Iridacyclopentadiene Reactions with Terminal Alkynes: Tandem Cycloaromatization and Orthometalation

ARTICLE *in* ORGANOMETALLICS · JULY 2001

Impact Factor: 4.13 · DOI: 10.1021/om0102450

5 AUTHORS, INCLUDING:

Joseph M O'Connor
University of California, San Diego
101 PUBLICATIONS **2,071** CITATIONS

SEE PROFILE

Peter Gantzel
University of California, San Diego
94 PUBLICATIONS **2,991** CITATIONS

SEE PROFILE

Iridacyclopentadiene Reactions with Terminal Alkynes: Tandem Cycloaromatization and Orthometalation

Joseph M. O'Connor,* Adam Closson, Kristin Hiibner, Richard Merwin, and Peter Gantzel

Department of Chemistry and Biochemistry, 0358, 9500 Gilman Drive, University of California at San Diego, La Jolla, California 92093-0358

Dean M. Roddick*

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

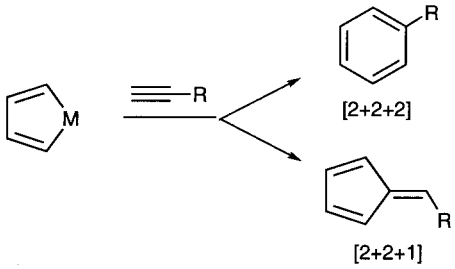
Received March 26, 2001

Treatment of the iridacyclopentadiene complex [{$(CH_3C(CH_2PPh_2)_3$}Ir(CR=CRCR=CR)Cl] (**1**, R = CO_2CH_3) with silver tetrafluoroborate, followed by addition of a terminal alkyne (ethyne, ethyl ethnynyl ether, methyl propargyl ether), yields iridium(III) aryl-hydride complexes[{$(CH_3C(CH_2PPh_2)_3$}Ir{C=C(C=OOMe)C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C(R^1)}H]BF_4 (**6**-H, R^1 = H; **6**-OEt, R^1 = OCH_2CH_3; **6**-CH_2OMe, R^1 = CH_2OCH_3). The structure of **6**-OEt was established by X-ray crystallographic analysis. Treatment of **6**-H with either HCl or carbon monoxide results in demetalation to give tetramethyl 1,2,3,4-benzenetetracarboxylate [$C_6(CO_2Me)_4H_2$]. When 3-butyn-2-ol and propargyl alcohol are employed as substrates, a similar reaction occurs with **1**/$AgBF_4$ to produce the phthalimidyl complexes [{$(CH_3C(CH_2PPh_2)_3$}Ir{C=C(C=OOMe)C(CO_2Me)=C(CO_2Me)C(C=O)=CCHR^1O}H]BF_4 (**7**-H, R^1 = H; **7**-Me, R^1 = CH_3). The lactone ring in **7** is generated from an intramolecular transesterification of the hydroxyl with an adjacent methyl ester. In all cases these products are attributed to tandem cycloaromatization and orthometalation processes.

Introduction

Metal-mediated [2+2+2] cyclotrimerization of alkynes to produce aromatic six-membered rings have been widely applied to the synthesis of natural products and novel organic materials.[1] Reactions of this type typically proceed via the intermediacy of metallacyclopentadiene complexes.[2] A potentially useful alternative to the [2+2+2] cyclotrimerization of alkynes is a [2+2+1] cyclotrimerization to give five-membered rings. This later process, which is exceedingly rare, may also be envisioned as proceeding via a metallacyclopentadiene intermediate (Scheme 1).[3]

Scheme 1



We previously reported the first evidence that metallacyclopentadienes may indeed undergo reaction with alkynes to generate fulvenes in what is formally a [2+2+1] cyclotrimerization process (Scheme 2).[4−6] For

(1) For leading references to metal-mediated alkyne cyclotrimerization see: (a) Yamamoto, Y.; Ogawa, R.; Itoh, K. *Chem. Commun.* **2000**, 549. (b) Ozerov, O. V.; Ladipo, F. T.; Partick, B. O. *J. Am. Chem. Soc.* **1999**, *121*, 7941. (c) Hecht, S.; Fréchet, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 4084. (d) Sherrill, A. B.; Lusvardi, V. S.; Barteau, M. A. *Langmuir* **1999**, *15*, 7615. (e) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (f) Sigman, M. S.; Fatland, A. W.; Eaton, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 5130. (g) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (h) Bönnemann, H. *Angew. Chem.* **1985**, *97*, 264.

(2) Diercks, R.; Eaton, B. E.; Gurtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247. (b) Baxter, R. J.; Knox, G. R.; Pauson, P. L.; Spicer, M. D. *Organometallics* **1999**, *18*, 197. (c) Takahashi, T.; Tsai, R. Y.; Li, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093. (d) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672. (e) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298.

(3) Other mechanistic possibilities, most notably the initial formation of a vinylidene ligand followed by addition of alkyne across the iridium−carbon double bond, are potentially viable [2+2+1] routes toward fulvenes; see ref 6.

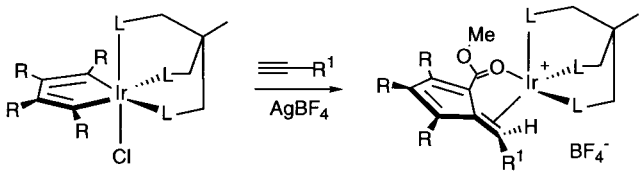
(4) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P.; Rheingold, A. L.; Fong, B. S. *J. Am. Chem. Soc.* **1997**, *119*, 3631.

(5) For an early-metal metallacyclopentadiene to fulvene cyclization see: Johnson, E. S.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 11086−11087.

(6) For other [2+2+1] alkyne cyclotrimerizations see: (a) Moran, G.; Green, M.; Orpen, A. G. *J. Organomet. Chem.* **1983**, *250*, C15. (b) Moreto, J.; Maruya, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1341. (c) Kim, H. J.; Choi, N. S.; Lee, S. W. *J. Organomet. Chem.* **2000**, *616*, 67. (d) Chukhadzhyan, G. A.; Abramyan, Zh. Igevorkyan, G. A. *Zh. Obshch. Khim.* **1973**, *43*, 2012. (e) Chukhadzhyan, G. A.; Abramyan, Zh. I.; Tonyan, G. M.; Matosyan, V. A. *Zh. Org. Khim.* **1974**, *10*, 1994. (f) Chukhadzhyan, G. A.; Abramyan, Zh. I.; Tonyan, G. M.; Sagradyan, L. I.; Elbakyan, T. S. *Zh. Org. Khim.* **1981**, *17*, 1831.

10.1021/om0102450 CCC: $20.00
Publication on Web 07/17/2001

Scheme 2



1 R = CO_2Me, L = PPh_2

2-Bu, $R^1 = Bu^t$

2-Ph, R^1 = Ph

example, treatment of the iridacyclopentadiene complex [{$(CH_3C(CH_2PPh_2)_3$}Ir(CR=CRCR=CR)Cl] (**1**, R = CO_2CH_3) with $AgBF_4$ and either 3,3-dimethylbut-1-yne or phenyl acetylene led to formation of the cationic fulvene complexes [{$CH_3C(CH_2PPh_2)_3$}Ir{CHR^1=CC(C(=O)OMe)=CRCR=CR}]BF_4 (**2**-Bu, $R^1 = Bu^t$, R = CO_2CH_3; **2**-Ph, R^1 = Ph, R = CO_2CH_3). The hydroxyl-substituted alkynes, 3-butyn-1-ol and 4-pentyn-1-ol, also underwent reaction with **1** and $AgBF_4$ to give fulvene-derived products.[4] The cationic iridacycle [{$CH_3C(CH_2PPh_2)_3$}Ir(CR=CRCR=CR)(NCMe)]BF_4 (**3**, R = CO_2CH_3) may be employed in place of **1**/$AgBF_4$ with similar results.

We now report that, quite unexpectedly in view of the fulvene chemistry described above, certain terminal alkynes (ethyne, ethyl ethynyl ether, methyl propargyl ether, propargyl alcohol, and 3-butyn-2-ol) undergo reaction with **3** or **1**/Ag^+ to generate [2+2+2] cyclization products. Thus, for reactions of **1**/Ag^+ or **3** with terminal alkynes there is a dramatic and highly selective partitioning between [2+2+1] and [2+2+2] cyclotrimerization pathways which depends solely on the nature of the alkyne substituent. The [2+2+2] products take the form of iridium aryl-hydrides which appear to arise from orthometalation of the newly formed aromatic ring.

Results

Synthesis of Triphos-Iridacyclopentadiene Complexes. We previously examined the reactions of bis(triphenylphosphine)iridacyclopentadiene complexes such as [$(PPh_3)_2$Ir(CR=CRCR=CR)Cl] (**4**, R = CO_2CH_3)[7] and the cationic analogue [$(PPh_3)_2$Ir(CR=CRCR=CR)(CO)(NCMe)]BF_4 (**5**, R = CO_2CH_3)[7a,8] with terminal alkynes in an effort to develop the chemistry of metallacycle-carbene and metallacycle-vinylidene complexes. In no instance was evidence obtained for the coupling of vinylidene and buta-1,3-dien-1,4-diyl ligands. Intrigued by the possibility that the metallacycle stereochemistry would have a pronounced effect on the reactions of alkynes and iridacycles and encouraged by literature examples in which tridentate tris(phosphine) ligands [$Me(CH_2PPh_2)_3$] and [$PhP(CH_2CH_2PPh_2)_2$] were successfully utilized to control stereochemistry in octahedral complexes,[9] we set out to prepare triphos-iridacyclopentadiene complexes related to **4** and **5**.

The air-stable triphos-metallacyclopentadiene complex **1** proved to be readily accessible on a one gram scale in 95% isolated yield by simply heating a toluene solution of **4** and [$Me(CH_2PPh_2)_3$] at reflux for 24 h (Scheme 3). Despite the rather harsh conditions of this procedure there was no evidence for the formation of cyclobutadiene complexes as is commonly observed upon thermolysis of cobaltacyclopentadienes.[10] The cationic facial-iridacyclopentadiene complex [{$CH_3C(CH_2PPh_2)_3$}Ir(CR=CRCR=CR)(NCMe)]BF_4 (**3**, R = CO_2CH_3) was subsequently prepared as an air-stable off-white solid in 86% isolated yield by treatment of **1** with $AgBF_4$ in acetonitrile solution. A related procedure was carried out with [$PhP(CH_2CH_2PPh_2)_2$] to give a cationic meridional-iridacyclopentadiene complex as reported previously.[11]

Synthesis of Iridium Aryl-Hydride Complexes. When ethyl ethynyl ether (6 μL, 0.06 mmol) was added to a $CDCl_3$ solution of the cationic metallacycle **3** (0.004 mmol, 0.011 mM) and the solution monitored by ^1H NMR spectroscopy, the aryl-hydride complex **6**-OEt was observed to form over the course of several hours at room temperature (Scheme 4). Integration of the methyl-ester hydrogen resonances in the ^1H NMR spectrum, relative to 1,4-bis(trimethylsilyl)benzene as internal standard, indicated a 97% yield of **6**-OEt. A related preparative scale reaction of iridacycle **1** (300 mg, 0.26 mmol, 17.3 mM), $AgBF_4$ (0.29 mmol), and ethyl ethynyl ether (1.3 mmol) gave **6**-OEt as a pale yellow air-stable solid in 82% yield. Metallacycle **3** also underwent a room-temperature reaction with both acetylene and methyl propargyl ether to give the corresponding hydride complexes **6**-H and **6**-CH_2OMe in 97% and 96% NMR yields, respectively (Scheme 4).

The observation of four singlets at δ 3.89, 3.86, 3.69, and 3.42 (3H each), and a hydride resonance at −8.57 (ddd, J_{PH} = 140, 13, 10 Hz) in the ^1H NMR spectrum ($CDCl_3$) of **6**-OEt, is consistent with the assigned structure. For comparison, the Ir(III) hydride ligand in the carbonyl(1,2-phenylen)methylene complex [{$CH_3C(CH_2PPh_2)_3$}Ir{C(=O)$C_6H_4CH_2$}(H)] is observed as a doublet of triplets at δ −9.05 with J_{PH} = 129, 13 Hz.[12] The presence of the chelating ester substituent in **6**-OEt was established by a single-crystal X-ray diffraction study (Figure 1, Tables 1 and 2).[13] The quality of the structural data precludes a detailed analysis of bond lengths and bond angles; however, the three iridium−phosphorus bond distances vary significantly with the longest bond for the phosphorus *trans* to the hydride ligand [2.427 (4) Å] and the shortest bond length to the phosphorus *trans* to the oxygen ligand [2.259 (4) Å].

(7) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232. (b) O'Connor, J. M.; Pu, L.; Woolard, S.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 6731. (c) O'Connor, J. M.; Hiibner, K.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1209. (d) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 8861.

(8) O'Connor, J. M.; Pu, L.; Chadha, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 543. (b) O'Connor, J. M.; Pu, L. *J. Am. Chem. Soc.* **1990**, *112*, 9013. (c) O'Connor, J. M.; Pu, L.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 9627. (d) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 9663.

(9) Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239.

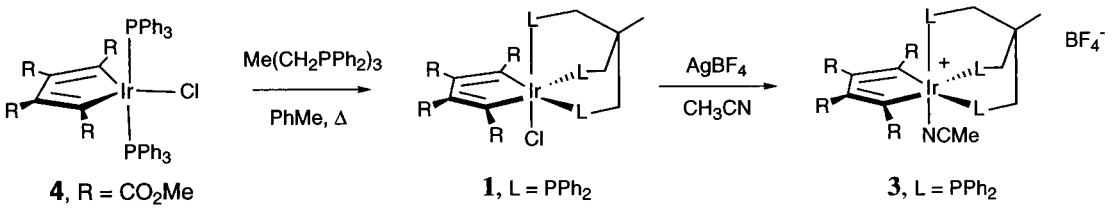
(10) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1967**, *7*, 22. (b) Ville, G.; Vollhardt, K. P. C.; Winter, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 5267.

(11) O'Connor, J. M.; Hiibner, K.; Closson, A.; Gantzel, P. *Organometallics* **2001**, *20*, 1482.

(12) Arpac, E.; Dahlenburg, L. *Chem. Ber.* **1985**, *118*, 3188.

(13) For details of the X-ray crystallographic analysis see Supporting Information.

Scheme 3



4, R = CO_2Me **1**, L = PPh_2 **3**, L = PPh_2

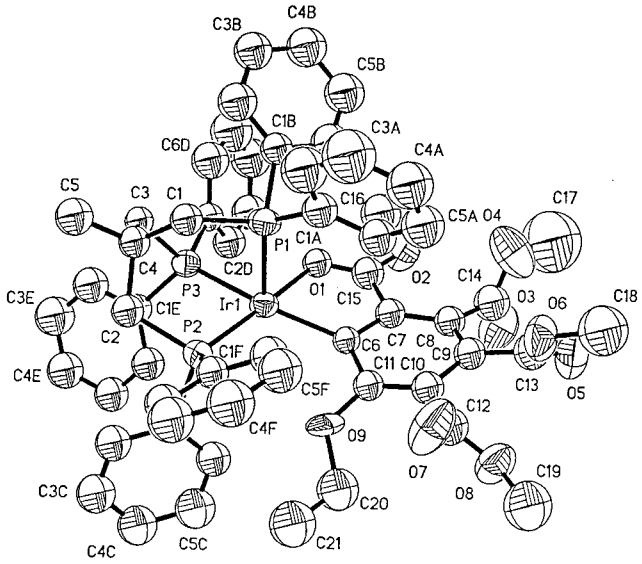
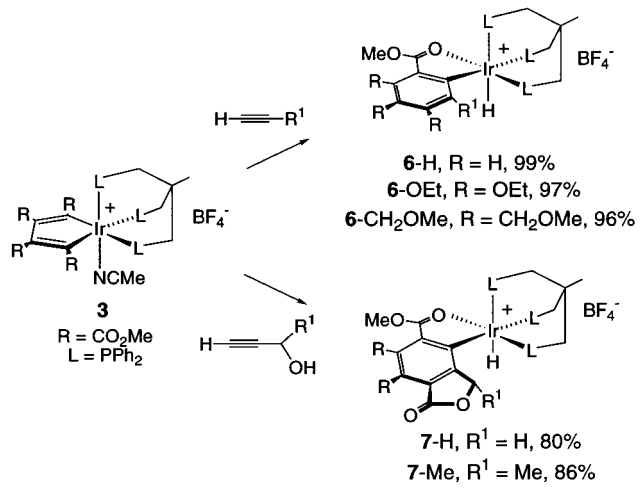


Figure 1. ORTEP view of the cation of [{(MeC(CH_2-PPh_2)$_3$}Ir{C=C(C=OOMe)CR=CRCR=C(OEt)}H]BF_4 (**6**-OEt, R = CO_2Me).

Scheme 4



Propargyl alcohol and 3-butyn-2-ol also undergo a clean reaction with **3** at room temperature to give hydride complexes; however, in both cases only three methyl-ester resonances are observed in the ^1H NMR spectrum of the product. When the room-temperature reaction of excess propargyl alcohol (48.5 mM) and **3** (9.2 mM) was monitored by ^1H NMR spectroscopy ($CDCl_3$), the phthalidyl complex **7**-H and methanol (δ 3.48) are observed to form in 92% NMR yield (Scheme 4). The methanol byproduct is consistent with a transesterification involving the alkynol and one of the methyl ester ring substituents. In a preparative scale reaction **7**-H was isolated as a pale yellow solid in 79% yield from reaction of **1**/$AgBF_4$ and propargyl alcohol. In addition to the observation of only three methyl hydrogen resonances between δ 4.0 and 3.2 in the ^1H NMR spectrum of isolated **7**-H, a strong band in the infrared spectrum at 1768 cm^{-1} is consistent with the presence of the lactone ring. In the reaction of 3-butyn-2-ol and **3**, the substituted phthalidyl complex **7**-Me is formed as a single diastereomer, in 86% isolated yield (Scheme 4). Presumably the favored diastereomer has the methyl substituent of the lactone ring pointed down toward the hydride ligand and away from the bulky phosphine ligand as shown in Scheme 4, but this assignment has not been unambiguously established.

To test for the presence of a noncoordinated arene prior to the orthometalation step, we examined the reaction of **3**-d_{12} (0.007 mM in $CDCl_3$), in which the four ester-methyl groups were deuterium enriched, and ethyne (1 atm) in the presence of added 1,2,3,4-tetrakis-(methoxycarbonyl)benzene[14] (**8**, 0.07 mM). Upon completion of reaction, excess **8** was removed by precipitation of the iridium product, which was than recovered by

Table 1. Crystal and Data Collection and Refinement Parameters for 6-OEt and 9

	6-OEt	**9**
empirical formula	$C_{31}H_{28}B_{0.50}F_2Ir_{0.50}O_{5.13}P_{1.50}$	$C_{58}H_{82}Cl_2Ir_2P_2P_6$
lattice type	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	16.046(9)	12.084(2)
b Å	22.031(14)	14.577(3)
c, Å	18.461(12)	15.080(3)
α, deg	90	96.62(3)
β, deg	100.09(5)	107.59(3)
γ, deg	90	113.56(3)
V, Å^3	6425 (7)	2234.7(7)
Z	8	1
F(000)	2692	1048
cryst dimens, mm	0.14 × 0.36 × 0.70	0.20 × 0.24 × 0.39
cryst color	yellow plate	yellow prism
D(calc), Mg/m^3	1.382	1.575
abs coeff, mm^{-1}	2.218	3.380
temp	23 °C	296 K
radiation type	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
θ range, deg	1.5 to 22.57	4.0 to 45.0 (2θ)
no. of reflns collected	8460	6164
no. of ind reflns	8259 (R_{int} = 0.0725)	5829 (R_{int} = 0.0574)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares
no. of data/params	8252/309	12.0/1
final *R* indices ($I > 2\sigma(I)$])	R1 = 0.0773, wR2 = 0.1850	R1 = 0.0760, wR2 = 0.0947
R indices (all data)	R1 = 0.1380, wR2 = 0.2291	R1 = 0.1214, wR2 = 0.1104
GOF	1.044	1.06

Table 2. Selected Bond Lengths and Angles for [{(MeC(CH$_2$PPh$_2$)$_3$}Ir{C=C(C=OOMe)CR=CRCR=C(OEt)}H]BF$_4$ (6-OEt, R = CO$_2$Me)

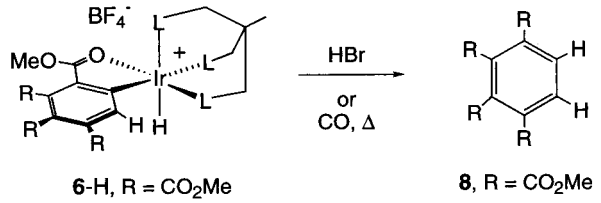
Bond Lengths (Å)

A	B	distance	A	B	distance
Ir	P(1)	2.427 (4)	C(9)	C(10)	1.43 (2)
Ir	P(2)	2.259 (4)	C(10)	C(11)	1.40 (2)
Ir	P(3)	2.361 (4)	C(7)	C(15)	1.48 (2)
Ir	O(1)	2.114 (9)	C(15)	O(1)	1.25 (2)
Ir	C(6)	2.124 (14)	C(15)	O(2)	1.30 (2)
C(6)	C(7)	1.42 (2)	C(11)	O(9)	1.38 (2)
C(7)	C(8)	1.43 (2)	O(9)	C(20)	1.45 (2)
C(8)	C(9)	1.38 (2)			

Bond Angles (deg)

A	B	C	angle	A	B	C	angle
P(1)	Ir	P(2)	90.0 (2)	O(1)	Ir	C(6)	78.4 (5)
P(1)	Ir	P(3)	88.61 (14)	Ir	C(6)	C(7)	111.5 (10)
P(2)	Ir	P(3)	88.7 (2)	Ir	O(1)	C(15)	116.8 (10)
P(2)	Ir	O(1)	175.2 (3)	C(6)	C(7)	C(15)	115.3 (14)
P(1)	Ir	O(1)	93.1 (3)	C(7)	C(15)	O(1)	117.7 (14)
P(3)	Ir	O(1)	87.8 (3)	C(6)	C(7)	C(8)	122.7 (14)
P(2)	Ir	C(6)	104.7 (4)	C(7)	C(8)	C(9)	118.9 (14)
P(1)	Ir	C(6)	98.7 (4)	C(8)	C(9)	C(10)	119 (2)
P(3)	Ir	C(6)	164.7 (4)	C(10)	C(11)	C(6)	121.4 (14)

Scheme 5



filtration and analyzed by ^{1}H NMR spectroscopy. The absence of methyl hydrogen resonances in the region of the NMR spectrum between δ 3.8 and 3.6 ppm indicates less than 5% crossover between **8** and the aryl ligand of **6**-H-d_{12}. Even upon heating a sample of **6**-H-d_{12} and **8** at 60 °C for 192 h, there was no spectroscopic evidence for exchange of the aryl ligand in **6**-H-d_{12} with **8**.

Liberation of the Aryl Ligand from Iridium. The reactions of **6**-H with CO and with HCl were examined as a possible means of liberating the highly substituted aryl ligand from iridium (Scheme 5). Heating a $CDCl_3$ solution of **6**-H under an atmosphere of carbon monoxide at 70 °C led to reductive elimination of the aryl and hydride ligands[15] to give tetramethyl 1,2,3,4-benzenetetracarboxylate[16] (**8**, 82% yield) and the known dicarbonyl complex[17] [Ir(triphos)(CO)$_2$]BF$_4$ (73% yield). Bubbling HCl gas through a CD_2Cl_2 solution of **6**-H at room temperature also cleanly generated **8** (95% yield).

When $CHCl_3$ solutions of **6** are heated at 90 °C for 2 weeks, the iridium hydride dimer [{CH$_3$C(CH$_2$PPh$_2$)$_3$}-Ir(μ-Cl)H]$_2$[BF$_4$]$_2$ (**9**) precipitated from solution in 31% yield. In the ^{1}H NMR spectrum (acetone-d_6) of **9** the hydride resonance is observed at δ −6.63 as a dt with J_{PH} = 165 and 10 Hz. The tetraphenylborate salts of **9**

(14) Stephan, C.; Munz, C.; tom Dieck, H. *J. Organomet. Chem.* **1993**, *452*, 223.

(15) For a detailed mechanistic study on reductive elimination of aromatics from Ir(III) aryl-hydride complexes see: Rosini, G. P.; Wang, K.; Patel, B.; Goldman, A. S. *Inorg. Chim. Acta* **1998**, *270*, 537.

(16) Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8494

(17) Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227.

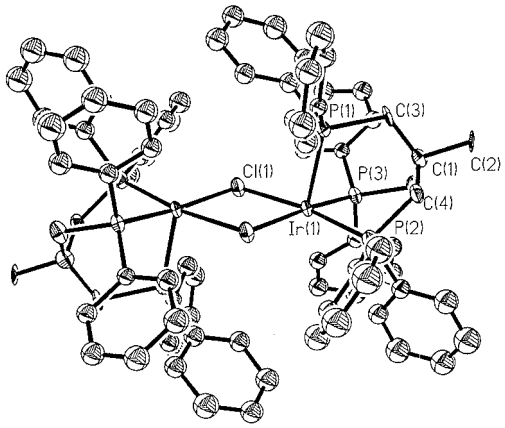


Figure 2. ORTEP view of the cation of [{(MeC(CH$_2$-PPh$_2$)$_3$}Ir(μ-Cl)$_2$H][BF$_4$]$_2$ (**9**).

Table 3. Selected Bond Lengths and Angles for [{(MeC(CH$_2$PPh$_2$)$_3$}Ir(μ-Cl)H]$_2$[BF$_4$]$_2$ (9)

Bond Lengths (Å)

A	B	distance	A	B	distance
Ir	P(1)	2.406 (6)	Ir	Cl1(1A)	2.441 (6)
Ir	P(2)	2.272 (7)	P(1)	C(3)	1.889 (17)
Ir	P(3)	2.277 (6)	P(2)	C(5)	1.829 (16)
Ir	Cl(1)	2.442 (6)	P(3)	C(4)	1.850 (19)

Bond Angles (deg)

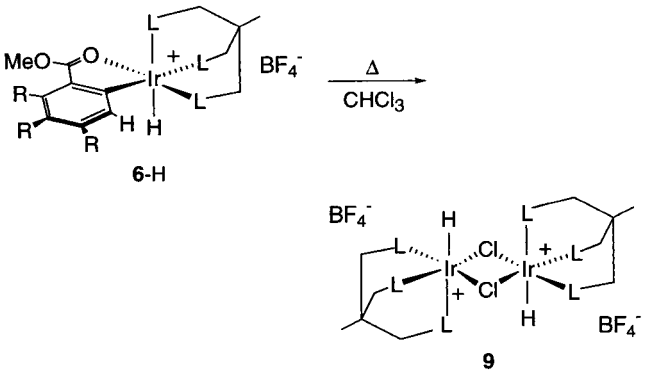
A	B	C	angle	A	B	C	angle
P(1)	Ir	P(2)	92.4 (2)	Ir	P(1)	C(3)	107.8 (8)
P(1)	Ir	P(3)	87.8 (2)	Ir	P(2)	C(5)	110.4 (9)
P(2)	Ir	P(3)	88.8 (2)	Ir	P(3)	C(4)	78.4 (5)
P(1)	Ir	Cl(1)	94.4 (2)	C(11)	P(1)	C(21)	99.4 (13)
P(2)	Ir	Cl(1)	171.5 (2)	C(31)	P(2)	C(41)	98.7 (13)
P(3)	Ir	Cl(1)	96.6 (2)	C(51)	P(3)	C(61)	98.2 (12)

were previously isolated as a mixture of *cis* and *trans* isomers from reaction of [{CH$_3$C(CH$_2$PPh$_2$)$_3$}Ir(η^2-CH$_2$=CH$_2$)Cl] with HOSO$_2$CF$_3$ followed by treatment with NaBPh$_4$.[17] Upon heating CD_3NO_2 solutions of the *cis*/*trans* mixture at 90 °C, one isomer was converted to the other. Since it was not possible in the earlier work to unambiguously correlate the NMR data with the specific *cis* or *trans* isomer, we carried out a single-crystal X-ray analysis of **9** (Figure 2, Table 1, Table 3). As shown in Figure 2, **9** exists as the *trans*-isomer. The iridium−phosphorus bond distance of 2.406(6) Å for the phosphine *trans* to the hydride is significantly longer than the 2.277(6) and 2.272(7) Å distances observed for the iridium−phosphorus bonds *trans* to the bridging halide ligands.

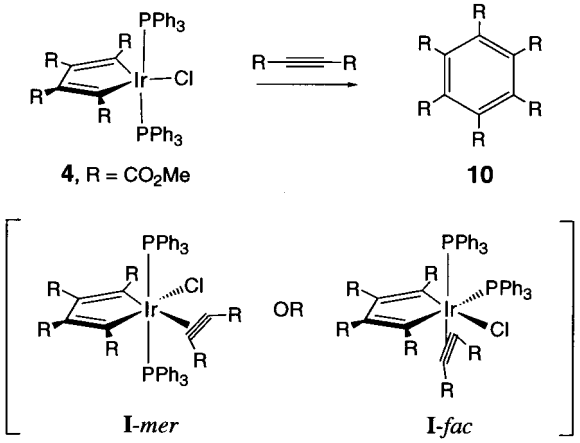
Discussion

Iridacyclopentadienes and Internal Alkynes. In 1968 Collman and co-workers first reported the reaction of an iridacyclopentadiene complex and an alkyne to give an aromatic product.[2e] Thus, [(PPh$_3$)$_2$Ir(CR=CRCR=CR)Cl] (**4**, R = CO$_2$CH$_3$) underwent a slow reaction with dimethyl acetylenedicarboxylate (DMAD) at 80 °C to give hexacarbomethoxybenzene, C$_6$(CO$_2$Me)$_6$ (**10**, Scheme 7). The sensitivity of this reaction to steric congestion was demonstrated by the observation that diphenylacetylene failed to react with **4**, and [(PPh$_3$)$_2$Ir(CR=CRCR=CR)Cl] (R = CO$_2$Et) and diethyl acetylenedi-

Scheme 6



Scheme 7

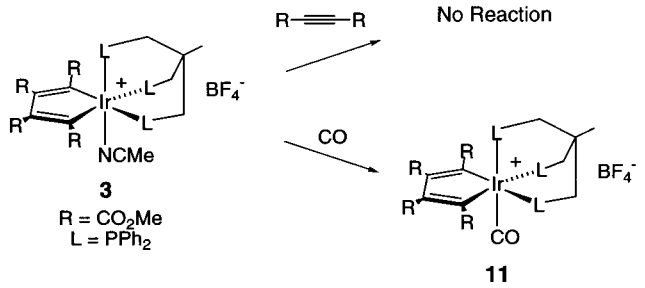


carboxylate gave only low yields of $C_6(CO_2Et)_6$. Two stereoisomeric complexes were suggested for the key metallacycle-alkyne intermediate in this cyclotrimerization reaction: the meridional isomer **I**-*mer* and the facial isomer **I**-*fac*, which appears to be an ideal geometry for concerted ring closure. Alternatively, a stepwise insertion/reductive elimination mechanism is possible from either isomer of **I**.

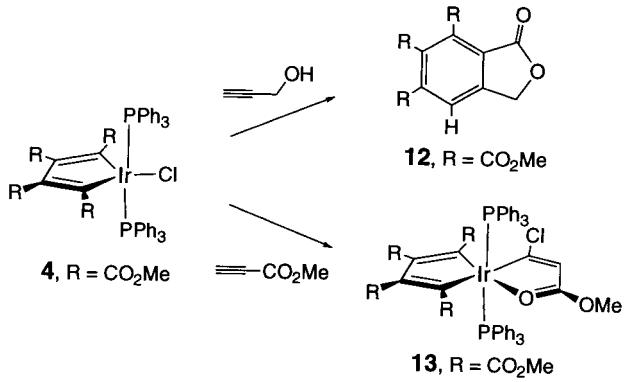
One method for enforcing a facial stereochemistry in an iridacyclopentadiene-alkyne intermediate related to **I**-*fac* is to prepare a triphos analogue of **4** or **5**. Simply heating toluene solutions of **4** and $[MeC(CH_2PPh_2)_3]$ at reflux leads to high yields of the coordinatively saturated metallacycle $[\{(CH_3C(CH_2PPh_2)_3\}Ir(CR{=}CRCR{=}CR)Cl]$ (**1**, R = CO_2CH_3). Treatment of **1** with $AgBF_4$ in acetonitrile gives the isolable cationic acetonitrile complex $[\{CH_3C(CH_2PPh_2)_3\}Ir(CR{=}CRCR{=}CR)(NCMe)]BF_4$ (**3**, R = CO_2CH_3). The labile nature of the acetonitrile ligand is apparent from the reaction of **3** with 1 atm of carbon monoxide to give the carbonyl complex $[\{CH_3C(CH_2PPh_2)_3\}Ir(CR{=}CRCR{=}CR)(CO)]BF_4$ (**11**, R = CO_2CH_3) in 86% isolated yield.[18] Heating $CDCl_3$ solutions of **3** (5.4 mg, 0.004 mmol, 0.008 mM) with DMAD (0.08 mM) for 18 h at 60 °C failed to give an observable reaction as determined by ^1H NMR spectroscopic analysis of the crude reaction mixture. Presumably this lack of reactivity is related to increased steric congestion at iridium in the triphos complex

(18) O'Connor, J. M.; Closson, A., unpublished observation.

Scheme 8



Scheme 9



relative to that in the bis(triphenylphosphine) system examined by Collman.

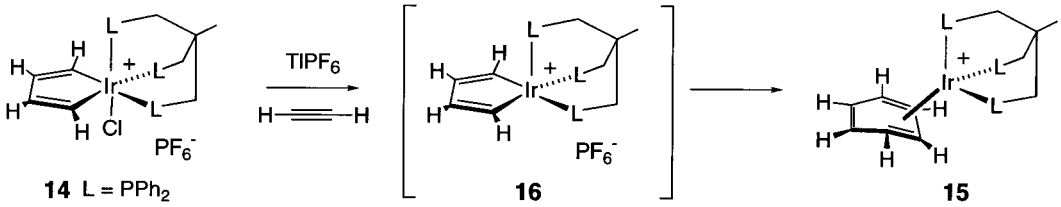
Iridacyclopentadienes and Terminal Alkynes. To date, the only terminal alkyne to undergo a cyclization reaction with the buta-1,3-dien-1,4-diyl ligand of **4** is propargyl alcohol, which gives a quantitative yield of 5,6,7-tri(carbomethoxy)phthalide (**12**) when the reaction is carried out in anhydrous CH_2Cl_2 at room temperature (Scheme 9).[7c] More typically, terminal alkynes undergo reaction with **4** to give products that do not involve carbocycle formation. For example, the room-temperature reaction of methylpropiolate with **4** gives the oxametallacycle $[(PPh_3)_2Ir(CR{=}CRCR{=}CR)(CCl{=}CHC(OMe){=}O)]$ (**13**, R = CO_2CH_3), the formation of which is consistent with an iridium(III) vinylidene intermediate which undergoes an insertion of the vinylidene ligand into the iridium−chloride bond.[7d]

A close analogy to the work reported herein is Bianchini's observation that reaction of the iridium triphos metallacycle $[\{(CH_3C(CH_2PPh_2)_3\}Ir(CH{=}CHCH{=}CH)Cl]$ (**14**) and ethyne, in the presence of $TlPF_6$, gives an isolable η^4-benzene complex $[\{(CH_3C(CH_2PPh_2)_3\}Ir(\eta^4\text{-}C_6H_6)]PF_6$ (**15**, Scheme 10).[19] Complex **15** was suggested to form via the unsaturated cationic intermediate **16**, which undergoes reaction with ethyne by a process involving a concerted formation of the Ir−C and C−C bonds.

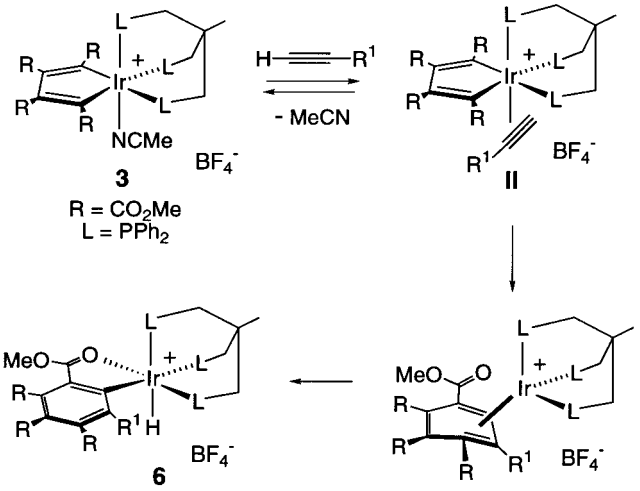
We suggest that an η^4-benzene intermediate may be pertinent to the conversion of **3** to **6** (Scheme 11). The η^4-arene complex would in turn arise either via a

(19) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M. L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010. (b) Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127.

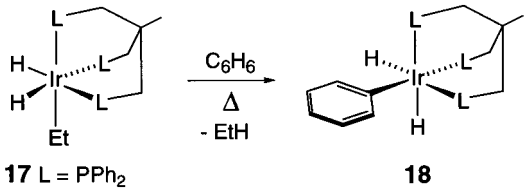
Scheme 10



Scheme 11



Scheme 12



concerted formation of iridium−carbon and carbon−carbon bonds, as proposed by Bianchini for **14**, or from a discrete η^2-alkyne intermediate (**II**) as shown in Scheme 11.

The ester substituent in the putative η^4-benzene intermediate presumably directs the insertion of iridium into the ortho carbon−hydrogen bond. The lack of a crossover product from the reaction of **3**-d_{12} and ethyne in the presence of added 1,2,3,4-tetrakis(methoxycarbonyl)benzene (**8**) supports an intramolecular rearrangement of the η^4-arene intermediate to the orthometalated product (**6**-H).

Chelation of the ester oxygen in **6** and **7** is likely to be responsible for the stability of the aryl-hydride structure relative to the η^4-arene isomer related to [{$(CH_3C(CH_2PPh_2)_3$}Ir(η^4-C_6H_6)]PF_6 (**14**). Carbon−hydrogen bond activation involving iridium alkyl-hydride intermediates is well precedented,[20] and isotopic incorporation of deuterium into substituted aromatics such as benzamides[21] and 4-phenylbenzoic acid[22] has been proposed to proceed via unobserved five-membered orthometalated intermediates. Iridium complexes containing four- or five-membered rings formed via an orthometalation reaction have also been isolated in a number of cases.[23] With respect to the triphos iridium complexes examined herein, the best precedent for the C−H activation step is the thermal conversion of iridium ethyl-dihydride **17** and benzene to aryl-dihydride **18** (Scheme 12).[24] This transformation presumably involves an unsaturated iridium(I) monohydride intermediate which undergoes insertion into the C−H bond of benzene, although cationic Ir(III) alkyls have recently been observed to give isolable Ir(V) aryl hydrides by metal insertion into an aryl−hydride bond.[25]

In summary, we have established an unusual partitioning between [2+2+2] and [2+2+1] cyclization pathways in iridacycle complexes that depends solely on the nature of the alkyne substituent. Studies are underway to establish the factors important for controlling this remarkable partitioning and to clarify the mechanistic details of both alkyne cyclization pathways.

Experimental Section

General Considerations. All experiments were performed under a nitrogen atmosphere using standard Schlenk, vacuum line, and drybox techniques. Solvents were degassed and dried by standard procedures. The iridium starting complex, [$(PPh_2)_2$Ir(CR=CRCR=CR)Cl] **4**, (R = CO_2Me) was prepared as described in the literature.[2e] 1,1,1-Tris(diphenylphosphinomethyl)ethane was obtained from either Organometallics, Inc. or Strem Chemicals, Inc. and used without further purification. Terminal alkynes and silver tetrafluoroborate were obtained from Aldrich Chemical Co. and used without further purification. Commercial grade acetylene gas was purified by passing through a liquid nitrogen trap, then bubbling through H_2SO_4, and finally passing over KOH pellets. All reaction workups were performed in the air unless otherwise noted. Infrared (IR) spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. Melting points are uncorrected and were determined in sealed capillaries using an Electrothermal melting point apparatus. Elemental analyses were performed by either Desert Analytics or Galbraith Laboratories, Inc. ^{1}H and ^{31}P NMR spectra were obtained on a GE QE 300 (^{1}H 300 MHz, ^{31}P, 122 MHz) spectrometer, and ^{13}C NMR spectra were obtained on a Varian UNITY 500 (126 MHz) spectrometer or a GE QE 300 (76 MHz). ^{1}H and ^{13}C NMR chemical shifts were referenced to the residual protio solvent signal, and ^{31}P NMR chemical shifts were referenced to 85%

(20) Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Alaimo, P. J.; Arndtsen, B. A.; Bergman, R. G. *Organometallics* **2000**, *19*, 2130. (c) Fuchen, L.; Pak, E. B.; Singh, B.; Jensen, C. M.; Goldman, A. S. *J. Am. Chem. Soc.* **1999**, *121*, 4086. (d) Aoki, T.; Crabtree, R. H. *Organometallics* **1993**, *12*, 294.

(21) Shu, A. Y. L.; Chen, W.; Heys, J. R. *J. Organomet. Chem.* **1996**, *524*, 87.

(22) Kingston, L. P.; Lockley, W. J. S.; Mather, A. N.; Spink, E.; Thompson, S. P.; Wilkinson, D. J. *Tetrahedron Lett.* **2000**, *41*, 2705.

(23) Ainscough, E. W.; Robinson, S. D.; Levison, J. J. *J. Chem. Soc. (A)* **1971**, 3413. (b) Deuton, K.; Dahlenburg, L. *Transition Met. Chem.* **1980**, *5*, 222, (c) Dahlenburg, L. *J. Organomet. Chem.* **1983**, *251*, 215. (d) Aizenberg, M.; Milstein, D. *Organometallics* **1996**, *15*, 3317. (e) Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974.

(24) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, *12*, 2505.

(25) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816. (b) Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1998**, *120*, 6169.

H_3PO_4. Mass spectra were obtained at the University of California Riverside Mass Spectroscopy Facility.

[{$CH_3C(CH_2PPh_2)_3$}Ir(CR=CRCR=CR)Cl] (1, R = CO_2CH_3). A 100 mL round-bottom flask was charged with $(PPh_3)_2$Ir(CR=CRCR=CR)Cl (R = CO_2Me; 1.0 g, 0.96 mmol), [$CH_3C(CH_2PPh_2)_3$] (0.75 g), and toluene (20 mL). The reaction mixture was refluxed for 24 h, during which time the opaque orange solution turned to a clear pale yellow color and a cream-colored precipitate formed. The precipitate was collected by filtration and washed with Et_2O to give **1** (1.1 g, 95% yield) as a white solid, mp 266−276 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.88−6.69 (m, 30H), 3.70 (s, 6H), 2.86 (m, 4H), 2.52 (s, 6H), 2.33 (m, 2H), 1.59 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 172.4, 167.7, 149.7 (br s), 137.8 (br s), 136.3 (d, J = 56.4 Hz), 134.0 (br s), 132.3 (d, J = 8.1), 132.2 (t, J = 4.9), 129.8 (br s), 129.4 (br s), 128.8 (br s), 128.5 (d, J = 10.2), 127.9 (t, J = 4.9), 127.4 (t, J = 4.6), 51.5, 50.2, 39.7 (m), 38.2 (br s), 35.3 (m), 31.0 (m). Anal. Calcd for $C_{53}H_{51}O_8P_3IrCl$: C, 56.01; H, 4.52. Found: C, 55.89; H, 4.60.

[{$CH_3C(CH_2PPh_2)_3$}Ir(CR=CRCR=CR)(NCMe)]BF_4 (3, R = CO_2CH_3). A 50 mL round-bottom flask was charged with **1** (125 mg, 0.11 mmol), $AgBF_4$ (23 mg, 0.12 mmol), and CH_3CN (25 mL). After stirring the solution at room temperature (3 h), the volatiles were removed in vacuo and CH_2Cl_2 (20 mL) was added to the residue to give a slurry. The mixture was filtered through Celite and concentrated to ca. 5 mL. Addition of Et_2O gave a precipitate, which was washed with Et_2O and dried in vacuo to give **3** (113.9 mg, 88% yield) as a pinkish white solid, mp 191 °C dec. IR (KBr): 1731 (vs), 1696 (vs), 1434 (vs), 1212 (vs), 1061 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.00 (m, 4H), 7.59 (t, J = 8.5 Hz, 4H), 7.49 (m, 6H), 7.36−7.29 (m, 6H), 7.16 (m, 2H), 6.83 (t, J = 7.2 Hz, 4H), 6.23 (dd, J = 11.0, 8.0 Hz, 4H), 3.76 (s, 6H), 3.08−3.02 (m, 4H), 2.67 (s, 6H), 2.09 (m, 2H), 2.06 (s, 3H), 1.71 (d, J = 2.5 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz): δ 173.0, 166.5 (d, J = 3.0 Hz), 149.6 (m), 149.0 (m), 148.3 (m), 133.9 (d, J = 59.5 Hz), 133.2 (br s), 132.8 (t, J = 5.0 Hz), 132.0 (d, J = 8.4 Hz), 131.9 (d, J = 51.2 Hz), 131.1 (d, J = 9.2 Hz), 130.1, 129.5 (d, J = 10.7 Hz), 128.8 (br s), 128.5 (t, J = 4.97 Hz), 127.6 (d, J = 48.9 Hz), 52.0, 51.0, 38.6 (br s), 38.4 (q, J = 11.5 Hz), 34.9 (m), 27.7 (br d, J = 45.9 Hz), 3.7. Anal. Calcd for $C_{55}H_{54}O_8P_3NIrBF_4$: C, 53.75; H, 4.43. Found: C, 53.92; H, 4.71.

[{$CH_3C(CH_2PPh_2)_3$}Ir{$C_6R_4(OCH_2CH_3)$}H]BF_4 (6-OEt, R = CO_2CH_3). A 25 mL round-bottom flask was charged with **1** (300 mg, 0.26 mmol), $AgBF_4$ (56 mg, 0.29 mmol), and $CHCl_3$ (15 mL). After 15 min at room temperature, ethyl ethynyl ether (127 mL, 1.30 mmol) was added via syringe and the solution was stirred for 11 h. The solvent was removed in vacuo, and $CHCl_3$ (40 mL) was added to give a slurry, which was filtered through Celite. The solution was concentrated to ca. 5 mL, and addition of Et_2O (30 mL) led to precipitation of a pale yellow solid. The powder was collected by filtration and washed with Et_2O to give **6**-OEt (270 mg, 82% yield) as a yellow powder. An analytically pure sample was obtained by chromatography (2000μ silica gel plate, 20% acetone/CH_2Cl_2; R_f = 0.6), mp 180 °C dec. IR (KBr): 1734 (s), 1600 (s), 1436 (s), 1383 (s), 1228 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.76 (ddd, J = 24.9, 11.1, 8.4 Hz, 4H), 7.43−7.05 (m, 20 H), 6.92 (t, J = 9.0 Hz, 2H), 6.66 (m, 4H), 3.89 (s, 3H), 3.86 (s, 3H), 3.82 (q, J = 6.9 Hz, 2H), 3.69 (s, 3H), 3.42 (s, 3H), 3.27−2.33 (m, 6H), 1.79 (s, 3H), 0.31 (t, J = 6.9 Hz, 3H), −8.57 (ddd, J = 139.7, 12.6, 10.2 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz): δ 167.5, 166.8, 165.5, 162.7, 134.1 (m), 133.9 (m), 133.4 (m), 133.1 (m), 132.9 (d, J = 9.6 Hz), 132.4 (d, J = 7.8 Hz), 132.2 (d, J = 10.9 Hz), 132.0 (d, J = 9.7 Hz), 131.6, 131.5, 131.3 (br s), 131.2, 131.0 (m), 130.9 (m), 130.7 (br s), 130.6 (m), 130.4 (br s), 130.2, 128.7 (d, J = 10.1 Hz), 128.5 (d, J = 10.9 Hz), 128.1 (d, J = 11.4 Hz), 127.5 (d, J = 11.4 Hz), 125.8, 68.9, 56.4, 53.0, 52.7, 52.5, 40.5, 38.6 (dd, J = 71.2, 10.5 Hz), 38.6 (m), 31.6 (d, J = 26.1 Hz), 27.2 (d, J = 29.3 Hz), 13.8. Anal. Calcd for $[C_{57}H_{57}O_9P_3Ir]BF_4$: C, 54.42; H, 4.57. Found: C, 54.35; H, 4.60.

[{$CH_3C(CH_2PPh_2)_3$}Ir(C_6R_4H)H]BF_4 (6-H, R = CO_2CH_3). A 50 mL round-bottom flask was charged with **1** (530 mg, 0.47 mmol), $AgBF_4$ (100 mg, 0.51 mmol), and CH_2Cl_2 (20 mL). After 20 min at room temperature the slurry was blanketed under an atmosphere of ethyne and stirred an additional 6 h. The solvent was removed in vacuo and $CHCl_3$ (30 mL) added to the residue. Filtration through Celite, concentration of the filtrate to ca. 10 mL, and addition of Et_2O (30 mL) gave a precipitate, which was collected by filtration and washed with Et_2O to give **6**-H (490 mg, 88% yield) as a white powder, mp 170 °C dec. IR (KBr): 1735 (s), 1602 (s), 1436 (vs), 1389 (s), 1278 (vs), 1235 (s), 1095 (vs), 1060 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.49 (m, 8H), 7.26−7.96 (m, 19 H), 6.59 (m, 4H), 3.94 (s, 3H), 3.80 (s, 3H), 3.77 (s, 3H), 3.66 (s, 3H), 2.93 (m, 4H), 2.47 (dm, J = 15.6 Hz, 2H), 1.88 (br s, 3 H), −7.93 (dt, J = 134.4, 11.5 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 183.5 (d, J = 6.1 Hz), 169.2 (dt, J = 83.16, 5.34 Hz), 167.4, 166.0, 137.9, 136.5 (d, J = 2.3 Hz), 134.8 (d, J = 4.7 Hz), 133.4 (dd, J = 42.7, 4.6 Hz), 132.3 (d, J = 9.2 Hz), 132.2 (d, J = 9.9 Hz), 132.0 (d, J = 43.5 Hz), 132.0 (d, J = 9.9 Hz), 131.7 (d, J = 36.6 Hz), 131.2 (br s), 131.0 (d, J = 9.9 Hz), 130.9 (br s), 130.8 (d, J = 10.6 Hz), 130.8 (br s), 130.5 (d, J = 1.5 Hz), 130.4 (br s), 130.0 (br s), 129.2 (d, J = 9.9 Hz), 128.8 (d, J = 9.9 Hz), 128.6 (J = 9.9 Hz), 128.2 (d, J = 11.4 Hz), 128.5−127.8 (m, 9 peaks), 124.1, 56.8, 52.9 (t, J = 3.1 Hz), 52.8, 52.5, 40.3 (t, J = 4.2 Hz), 38.3 (q, J = 10.7 Hz), 31.8 (dd, J = 38.9, 9.9 Hz), 30.9 (dd, J = 27.1, 7.3 Hz), 28.0 (dd, J = 29.4, 4.2 Hz). Anal. Calcd for $[C_{55}H_{53}O_8P_3Ir]BF_4$: C, 54.42; H, 4.40. Found: C, 54.02, H, 4.35. LRMS (FAB) m/z calcd for $C_{55}H_{53}O_8P_3Ir$ 1127; found 1127.

[{$CH_3C(PPh_2CH_2)_3$}Ir{$C_6R_4(CH_2OCH_3)$}H]BF_4 (6-CH_2O-Me, R = CO_2CH_3). A 100 mL round-bottom flask was charged with **3** (305 mg, 0.24 mmol) and CH_2Cl_2 (50 mL). Methyl propargyl ether (0.21 mL, 2.4 mmol) was added via syringe and the solution stirred at room temperature for 18 h. The red solution was then filtered through Celite, concentrated in vacuo, and chromatographed (silica gel, 5% MeOH/$CHCl_3$) to give 189.3 mg of a red powder. Recrystallization (THF/Et_2O) in the drybox gave **6**-CH_2OMe (50 mg, 16% yield) as tan solid, mp 196−198 °C. IR (KBr): 1737 (s), 1597 (s), 1440 (s), 1230 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80 (dd, J = 10.8, 7.6 Hz, 2H), 7.60 (dd, J = 11.2, 8.0 Hz, 2H), 7.48−7.40 (m, 3H), 7.29−7.18 (m, 9H), 7.12−7.01 (m, 6H), 6.88−6.80 (m, 6H), 6.39 (dd, J = 12.4, 8.4 Hz, 2H), 3.99 (d, J = 10.8 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.72 (s, 3H), 3.21 (s, 3H), 3.18−3.14 (m, 1H), 2.96, (d, J = 10.4 Hz, 1H), 2.92 (m, 1H), 2.86−2.68 (m, 3H), 2.65 (s, 3H), 2.24 (dd, J = 16, 8.8 Hz, 1H), 1.87 (d, J = 2.8 Hz, 3H), −8.69 (ddd, J = 140.0, 13.6, 9.6 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 183.41 (d, J = 7.3 Hz), 174.86, (d, J = 76.9 Hz), 167.59, 167.07, 165.59, 146.16, 137.65 (d, J = 5.9 Hz), 135.53, 133.07 (d, J = 4.6 Hz), 132.93 (d, J = 5 Hz), 132.66 (d, J = 4.1 Hz), 132.48, 132.39, 132.06 (d, J = 9.1 Hz), 131.80 (d, J = 9.1 Hz), 131.62 (m), 131.34 (d, J = 2.7 Hz), 131.15, 131.04 (m), 130.72 (d, J = 2.7 Hz), 130.45, 130.15 (m), 129.89 (d, J = 13.7 Hz), 129.87 (d, J = 2.3 Hz), 129.64, 129.59, 129.43, 129.42 (d, J = 9.6 Hz), 128.95 (d, J = 9.1 Hz), 128.73, 128.62 (d, J = 1 Hz), 128.50, 128.42 (d, J = 10.5 Hz), 127.71 (m), 127.10 (m), 124.97, 77.66, 57.89, 56.50, 53.07, 52.77, 52.33, 40.25 (d, J = 3.6 Hz), 38.18 (m), 37.61 (m), 30.81 (d, J = 27.8 Hz), 26.85 (d, J = 29.6 Hz). Anal. Calcd for $C_{57}H_{57}O_9P_3IrBF_4$: C, 54.42; H, 4.57. Found: C, 53.94; H, 4.36. HRMS (FAB) m/z calcd for $C_{57}H_{57}O_9P_3Ir$ (M^+) 1169.2794; found 1169.2822.

[{$CH_3C(PPh_2CH_2)_3$}Ir{5,6,7-tri(carbomethoxy)phthalidyl}H]BF_4 (7-H, R = CO_2CH_3). A 100 mL round-bottom flask was charged with **1** (250 mg, 0.22 mmol), $AgBF_4$ (47 mg, 0.24 mmol), and $CHCl_3$ (30 mL). After 15 min at room temperature, propargyl alcohol (64 μL, 1.09 mmol) was added via syringe and the reaction stirred for an additional 40 h. The solvent was removed and the residue dried in vacuo for 2 h. $CHCl_3$

(20 mL) was added to the residue and the mixture filtered through Celite. The filtrate was concentrated to ca. 5 mL, and addition of Et_2O (30 mL) led to formation of a pale yellow precipitate. The precipitate was isolated by filtration, washed with Et_2O, and dried in vacuo to give **7**-H (210 mg, 79% yield), mp 219−221 °C. IR (KBr): 1777 (vs), 1736 (vs), 1611 (vs), 1436 (s), 1383 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.63−7.50 (m, 4H), 7.40 (t, J = 6.6 Hz, 2H), 7.26−7.10 (m, 18 H), 7.05−7.00 (m, 2H), 6.89−6.84 (m, 2H), 6.60 (dd, J = 11.6, 8.3, 2H), 4.23 (d, J = 16.2, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 3.44 (dd, J = 16.1, 10.1, 1H), 3.34 (d, J = 16.2, 1H), 3.24 (s, 3H), 3.14−2.78 (m, 4H), 2.39 (m, 1H), 1.96 (d, J = 2.1, 3H), −8.42 (ddd, J = 133.6, 13.1, 10.2, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 168.0, 166.7, 165.4, 158.2, 135.9, 134.7, 133.6 (d, J = 9.2 Hz), 133.3 (d, J = 5.4 Hz), 132.7 (d, J = 6.2 Hz), 132.6 (d, J = 3.8 Hz), 132.2 (d, J = 9.2 Hz), 131.9 (d, J = 11.4 Hz), 131.8 (d, J = 9.9 Hz), 131.8 (d, J = 9.2 Hz), 131.7 (d, J = 9.2 Hz), 131.6 (br s), 131.5 (br s), 131.2 (d, J = 2.3 Hz), 130.8 (d, J = 2.4 Hz), 130.2 (d, J = 3.1 Hz), 130.2 (br s), 129.6 (d, J = 9.9 Hz), 129.3 (d, J = 52.5 Hz), 129.3 (d, J = 52.5 Hz), 129.2 (d, J = 48.1 Hz), 129.1 (d, J = 9.9 Hz), 128.9 (d, J = 11.4 Hz), 128.6 (d, J = 11.3 Hz), 128.6 (d, J = 10.7 Hz) 128.5 (d, J = 58.8 Hz), 128.3 (d, J = 35.8 Hz), 73.0, 56.6, 53.3, 53.1, 41.3 (br s), 38.4 (m), 31.8 (d, J = 27.5 Hz), 30.8 (m), 27.2 (d, J = 25.3 Hz). HRMS (FAB) m/z calcd for $C_{55}H_{51}O_8P_3Ir$ (M^+) 1125.2426; found 1125.2404.

[{$CH_3C(PPh_2CH_2)_3$}Ir{5,6,7-tri(carbomethoxy)-2-methyl-phthalidyl}H]BF_4 (7-Me). A 100 mL round-bottom flask was charged with **3** (305.3 mg, 0.25 mmol) and CH_2Cl_2 (50 mL). 3-Butyn-2-ol (0.193 mL, 2.4 mmol) was added via syringe and the solution stirred for 24 h. The yellow solution was filtered through Celite, the volatiles were evaporated, and the residue was chromatographed (silica gel, 15% $MeCN/CH_2Cl_2$) to give **7**-Me (122 mg, 40% yield) as a yellow powder. Recrystallization (THF/MeOH/Et_2O) gave 74.2 mg of analytically pure yellow crystals, mp 186−188 °C dec. IR (KBr): 1763 (s), 1607 (s), 1433 (s), 1384 (s), 1260 (s), cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.83 (t, J = 10 Hz, 2H), 7.62 (dd, J = 11, 8 Hz, 2H), 7.58−7.52 (m, 3H), 7.45−7.42 (m, 2H), 7.37−7.34 (m, 3H), 7.29−7.26 (m, 2H), 7.23−7.13 (m, 5H), 7.06−6.96 (m, 5H), 6.87 (t, J = 7.5 Hz, 2H), 6.47 (t, J = 9 Hz, 2H), 5.93 (dd, J = 10.5, 8 Hz, 2H), 3.96 (s, 3H), 3.74 (s, 3H), 3.30 (s, 3H), 3.26−3.19 (m, 3H), 3.04−3.00 (m, 1H), 2.92 (dd, J = 16, 3.5 Hz, 1H), 2.46 (dd, J = 16, 8.5 Hz, 1H), 2.33 (dd, J = 16.5, 4.5 Hz, 1H), 1.95 (d, J = 1.5 Hz, 3H), 1.15, (d, J = 6 Hz, 3H), −8.64 (ddd, J = 140, 15, 8.7 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 183.63, (d, J = 7.8 Hz), 167.35, 166.30, 165.32, 161.36 (d, J = 1.3 Hz), 135.38 (d, J = 1.8 Hz), 135.29 (d, J = 2.5 Hz), 132.84 (t, J = 9.1 Hz), 132.51−132.20 (m), 132.06, 131.90 (d, J = 9.1 Hz), 131.80 (d, J = 1.8 Hz), 130.66−130.57 (m), 130.28, 129.98 (d, J = 1.8 Hz), 129.87 (d, J = 9.7 Hz), 128.84, 128.64 (d, J = 10.3 Hz), 127.04, 126.71, 126.42, 125.19 (m), 124.70 (m), 123.66, (d, J = 3.6 Hz), 57.35, 53.27, 52.90, 39.51, (d, J = 3.3 Hz), 38.01−37.91 (m), 36.43 (d, J = 13 Hz), 36.16 (d, J = 3 Hz), 30.15 (m), 26.47 (m), 21.05. Anal. Calcd for $C_{56}H_{53}O_8P_3IrBF_4$: C, 54.86; H, 4.36. Found: C, 54.56; H, 4.26.

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE-9975939) and the donors of the Petroleum Research Fund administered by the American Chemical Society, for financial support of this work. We thank Dr. Richard Kondrat (Mass Spectrometry Facility, University of California, Riverside) for determining the mass spectra.

Supporting Information Available: Tables of crystallographic data for **6**-OEt and **9**. These materials are available free of charge via the Internet at http://pubs.acs.org.

OM0102450