, 3H), 3.38 (s, 3H), 3.14−2.86 (m, 4H), 2.36 (s, 3H), 1.78 (t, 2H, J = 7.7 Hz), 1.07 (quintet, J = 7.9 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 79.27 (br s, 1P), 10.47 (d, 2P, J = 2.8 Hz). Anal. Calcd for $[C_{50}H_{51}O_9P_3Ir]^+BF_4^-$: 51.42% C, 4.40% H. Found: 51.17% C, 4.06% H.

X-ray Structure Determination for $[\{PPh(CH_2CH_2PPh_2)_2\}\overline{Ir(CR{=}CRCR{=}C}R)({=}\overline{COCH_2CH_2C}H_2)]BF_4$ (9, R = CO_2CH_3). Crystals of **9** were obtained by slow diffusion from CH_2Cl_2/Et_2O. The crystals were found to rapidly lose solvent when removed from the mother liquor. Therefore, a satisfactory crystal for diffraction studies was obtained by removal of the crystal from the mother liquor, followed by rapid placement in paratone, and data collection at low temperature. Data were collected at the University of California−San Diego X-ray Facility with a Siemens R3m/V automated diffractometer system with a dedicated Microvax II computer system. The parameters used during the data collection are summarized in the Supporting Information. All computations used the SHELTXTL PLUS (Version 3.4) program library (Siemens Corp., Madison, WI). The structures were solved by direct methods and refined by full matrix-least-squares methods. All nonhydrogen atoms were located on a series of difference Fourier maps. Hydrogen atom positions were added in ideal calculated positions with d(C−H) = 0.96 Å and with fixed isotropic thermal parameters set at 1.2 to 1.3 times the isotropic equivalent of the attached carbon atom, with a maximum value of $U = 0.10$. Crystal data for **9**: $C_{50}H_{51}BF_4IrO_9P_3$, M_w= 1167.83, monclinic, $C2/c$, a = 26.10(3) Å, b = 28.42(3) Å, c = 15.19(2) Å, β = 124.64(9), V = 9268(21) Å^3, Z = 8, d_{calcd} = 1.674 g cm^{-3}, R1 = 0.0664 ($I > 2\sigma$(I)), wR2 = 0.1434.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **9**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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