Regio- and Stereoselective C−C Bond Formation between Alkynes: Synthesis of Linear Dienynes from Alkynes

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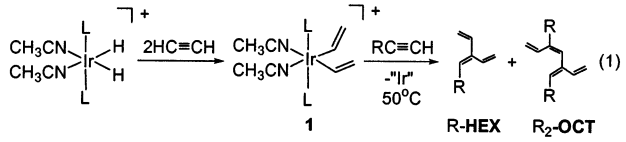
Reactions of the iridacyclopentadienes $[Ir(-CH=CHCH=CH)(NCCH_3)(CO)(PPh_3)_2]^+$ (**2a**) and $[Ir(-CH=C(CH_2)_4C=CH)(NCCH_3)(CO)(PPh_3)_2]^+$ (**2b**) with RC≡CH (R = C_6H_5, *p*-$C_6H_4CH_3$) give linear conjugated dienynes (RC≡CCH=CHCH=CH_2 (**3**) and RC≡CCH=$C(CH_2)_4C$=CH_2 (**5**)) and benzene derivatives (RC_6H_5 (**4**) and $RC_6H_3C_6H_8$ (**6**, 6-aryl-1,2,3,4-tetrahydronaphthalene)). Linear conjugated dienynes **3** and **5** are exclusively obtained from the reactions of alkynyl iridacyclopentadienes $[Ir(-CH=CHCH=CH)(C\equiv CR)(CO)(PPh_3)_2]$ (**7**) and $[Ir(-CH=C(CH_2)_4C=CH)(C\equiv CR)(CO)(PPh_3)_2]$ (**8**) (R = C_6H_5 (**a**), *p*-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**)) with HOTf, respectively. The di- and trinuclear alkynyl iridacyclopentadienes *p*-$C_6H_4(C\equiv CIr(-CH=CHCH=CH)L_3)_2$ (**9a**), *p*-$C_6H_4(C\equiv CIrCH=C(CH_2)_4C=CH)L_3)_2$ (**9b**), and *m,m*-$C_6H_3(C\equiv CIr(-CH=CHCH=CH)L_3)_3$ (**10**) (L_3 = $(CO)(PPh_3)_2$) react with HOTf to produce the extended and conjugated dienynes *p*-$C_6H_4(C\equiv CCH=CHCH=CH_2)_2$ (**11**), *p*-$C_6H_4(C\equiv CCH=C(CH_2)_4C=CH_2)_2$ (**12**), and *m,m*-$C_6H_3(C\equiv CCH=CHCH=CH_2)_3$ (**13**), respectively, in high yields. Iridacyclohexadienes $[Ir(-CH=CHCH=CHC(=CH\text{-}p\text{-}C_6H_4R')(CO)(PPh_3)_2]BF_4$ (**17**, R′ = H (**a**), CH_3 (**b**)) are obtained from the reactions of **7** with HBF_4 through a C−C bond-forming reaction between the α-carbons of alkynyl and 1,3-butadiene-1,4-diyl ligands. Plausible reaction pathways are suggested for the C−C bond-forming reaction between RC≡CH and 1,3-butadiene-1,4-diyl ligands of iridacyclopentadienes to produce linear dienynes.

Introduction

Transition-metal-mediated C−C bond formation between alkynes has been extensively investigated as an efficient method for the synthesis of highly conjugated organic compounds,[1] which have attracted great interest because of their utility in organic synthesis and unique physical properties.[2]

During the investigation on iridium-mediated C−C bond formation involving alkynes,[3] we observed cross-conjugated hexatrienes (RCH=C(CH=$CH_2)_2$, R-**HEX**) and octatetraenes (H_2C=CHCR=CHC(−CH=CH_2)=CHR, R_2-**OCT**) produced from reactions of HC≡CH and RC≡CH (R = C_6H_5, *p*-$C_6H_4CH_3$, cyclohex-1-enyl, $C(CH_3)$=CH_2, $C(CH_3)_3$) in the presence of the *cis*-dihydridoiridium(III) complex $[Ir(H)_2(NCCH_3)_2(PPh_3)_2]^+$, which proceeds via the bis(alkenyl) complex **1** as depicted in eq 1.[4]



R = C_6H_5 (**a**), *p*-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**), $C(CH_3)$=CH_2 (**d**), $C(CH_3)_3$ (**e**)

This prompted us to look into the reactions of RC≡CH with other types of bis(alkenyl) complexes,

(1) (a) Burrows, A. D.; Green, M.; Jeffery, J. C.; Lynam, J. M.; Mahon, M. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3043. (b) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035. (c) Haskel, A.; Wang, J. Q.; Straub, T.; Neyroud, T. G.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 3025. (d) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525. (e) Guérin, F.; McConville, D. H.; Vittal, J. J.; Yap, G. A. P. *Organometallics* **1998**, *17*, 1290. (f) Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 4290. (g) Werner, H.; Schäfer, M.; Wolf, J.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 191. (h) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098. (i) Klein, H.-F.; Mager, M. *Organometallics* **1992**, *11*, 3174.

(2) (a) Mawatari, Y.; Tabata, M.; Sone, T.; Ito, K.; Sadahiro, Y. *Macromolecules* **2001**, *34*, 3776. (b) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998. (c) Schulz, M.; Tretiak, S.; Chernyak, V.; Mukamel, S. *J. Am. Chem. Soc.* **2000**, *122*, 452. (d) Zhao, Y.; Tykwinski, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 458. (e) Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167.

(3) (a) Chin, C. S.; Won, G.; Chong, D.; Kim, M.; Lee, H. *Acc. Chem. Res.* **2002**, *35*, 218. (b) Chin, C. S.; Kim, M.; Lee, H. *Organometallics* **2002**, *21*, 1679. (c) Chin, C. S.; Cho, H.; Won, G.; Oh, M.; Ok, K. M. *Organometallics* **1999**, *18*, 4810. (d) Chin, C. S.; Maeng, W.; Chong, D.; Won, G.; Lee, B.; Park, Y. J.; Shin, J. M. *Organometallics* **1999**, *18*, 2210.

(4) Chin, C. S.; Lee, H.; Park, H.; Kim, M. *Organometallics* **2002**, *21*, 3889.

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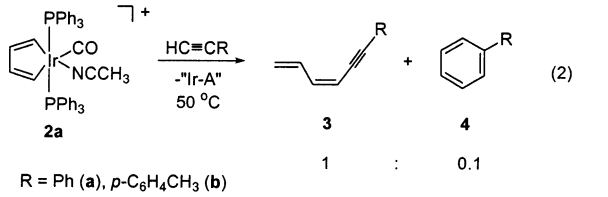
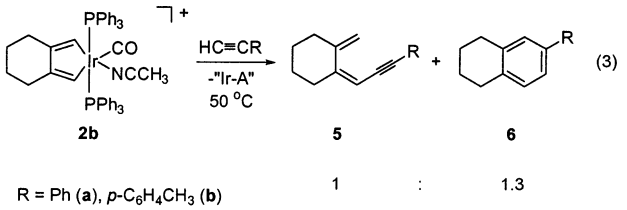
iridacyclopentadienes prepared by reactions of $[Ir(NCCH_3)(CO)(PPh_3)_2]^+$ with HC≡CH and HC≡C$(CH_2)_4$C≡CH.[5] We now wish to report the formation of linear dienynes that are regio- and stereoselectively produced from the reactions of iridacyclopentadienes with terminal alkynes and suggest plausible reaction mechanisms.

Results and Discussion

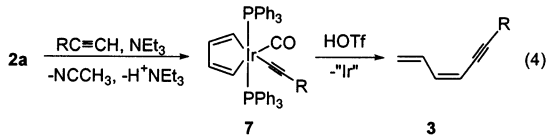
Iridacyclopentadienes **2**[5] react with RC≡CH to give linear conjugated dienynes (**3** and **5**) and cyclization products (**4** and **6**) at 50 °C (eqs 2 and 3).



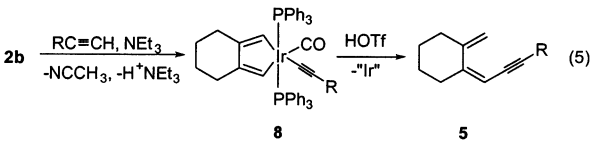


Z dimers (RC≡CCH=CHR) of RC≡CH are exclusively and catalytically obtained after the production of **3** and **4** in the presence of excess RC≡CH. Complexes **2a** and **2b** are recovered in high yields from the reactions of "Ir−A" with HC≡CH and HC≡C$(CH_2)_4$C≡CH, respectively.

Linear dienynes **3** and **5** are exclusively obtained from the reactions of HOTf with alkynyl iridacyclopentadienes **7** and **8**, which are prepared in high yields from the reactions of **2a** and **2b**, respectively[6] (eqs 4 and 5).



R = Ph (**a**), *p*-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**)



R = Ph (**a**), *p*-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**)

To the best of our knowledge, no example has been reported thus far for reactions of alkynes with metallacyclopentadienes to give linear dienynes, while metallacyclopentadienes are well-known to serve as intermediates for cyclotrimerization of alkynes to give benzene[7] and fulvene[8] derivatives.

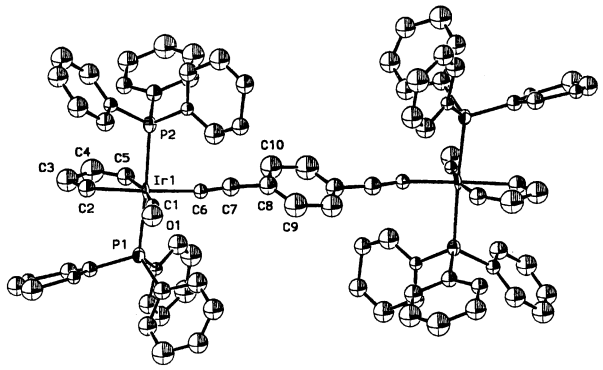
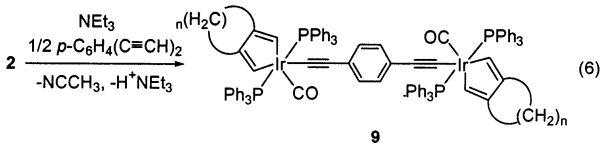
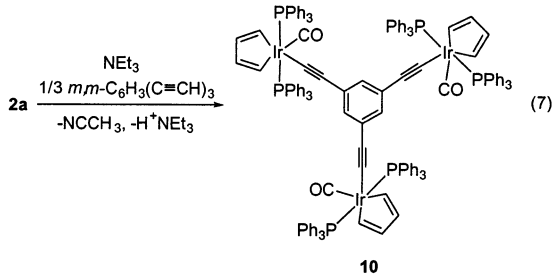


Figure 1. ORTEP drawing of *p*-C_6H_4(C≡CIr(−CH=CHCH=CH)L_3)$_2$ (**9a**, L_3 = $(CO)(PPh_3)_2$). Selected bond lengths (Å): Ir1−C1, 1.868(27); Ir1−C2, 2.131(42); Ir1−C5, 1.976(52); Ir1−C6, 2.056(37). Selected bond angles (deg): C2−Ir1−C1, 89.4(16); C5−Ir1−C1, 166.3(18); C5−Ir1−C2, 77.1(18); C6−Ir1−C1, 98.7(15); C6−Ir1−C2, 171.8(16); C6−Ir1−C5, 94.8(18).

To see further C−C coupling between alkynyl and 1,3-butadiene-1,4-diyl groups to produce highly extended and conjugated dienynes, di- and trinuclear alkynyl iridacyclopentadienes **9** and **10** have been prepared in the same manner used to prepare **7** and **8** (eqs 6 and 7).





These iridium(III) complexes **9** and **10** have been unequivocally identified by detailed spectral data (^{1}H, ^{13}C, ^{31}P NMR and ^{1}H,^{13}C-2D HETCOR) and FAB-mass measurements and also by the crystal structure of **9a** (see Figure 1, Experimental Section, and Supporting Information).

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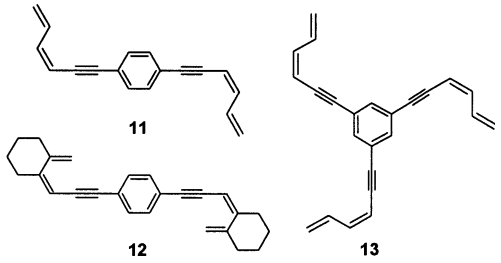
(6) Chin, C. S.; Lee, H.; Oh, M. *Organometallics* **1997**, *16*, 816. Compounds **8** were also prepared in the same manner as described for **7** in this reference. See the Experimental Section for a detailed characterization of **8**.

(7) (a) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 6055. (b) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093. (c) O'Connor, J. M.; Closson, A.; Hiibner, K.; Merwin, R.; Gantzel, P. *Organometallics* **2001**, *20*, 3710. (d) Baxter, R. J.; Knox, G. R.; Pauson, P. L.; Spicer, M. D. *Organometallics* **1999**, *18*, 197. (e) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.

(8) (a) Johnson, E. S.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 11086. (b) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P. K.; Fong, B. S. *J. Am. Chem. Soc.* **1997**, *119*, 3631. (c) Kim, H.-J.; Choi, N.-S.; Lee, S. W. *J. Organomet. Chem.* **2000**, *616*, 67. (d) Radhakrishnan, U.; Gevorgyan, V.; Yamamoto, Y. *Tetahedron Lett.* **2000**, *41*, 1971. (e) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025.

Oligomeric organometallic compounds with conjugated bridges have been extensively studied with respect to their chemical and physical properties.[9] Those α,ω-diyl groups (−C≡C-*p*-C_6H_4C≡C− and −C≡C-*m*,*m*-$C_6H_3(C{\equiv}C)_2$−) are frequently introduced as bridging ligands to connect two and three metal units.[9f,10] Reactions of these metal complexes, on the other hand, have been rarely reported, except that the C−C coupling between a 1,3-butadiyne-1,4-diyl bridging ligand and RHC═C═ units of RHC═C═RhC≡CC≡CRh═C═CHR gives the novel dinuclear compounds [L_3RhC(═CHR)C≡CC≡CC(═CHR)RhL_3] (R = H, Ph, L_3 = (CO)(P_iPr$_3$)$_2$).[11]

Highly extended and conjugated dienynes **11**−**13** are obtained in high yields from reactions of **9** and **10** with HOTf.

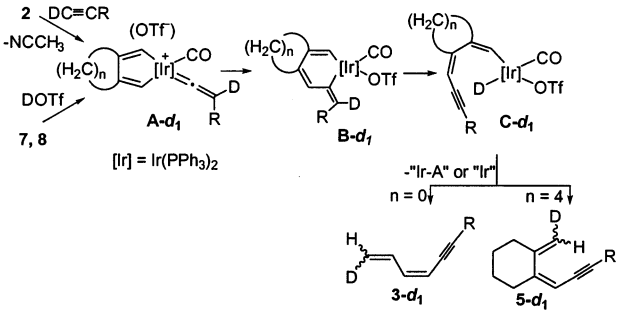


Dienynes **11**−**13** have been unequivocally identified by detailed data (^{1}H and ^{13}C NMR, ^{1}H decoupling, NOE spectral data, GC/MS and FD/MS measurements; see Experimental Section and Supporting Information).

Reactions of **2** with DC≡CR and of **7** and **8** with DOTf give the same products **3-*d*** (for **2a** and **7**) and **5-*d*** (for **2b** and **8**), respectively, containing one deuterium bound to the terminal olefinic carbon. These results led us to suggest the mechanism containing vinylidene intermediate **A**, as shown in Scheme 1.

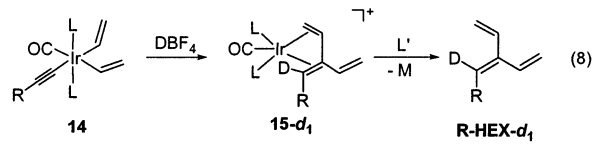
Metal−vinylidenes (M═C═CHR) are frequently observed and suggested in the reactions of metal alkynyls with H^+ and of metal compounds with terminal alkynes (RC≡CH).[12,13] The α-carbon (M═*C*═CHR) of the vinylidene group is known to be so electrophilic that it

Scheme 1



readily interacts with a neighboring hydrocarbyl ligand to form a new C−C bond.[13] The vinylidene intermediate **A** then undergoes the C−C bond-forming reaction between the vinylidene and the 1,3-butadiene-1,4-diyl groups to give the iridacyclohexadienes **B**. The hydrogen of the vinyl moiety of **B** (i.e., the deuterium of **B-*d***) seems close enough to the metal to interact with the metal to undergo β-H elimination[14] and thus give complex **C**. Finally, the intermediate **C** undergoes a reductive elimination to produce dienynes **3**.

We recently observed that H^+ exclusively attacks the β-carbon of the alkynyl ligand rather than an α-carbon of neighboring alkenyl ligands of the alkynyl bis(alkenyl) complexes **14** (eq 8).[4] Iridacyclopentadienes **2**



L = PPh_3
L' = Cl^-, CH_3CN, PPh_3
M = $[IrL'(CO)L_2]^{0,+}$
R = Ph (**a**), *p*-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**)

do not react with HOTf, while other metallacyclopentadienes (M = Ti, Pd, Zr) are known to react with electrophiles to give conjugated dienes.[7b,15] Reactions of **7** with HOTf in the presence of CH_3CN, however, give RC≡CH and **2a**. It is therefore not likely that H^+ attacks the α-carbon of the 1,3-butadiene-1,4-diyl group or the iridium metal center of **7**. The deuterium found at the terminal olefinic carbon of **3-*d*** may, therefore, be understood by the deuterium transfer through the

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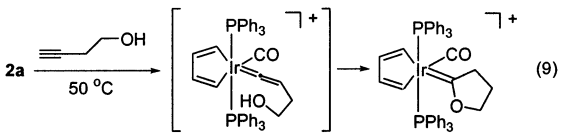
β-deuterium abstraction (**B-*d*** → **C-*d***) followed by the reductive elimination of **3-*d***, as shown in Scheme 1.

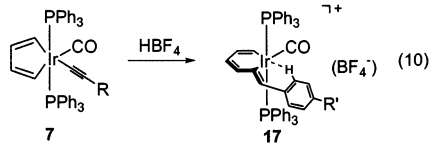
While attempts to isolate the vinylidene complexes **A** have been unsuccessful, the related carbene complex $[Ir(-CH{=}CHCH{=}CH)(=COCH_2CH_2CH_2)(CO)(PPh_3)_2]^+$ (**16**) could have been obtained from the reaction of 3-butyn-1-ol with **2a** presumably via the intramolecular trapping of a vinylidene group with the pendant hydroxyl group (eq 9), as shown in the previously reported $[Ir(CR{=}CRCR{=}CR)(=COCH_2CH_2CH_2)(CO)(PPh_3)_2]^+$ (R = CO_2CH_3) by O'Connor et al.[16]



(9)

16

Formation of the iridacyclohexadiene intermediate **B** from the C−C bond-forming reaction between α-carbons of alkynyl and 1,3-butadiene-1,4-diyl ligands is supported by the presence of the iridacyclohexadienes **17**, isolated from reactions of **7** with the acid (HBF_4) with noncoordinating base (BF_4^-) (eq 10).



(10)

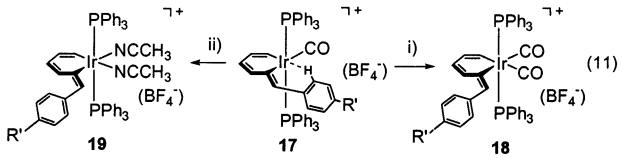
7 **17**

R = Ph (**a**), *p*-$C_6H_4CH_3$ (**b**) R' = H (**a**), CH_3 (**b**)

These 16-electron complexes **17** have been well characterized by detailed spectral (^1H, ^{13}C, ^{31}P NMR, ^1H,^{13}C-2D HETCOR, and ^1H NOE) and elemental analysis data and by X-ray crystallography of **17b** (see Figure 2, Experimental Section, and Supporting Information).

The crystal structure of **17b** shows an α-hydrogen of the aryl group close enough to the metal to have an agostic interaction in the absence of a base such as OTf^-. Only a few examples of agostic interaction by the aryl hydrogen have been reported in phosphinoaryl complexes, whereas agostic alkyl complexes are numerous.[17]

It is somewhat surprising not to observe dienynes **3** from reactions of **17** with OTf^- or bases such as CH_3CN and CO. The cis aryl group of **17**, however, flips outward to be in a position trans to the iridium center (eq 11).



(11)

19 **17** **18**

i) CO
ii) Me_3NO, CH_3CN/-CO_2, -NMe_3
R' = H (**a**), CH_3 (**b**)

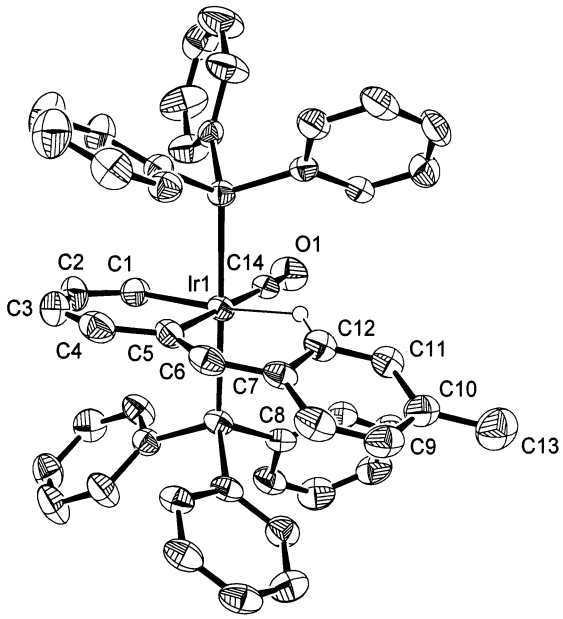
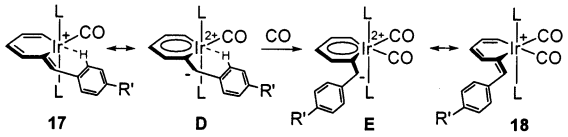


Figure 2. ORTEP drawing of $[Ir(-CH{=}CHCH{=}CHC(=CH\text{-}p\text{-}C_6H_4CH_3))(CO)(PPh_3)_2]^+$ (**17b**) with 50% probability thermal ellipsoids. Selected bond distances (Å): Ir1−C1, 2.030(6); Ir1−C5, 2.078(6); Ir1−C14, 1.933(7); Ir1−H12a, 1.945; C1−C2, 1.334(9); C2−C3, 1.422(10); C3−C4, 1.351(9); C4−C5, 1.422(9); C5−C6, 1.357(8); C6−C7, 1.437(9); C7−C12, 1.392(8); C12−H12a, 0.930; C14−O, 1.136(7). Selected bond angles (deg): C14−Ir1−C1, 89.3(3); C14−Ir1−C5, 179.6(2), C1−Ir1−C5, 90.5(3), Ir1−C14−O1, 177.8(6); C5−Ir1−H12a, 83.42; C14−Ir1−H12a, 96.33.

Scheme 2



17 **D** **E** **18**

L = PPh_3
R' = H (**a**), CH_3 (**b**)

^1H NMR spectra of **17** show an upfield signal at δ 4.74−4.78 due to the ortho protons (the agostic ones) of *p*-C_6H_4R', while the ortho protons of *p*-C_6H_4R' of **18** and **19** are seen in the phenyl region (δ 6.78−7.08).

These rearrangements (**19** ← **17** → **18**) may be understood by the resonance involving the iridabenzenes **D** and **E** (Scheme 2). The conversion **D** → **E** provides a vacant site for CO coordination to produce the 18-electron dicarbonyl complexes **18**. The related transformation of iridacyclohexadienes ($CPh{=}CPhCH{=}{}^{13}CH{}^{13}CH_2$)$IrL_4$ to ($CH_2CPh{=}CH{}^{13}CH{=}{}^{13}CPh$)$IrL_4$ (L_4 = $(PMe_3)_2$(acac)) via iridabenzene intermediates was previously reported by Hughes et al.[18]

(16) (a) O'Connor, J. M.; Hiibner, K.; Closson, A.; Gantzel, P. *Organometallics* **2001**, *20*, 1482. (b) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 7578.

(17) (a) Dani, P.; Toorneman, M. A. M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2000**, *19*, 5287. (b) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Y. *Organometallics* **2000**, *19*, 1734. (c) Matsubara, T.; Koga, N.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 12692. (d) Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539. (e) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317. (f) King, W. A.; Luo, X.-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782. (g) Cooper, A. C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 9069.

It seems that the agostic hydrogen of **17** is so strongly bound to the metal that the interaction is not broken by a base such as OTf^-, while both CH_3CN and CO coordinate to the metal to give the stable 18-electron complexes **18** and **19** to inhibit the β-hydrogen elimination of vinyl hydrogen to give linear dienynes.

In conclusion, iridacyclopentadienes can be utilized to prepare linear conjugated dienynes by C−C bond formation between 1,3-butadiene-1,4-diyl ligands and alkynes and reactions of this type can be further applied to reactions with diynes and triynes to prepare highly extended and conjugated organic compounds.

Experimental Section

General Information. A standard vacuum system and Schlenk type glassware were used in most of the experiments in handling metal complexes, although most of the compounds are stable enough to be handled in air.

PhC≡CD, HOTf, and DOTf were purchased from Aldrich, and 1,4-diethynylbenzene (p-$C_6H_4(C{\equiv}CH)_2$),[19] 1,3,5-triethynylbenzene (m,m-$C_6H_3(C{\equiv}CH)_3$),[10a] [Ir(−CH=CHCH=CH)(NCCH$_3$)(CO)(PPh$_3$)$_2$]OTf (**2a**),[5] [Ir(−CH=C(CH$_2$)$_4$C=CH)(NCCH$_3$)(CO)(PPh$_3$)$_2$]OTf (**2b**),[5] and Ir(−CH=CHCH=CH)(C≡CR)(CO)(PPh$_3$)$_2$ (**7**, R = C_6H_5 (**a**), p-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**))[6] were prepared by the literature methods.

Instruments. NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer for ^{1}H, a 75 or 126 MHz instrument for ^{13}C, and an 81 MHz spectrometer for ^{31}P. Infrared spectra were obtained on a Nicolet 205. Electronic absorption spectra were measured with a Hewlett-Packard HP8453 diode array spectrophotometer. Elemental analyses were carried out with a Carlo Erba EA1108 instrument. Gas chromatography/mass spectra were measured with a Hewlett-Packard HP 5890A VG-trio 2000 at the Organic Chemistry Center, Sogang University. FD mass measurements were carried out with a Micro Mass Co. Autospec-Q at the SK research center. FAB mass measurements were carried out with a JMS-HX110/110A tandem mass spectrometer at the Korea Basic Science Institute.

Synthesis. Preparation of Ir(−CH=C(CH$_2$)$_4$C=CH)(C≡CR)(CO)(PPh$_3$)$_2$ (8, R = Ph (a), p-$C_6H_4CH_3$ (b), Cyclohex-1-enyl (c)). These compounds were prepared in a manner similar to the literature method for **7**.[5] The yield of **8a** was 0.086 g (94%) based on Ir(−CH=C(CH$_2$)$_4$C=CH)(C≡CPh)(CO)(PPh$_3$)$_2$ (**8a**).

Ir(−CH=C(CH$_2$)$_4$C=CH)(C≡CPh)(CO)(PPh$_3$)$_2$ (8a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.7 (m, P(C_6H_5)$_3$, 30H), 7.04, 6.98, and 6.66 (m, IrC≡CC$_6$*H*$_5$, 5H), 6.51 and 6.45 (both br s, IrC*H*=C(CH$_2$)$_4$C=C*H*, 2H), 1.70, 1.23, 0.79, and 0.68 (m, IrCH=C(C*H*$_2$)$_4$C=CH, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3 (t, Ir*C*O, J(C−P) = 7.5 Hz), 153.1 (t, J(C−P) = 4.4 Hz) and 148.5 (s) (IrCH=*C*(CH$_2$)$_4$C=CH), 141.0 (t, J(C−P) = 7.4 Hz, IrCH=C(CH$_2$)$_4$C=*C*H), 129.7 (s, C_{ipso} of IrC≡C*C*$_6$H$_5$), 130.7, 127.4, and 124.0 (s, CH carbons of IrC≡C*C*$_6$H$_5$), 112.6 (s, IrC≡*C*Ph), 90.1 (t, J(C−P) = 14.6 Hz, Ir*C*≡CPh), 33.2, 31.9, 24.6, and 24.3 (s, IrCH=C(*C*H$_2$)$_4$C=CH), 134.7, 131.7, 129.6, and 127.1 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 7.04 → 127.4; 6.98 → 124.0; 6.66 → 130.7; 6.51, 6.45 → 140.1; 1.70 → 33.2; 1.23 → 31.9; 0.79 → 24.6; 0.68 → 24.3. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 0.07 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2112 (m, $\nu_{C\equiv C}$), 1992 (s, $\nu_{C\equiv O}$). Anal. Calcd for $IrP_2OC_{53}H_{45}$: C, 66.86; H, 4.76. Found: C, 66.89; H, 4.82.

Ir(−CH=C(CH$_2$)$_4$C=CH)(C≡C-p-C$_6$H$_4$CH$_3$)(CO)(PPh$_3$)$_2$ (8b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.7 (m, P(C_6H_5)$_3$, 30H), 6.58−6.87 (AB quartet with $\Delta\nu/J$ = 17.5, IrC≡C-p-C_6H_4CH$_3$, 4H), 6.52 and 6.50 (both br s, IrC*H*=C(CH$_2$)$_4$C=C*H*, 2H), 2.26 (s, IrC≡C-p-C$_6$H$_4$C*H*$_3$, 3H) 1.71, 1.24, 0.80, and 0.69 (m, IrCH=C(C*H*$_2$)$_4$C=CH, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3 (t, Ir*C*O, J(C−P) = 7.9 Hz), 153.1 (t, J(C−P) = 4.3 Hz) and 148.4 (s) (IrCH=*C*(CH$_2$)$_4$*C*=CH), 141.1 (t, J(C−P) = 6.7 Hz, Ir*C*H=C(CH$_2$)$_4$C=*C*H), 134.6 and 133.6 (both s, C_{ipso} of IrC≡C-p-*C*$_6$H$_4$CH$_3$), 130.6 and 128.1 (both s, CH carbons of IrC≡C-p-*C*$_6$H$_4$CH$_3$), 112.6 (s, IrC≡*C*-p-C$_6$H$_4$-CH$_3$), 88.1 (t, J(C−P) = 14.7 Hz, Ir*C*≡C-p-C$_6$H$_4$CH$_3$), 33.2, 31.9, 24.6, and 24.3 (s, IrCH=C(*C*H$_2$)$_4$C=CH), 21.2 (s, IrC≡C-p-C$_6$H$_4$*C*H$_3$), 134.7, 131.8, 129.6, and 127.0 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 6.86 → 128.1; 6.58 → 130.6; 6.52, 6.50 → 141.1; 2.26 → 21.2; 1.71 → 33.2; 1.24 → 31.9; 0.80 → 24.6; 0.69 → 24.3. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −0.07 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2112 (m, $\nu_{C\equiv C}$), 1991 (s, $\nu_{C\equiv O}$). Anal. Calcd for $IrP_2OC_{54}H_{47}$: C, 67.13; H, 4.90. Found: C, 67.15; H, 4.95.

Ir(−CH=C(CH$_2$)$_4$C=CH)(cyclohex-1-enyl)(CO)(PPh$_3$)$_2$ (8c). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.7 (m, P(C_6H_5)$_3$, 30H), 6.46 and 6.43 (both br s, IrC*H*=C(CH$_2$)$_4$C=C*H*, 2H), 5.14 (s, IrC≡CC=C*H*(CH$_2$)$_3$CH$_2$), 1.94, 1.63, and 1.44 (m, IrC≡CC=CH(C*H*$_2$)$_3$C*H*$_2$, 8H), 1.70, 1.17, 0.78, and 0.66 (m, IrCH=C(C*H*$_2$)$_4$C=CH, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.5 (t, Ir*C*O, J(C−P) = 7.3 Hz), 153.0 (br s) and 148.2 (s) (IrCH=*C*(CH$_2$)$_4$*C*=CH), 141.5 (t, J(C−P) = 7.5 Hz, Ir*C*H=C(CH$_2$)$_4$C=*C*H), 130.0 (s, IrC≡C*C*=CH(CH$_2$)$_3$CH$_2$), 125.8 (s, IrC≡CC=*C*H(CH$_2$)$_3$CH$_2$), 114.7 (s, IrC≡*C*C=CH(CH$_2$)$_3$CH$_2$), 83.0 (t, J(C−P) = 12.5 Hz, Ir*C*≡CC=CH(CH$_2$)$_3$CH$_2$), 33.2, 31.9, 24.6, and 24.3 (s, IrCH=C(*C*H$_2$)$_4$C=CH), 30.3, 25.4, 22.8, and 22.1 (s, IrC≡CC=CH(*C*H$_2$)$_3$*C*H$_2$), 134.8, 131.9, 129.5, and 127.0 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 6.46, 6.43 → 141.5; 5.14 → 125.8; 1.94 → 25.4; 1.70 → 33.2; 1.63 → 30.3; 1.44 → 22.8, 22.1; 1.17 → 31.9; 0.78 → 24.6; 0.66 → 24.3. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −0.50 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2094 (m, $\nu_{C\equiv C}$), 1997 (s, $\nu_{C\equiv O}$). Anal. Calcd for $IrP_2OC_{53}H_{49}$: C, 66.58; H, 5.17. Found: C, 66.50; H, 5.19.

Preparation of the Dinuclear Alkynyl Iridacyclopentadienes p-C$_6$H$_4$(C≡CIr(−CH=CHCH=CH)L$_3$)$_2$ (9a) and p-C$_6$H$_4$(C≡CIr(−CH=C(CH$_2$)$_4$C=CH)L$_3$)$_2$ (9b) (L$_3$ = (CO)(PPh$_3$)$_2$). Compounds **9a** and **9b** were prepared in the same manner as described below for **9a**. The reaction mixture of **2a** (0.20 g, 0.2 mmol) and p-$C_6H_4(C{\equiv}CH)_2$ (0.013 g, 0.1 mmol) in $CHCl_3$ (15 mL) was stirred in the presence of NEt_3 (0.04 mL, 0.3 mmol) at 25 °C for 12 h under nitrogen before the precipitation of beige microcrystals of **9a**, which were collected by filtration, washed with MeOH (3 × 10 mL), and dried under

(18) (a) Hughes, R. P.; Trujillo, H. A.; Egan, J. W., Jr.,; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 2261. (b) Hughes, R. P.; Trujillo, H. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 1583.

(19) Jung, J. K.; Kim, D. K.; Cho, D. H.; Yoon, B. I.; Kim, K. S. *Polymer (Korea)* **1993**, *17*, 67.

vacuum. The yield was 0.16 g (92%) based on *p*-C_6H_4(C≡CIr(−CH=CHCH=CH)L_3)$_2$ (**9a**, L = (CO)(PPh_3)$_2$).

***p*-C_6H_4(C≡CIr(−CH=CHCH=CH)L_3)$_2$ (9a, L = (CO)(PPh_3)$_2$).** ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.2−8.0 (m, P(C_6H_5)$_3$, 60H), 6.98 and 6.85 (both m, IrC*H*=CHCH=C*H*, 4H), 6.46 (s, IrC≡CC_6H_4, 4H), 6.18 and 5.71 (both m, IrCH=C*H*C*H*=CH, 4H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 174.2 (t, J(C−P) = 7.4 Hz, Ir*C*O), 149.8 (t, J(C−P) = 7.4 Hz) and 147.4 (t, J(C−P) = 12.6 Hz) (IrCH=CHCH=*C*H), 144.0 and 140.1 (both s, IrCH=*C*HCH=CH), 129.9 (s, CH carbons of IrC≡C*C*$_6$H$_4$), 127.4 (s, C_{ipso} of IrC≡C*C*$_6$H$_4$), 113.9 (s, IrC≡*C*$_6$H$_4$), 87.6 (t, J(C−P) = 10.2 Hz, Ir*C*≡C$_6$H$_4$), 134.8, 131.7, 129.8, and 127.2 (P(C_6H_5)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 6.98 → 147.4; 6.85 → 149.8; 6.46 → 129.9; 6.18 → 144.0; 5.71 → 140.1. ^{31}P-{^{1}H} NMR (81 MHz, $CDCl_3$): δ −1.91 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2107 (m, $\nu_{C\equiv C}$), 1997 (s, $\nu_{C\equiv O}$). MS (FAB): *m*/*z* 1718 [M$^+$]. Anal. Calcd for $Ir_2P_4O_2C_{92}H_{72}$: C, 64.32; H, 4.22. Found: C, 63.75; H, 4.10.

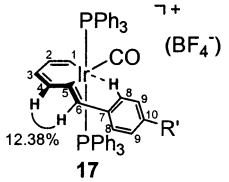
***p*-C_6H_4(C≡CIr(−CH=C(CH$_2$)$_4$C=CH)L_3)$_2$ (9b, L_3 = (CO)(PPh_3)$_2$).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.8 (P(C_6H_5)$_3$, 60H), 6.49 and 6.48 (both br s, IrC*H*=C(CH$_2$)$_4$C=C*H*, 4H), 6.39 (s, IrC≡CC_6H_4, 4H), 1.72, 1.22, 0.80, and 0.69 (IrCH=C(C*H*$_2$)$_4$C=CH, 16H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3 (t, Ir*C*O, J(C−P) = 7.0 Hz), 153.0 (br t, J(C−P) = 3.8 Hz) and 148.3 (s) (IrCH=*C*(CH$_2$)$_4$*C*=CH), 141.5 (br t, J(C−P) = 7.1 Hz, Ir*C*H=C(CH$_2$)$_4$C=*C*H), 129.8 (s, CH carbons of IrC≡C*C*$_6$H$_4$), 127.6 (s, C_{ipso} of IrC≡C*C*$_6$H$_4$) 113.4 (s, IrC≡*C*$_6$H$_4$), 88.6 (t, J(C−P) = 15.2 Hz, Ir*C*≡C$_6$H$_4$), 33.2, 31.9, 24.6, and 24.3 (s, IrCH=C(*C*H$_2$)$_4$C=CH), 134.7, 131.8, 129.5, and 127.0 (P(*C*$_6$H$_5$)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 6.49, 6.48 → 141.5; 6.39 → 129.8; 1.72 → 33.2; 1.22 → 31.9; 0.80 → 24.6; 0.69 → 24.3. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −0.21 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2106 (m, $\nu_{C\equiv C}$), 1995 (s, $\nu_{C\equiv O}$). MS (FAB): *m*/*z* 1626 [M$^+$]. Anal. Calcd for $Ir_2P_4O_2C_{100}H_{84}$: C, 65.77; H, 4.64. Found: C, 65.79; H, 4.68.

Preparation of the Trinuclear Alkynyl Iridacyclopentadiene *m*,*m*-C_6H_3(−C≡CIr(−CH=CHCH=CH)L_3)$_3$ (10, L_3 = (CO)(PPh_3)$_2$). This compound was prepared in the same manner as described above for **9a** by using *m*,*m*-C_6H_3(−C≡CH)$_3$. The yield was 0.11 g (95%) based on *m*,*m*-C_6H_3(−C≡CIr(CH=CHCH=CH)L_3)$_3$ (**10**, L_3 = (CO)(PPh_3)$_2$).

***m*,*m*-C_6H_3(C≡CIr(−CH=CHCH=CH)L_3)$_3$ (10, L_3 = (CO)(PPh_3)$_2$).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.2−8.0 (m, P(C_6H_5)$_3$, 90H), 7.06 and 6.74 (both m, IrC*H*=CHCH=C*H*, 6H), 6.52 (s, CH carbons of IrC≡CC_6H_3, 3H), 6.29 and 5.67 (both m, IrCH=C*H*C*H*=CH, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.1 (t, J(C−P) = 7.3 Hz, Ir*C*O), 150.6 (t, J(C−P) = 6.2 Hz) and 147.6 (t, J(C−P) = 12.2 Hz) (IrCH=CHCH=*C*H), 144.0 and 139.5 (both s, IrCH=*C*HCH=CH), 130.1 (s, CH carbons of IrC≡CC_6H_3) 128.0 (s, C_{ipso} of IrC≡CC_6H_3), 114.2 (s, IrC≡*C*$_6$H$_3$), 84.9 (t, J(C−P) = 14.6 Hz, Ir*C*≡C$_6$H$_3$), 134.8, 131.9, 129.8, and 127.2 (P(*C*$_6$H$_5$)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 7.06 → 147.6; 6.74 → 150.6; 6.52 → 130.1; 6.29 → 144.0; 5.67 → 84.9. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −2.75 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2103 (m, $\nu_{C\equiv C}$), 2000 (s, $\nu_{C\equiv O}$). MS (FAB): *m*/*z* 2538 [M$^+$]. Anal. Calcd for $Ir_3P_6O_3C_{135}H_{105}$: C, 63.89; H, 4.17. Found: C, 63.36; H, 3.90.

Preparation of [Ir(−CH=CHCH=CH)(=COCH$_2$-CH$_2$CH$_2$)(CO)(PPh_3)$_2$]OTf (16). A $CHCl_3$ (10 mL) solution of **2a** (0.10 g, 0.1 mmol) and HC≡CCH$_2$CH$_2$OH (0.01 mL, 0.14 mmol) was stirred at 50 °C for 1 h before *n*-pentane (20 mL) was added to precipitate beige microcrystals of **16**, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.10 g (97%) based on [Ir(−CH=CHCH=CH)(=COCH$_2$CH$_2$CH$_2$)(CO)(PPh_3)$_2$]OTf (**16**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.5 (m, P(C_6H_5)$_3$, 30H), 7.53 and 7.51 (both m, IrC*H*=CHCH=C*H*, 2H), 5.89 and 5.85 (both m, IrCH=C*H*C*H*=CH, 2H), 4.56 (t, J(H−H) = 8.0 Hz, Ir=COC*H*$_2$CH$_2$CH$_2$, 2H), 2.45 (t, J(H−H) = 8.0 Hz, Ir=COCH$_2$-CH$_2$C*H*$_2$, 2H), 1.10 (q, J(H−H) = 8.0 Hz, Ir=COCH$_2$C*H*$_2$CH$_2$, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 287.3 (t, J(C−P) = 6.5 Hz, Ir=*C*OCH$_2$CH$_2$CH$_2$), 172.6 (t, J(C−P) = 7.4 Hz, Ir*C*O), 153.2 (t, J(C−P) = 9.8 Hz) and 136.0 (t, J(C−P) = 9.8 Hz) (Ir*C*H=CHCH=CH), 148.7 and 148.1 (s, IrCH=*C*HCH=CH), 89.7 (s, Ir=CO*C*H$_2$CH$_2$CH$_2$), 55.8 (s, Ir=COCH$_2$CH$_2$*C*H$_2$), 19.6 (s, Ir=COCH$_2$*C*H$_2$CH$_2$), 134.3, 131.6, 128.2, and 128.0 (P(*C*$_6$H$_5$)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 7.53 → 153.2; 7.51 → 136.0; 5.89 → 148.1; 5.85 → 148.7; 4.56 → 89.7; 2.45 → 55.8; 1.10 → 19.6. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −1.15 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2032 (s, $\nu_{C\equiv O}$), 1265, 1151, and 1031 (s, due to uncoordinated OTf$^-$). Anal. Calcd for $IrP_2O_5SF_3C_{46}H_{40}$: C, 54.38; H, 3.97. Found: C, 54.40; H, 3.99.

Preparation of [Ir(CH=CHCH=CHC(=CH-*p*-C_6H_4R′))(CO)(PPh_3)$_2$]BF_4 (17, R′ = H (a), CH_3 (b)). These compounds were prepared in the same manner as described below for **17a**. A reaction mixture of **7a** (0.10 g, 0.1 mmol) and HBF_4 (0.016 mL, 54 wt % in Et_2O) in $CHCl_3$ (10 mL) was stirred for 1 h at 25 °C before Et_2O (30 mL) was added to precipitate reddish microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.102 g (93%) based on [Ir(CH=CHCH=CHC(=CHC$_6$H$_5$))(CO)(PPh_3)$_2$]BF_4 (**17a**).



17

NOE measurement for **17b**

[Ir(CH=CHCH=CHC(=CHC$_6$H$_5$))(CO)(PPh_3)$_2$]BF_4 (17a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.1−7.5 (m, P(C_6H_5)$_3$ and H_9, 32H), 6.92 (t, J(H−H) = 7.5 Hz, H_{10}), 6.82 (t, J(H−P) = 4 Hz, H_6), 6.64 (m, H_1), 5.88 (br d, J(H−H) = 10.0 Hz, H_4), 5.50 (br t, J(H−H) = 6.9 Hz, H_2), 5.20 (m, H_3), 4.74 (br m, H_8, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 176.6 (t, J(C−P) = 7.9 Hz, Ir*C*O), 165.0 (t, J(C−P) = 11.9 Hz, C_5), 149.0 and 127.2 (s, C_7 and C_9), 143.8 (t, J(C−P) = 7.3 Hz, C_6), 135.4 (s, C_4), 127.9 (t, J(C−P) = 9.8 Hz, C_1), 126.3 (br s, C_3), 122.0 (t, J(C−P) = 4.9 Hz, C_2), 119.8 (br s, C_8), 134.6, 131.8, 128.5, and 127.3 (P(*C*$_6$H$_5$)$_3$). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 2.41 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2052 (s, $\nu_{C\equiv O}$), 1064 (s, due to noncoordinated BF_4^-). Anal. Calcd for $IrP_2OBF_4C_{49}H_{40}$: C, 59.70; H, 4.09. Found: C, 59.36; H, 3.94.

[Ir(CH=CHCH=CHC(=CH-*p*-$C_6H_4CH_3$))(CO)(PPh_3)$_2$]-BF_4 (17b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.45 (m, P(C_6H_5)$_3$, 30H), 7.28 (br d, J(H−H) = 6.5 Hz, H_9, 2H), 6.78 (br t, J(H−P) = 3.8 Hz, H_6), 6.65 (m, H_1), 5.79 (br d, J(H−H) =

10.0 Hz, H_4), 5.55 (br t, J(H−H) = 6.5 Hz, H_2), 5.15 (m, H_3), 4.78 (br m, H_8, 2H), 2.25 (s, *p*-$C_6H_4CH_3$, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 176.5 (t, J(C−P) = 8.4 Hz, Ir*C*O), 163.7 (t, J(C−P) = 12.2 Hz, C_5), 147.2 and 137.7 (s, C_7 and C_{10}), 143.0 (t, J(C−P) = 7.6 Hz, C_6), 135.6 (s, C_9) 134.9 (s, C_4), 127.8 (t, J(C−P) = 9.4 Hz, C_1), 125.7 (br s, C_3), 122.1 (br s, C_2), 118.9 (br s, C_8), 20.6 (s, *p*-$C_6H_4CH_3$), 134.6, 131.7, 128.4, and 127.3 (P(C_6H_5)$_3$). HETCOR (^{1}H NMR (500 MHz) → ^{13}C NMR (126 MHz)): δ 7.28 → 135.6; 6.78 → 143.0; 6.65 → 127.7; 5.79 → 134.9; 5.55 → 122.1; 5.15 → 125.7; 4.78 → 118.9; 2.25 → 20.6. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 1.97 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2050 (s, $\nu_{C\equiv O}$), 1057 (s, due to noncoordinated BF_4^-). Anal. Calcd for $IrP_2OBF_4C_{50}H_{42}$: C, 60.06; H, 4.23. Found: C, 59.62; H, 4.04.

Preparation of [Ir(CH=CHCH=CHC(=CH-*p*-C_6H_4R'))(CO)$_2$(PPh$_3$)$_2$]BF$_4$ (18, R′ = H (a), CH$_3$ (b)). These compounds were prepared in the same manner as described below for **18a**. A 0.1 g (0.1 mmol) amount of **17a** in $CHCl_3$ (10 mL) was stirred under CO (1 atm) at 25 °C for 12 h before *n*-pentane (30 mL) was added to precipitate beige microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.10 g (97%) based on [Ir(CH=CHCH=CHC(=CHC_6H_5))(CO)$_2$(PPh$_3$)$_2$]BF$_4$ (**18a**).

[Ir(CH=CHCH=CHC(=CHC_6H_5))(CO)$_2$(PPh$_3$)$_2$]BF$_4$ (18a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.4−7.6 (m, P(C_6H_5)$_3$ and H_1, 31H), 7.23 (t, J(H−H) = 7.5 Hz, H_9, 2H), 7.20 (t, J(H−H) = 7.5 Hz, H_{10}), 6.90 (d, J(H−H) = 7.5 Hz, H_8, 2H), 6.40 (ddt, J(H−H) = 10 Hz, J(H−H) = 6.5 Hz, J(H−P) = 2.3 Hz, H_2), 6.24 (br s, H_6), 6.22 (d, J(H−H) = 11 Hz, H_4), 5.42 (dd, J(H−H) = 11 Hz, J(H−H) = 6.5 Hz, H_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.0 (t, J(C−P) = 6.9 Hz, Ir*C*O), 164.4 (t, J(C−P) = 6.3 Hz, Ir*C*O), 143.4 (t, J(C−P) = 7.5 Hz, C_6), 140.4 (s, C_7), 131.6 (br s, C_3), 130.9 (t, J(C−P) = 4.4 Hz, C_2), 129.0 (s, C_8), 128.1 (br s, C_4), 127.8 (s, C_9), 126.5 (s, C_{10}), 124.0 (t, J(C−P) = 10.7 Hz, C_5), 121.8 (t, J(C−P) = 11.3 Hz, C_1), 134.5, 132.0, 128.6, and 127.5 (P(C_6H_5)$_3$). HETCOR (^{1}H NMR (500 MHz) → ^{13}C NMR (126 MHz)): δ ca. 7.5 → 121.8; 6.39 → 130.9; 6.24 → 143.4; 6.22 → 128.1; 5.42 → 131.6. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −15.13 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2114, 2075 (s, $\nu_{C\equiv O}$), 1060 (s, due to noncoordinated BF_4^-). Anal. Calcd for $IrP_2O_2BF_4C_{50}H_{40}$: C, 59.23; H, 3.98. Found: C, 59.15; H, 3.91.

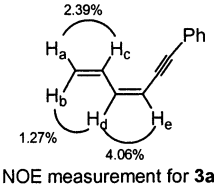
[Ir(CH=CHCH=CHC(=CH-*p*-$C_6H_4CH_3$))(CO)$_2$(PPh$_3$)$_2$]BF$_4$ (18b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.5 (m, P(C_6H_5)$_3$ and H_1, 31H), 6.8−7.1 (AB quartet with $\Delta\nu/J$ = 21.31, *p*-C_6H_4-CH_3, 4H), 6.40 (ddt, J(H−H) = 10 Hz, J(H−H) = 6.5 Hz, J(H−P) = 2.5 Hz, H_2), 6.22 (br s, H_6), 6.21 (d, J(H−H) = 10.5 Hz, H_4), 5.37 (dd, J(H−H) = 10.5 Hz, J(H−H) = 6.5 Hz, H_3), 2.34 (s, *p*-$C_6H_4CH_3$, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.1 (t, J(C−P) = 7.4 Hz, Ir*C*O), 164.5 (t, J(C−P) = 5.5 Hz, Ir*C*O), 143.5 (t, J(C−P) = 7.5 Hz, C_6), 137.5 and 136.4 (s, C_7 and C_{10}), 131.3 (br s, C_3), 131.0 (t, J(C−P) = 5.0 Hz, C_2), 128.9 and 128.5 (s, C_8 and C_9), 128.2 (br s, C_4), 124.5 (t, J(C−P) = 10.7 Hz, C_5), 121.3 (t, J(C−P) = 11.3 Hz, C_1), 21.1 (s, *p*-$C_6H_4CH_3$), 134.5, 132.0, 128.6, and 127.4 (P(C_6H_5)$_3$). HETCOR (^{1}H NMR (500 MHz) → ^{13}C NMR (126 MHz)): δ ca. 7.4 → 121.3; 6.37 → 131.0; 6.22 → 143.5; 6.21 → 128.2; 5.37 → 131.3; 2.34 → 21.1. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −15.16 (s, Ir*P*Ph$_3$). IR (KBr, cm^{-1}): 2116, 2080 (s, $\nu_{C\equiv O}$), 1057 (s, due to noncoordinated BF_4^-). Anal. Calcd for $IrP_2O_2BF_4C_{54}H_{42}$: C, 60.96; H, 3.98. Found: C, 60.73; H, 3.87.

Preparation of [Ir(CH=CHCH=CHC(=CH-*p*-C_6H_4R'))(NCCH$_3$)$_2$(PPh$_3$)$_2$]BF$_4$ (19, R′ = H (a), CH$_3$ (b)). These compounds were prepared by the same method as described below for **19a**. To a solution of **17a** (0.1 g, 0.1 mmol) and CH_3CN (0.010 g, 0.24 mmol) in $CHCl_3$ (10 mL) was added Me_3NO (0.019 g, 0.25 mmol), and the reaction mixture was stirred at 25 °C under N_2 for 30 min before the reddish solution turned light brown. Excess Me_3NO and NMe_3 were removed by extraction with H_2O (2 × 10 mL). Addition of *n*-pentane (20 mL) resulted in precipitation of beige microcrystals that were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.09 g (85%) based on [Ir(CH=CHCH=CHC(=CHC_6H_5)(NCCH$_3$)$_2$(PPh$_3$)$_2$]BF$_4$ (**19a**).

[Ir(CH=CHCH=CHC(=CHC_6H_5)(NCCH$_3$)$_2$(PPh$_3$)$_2$]BF$_4$ (19a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (br d, J(H−H) = 9.0 Hz, H_1), 7.3−7.5 (m, P(C_6H_5)$_3$, 30H), 7.22 (t, J(H−H) = 7.8 Hz, H_9, 2H), 7.05 (t, J(H−H) = 7.5 Hz, H_{10}), 6.85 (d, J(H−H) = 7.5 Hz, H_8, 2H), 6.29 (ddt, J(H−H) = 9.0 Hz, J(H−H) = 6.5 Hz, J(H−P) = 2.0 Hz, H_2), 5.98 (d, J(H−H) = 10.5 Hz, H_4), 5.66 (s, H_6), 5.38 (dd, J(H−H) = 10.5 Hz, J(H−H) = 6.5 Hz, H_3), 1.72 (br s, CH_3CN, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 133.7 (t, J(C−P) = 7.6 Hz, C_6), 131.0 (s, C_3), 130.0 (t, J(C−P) = 10.4 Hz, C_1), 128.0 (br s, C_2), 126.7 (br s, C_4), 123.3 (t, J(C−P) = 10.4 Hz, C_5), 120.5 and 120.0 (s, CH_3CN), 2.8 and 2.5 (s, CH_3CN), 134.9, 131.3, 130.2, and 127.7 (P(C_6H_5)$_3$). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −7.40 (s, Ir*P*Ph$_3$). ^{1}H NOE: irradiation of the signal at 6.01 ppm (H_4) shows a negative NOE effect on the signal at 5.68 ppm (H_6). Anal. Calcd for $IrP_2N_2BF_4C_{52}H_{46}$: C, 60.06; H, 4.46; N, 2.69. Found: C, 59.95; H, 4.38; N, 2.54.

[Ir(CH=CHCH=CHC(=CH-*p*-$C_6H_4CH_3$)(NCCH$_3$)$_2$(PPh$_3$)$_2$]BF$_4$ (19b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (br d, J(H−H) = 9.0 Hz, H_1), 7.3−7.6 (m, P(C_6H_5)$_3$, 30H), 6.77−7.06 (AB quartet with $\Delta\nu/J$ = 34.24, *p*-$C_6H_4CH_3$, 4H), 6.29 (ddt, J(H−H) = 9.0 Hz, J(H−H) = 6.5 Hz, J(H−P) = 2.0 Hz, H_2), 6.02 (d, J(H−H) = 10.5 Hz, H_4), 5.60 (br s, H_6), 5.36 (dd, J(H−H) = 10.5 Hz, J(H−H) = 6.5 Hz, H_3), 2.33 (s, *p*-$C_6H_4CH_3$, 3H), 1.77 and 1.72 (br s, CH_3CN, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 133.7 (t, J(C−P) = 7.0 Hz, C_6), 130.8 (s, C_3), 129.7 (t, J(C−P) = 10.1 Hz, C_1), 127.9 (t, J(C−P) = 5.5 Hz, C_2), 127.0 (br s, C_4), 122.0 (t, J(C−P) = 10.4 Hz, C_5), 120.4 and 119.7 (s, CH_3CN), 21.0 (s, *p*-$C_6H_4CH_3$), 3.1 and 2.7 (s, CH_3CN), 134.9, 130.9, 130.2, and 127.6 (P(C_6H_5)$_3$). HETCOR (^{1}H NMR (500 MHz) → ^{13}C NMR (126 MHz)): δ 8.18 → 129.7; 6.29 → 127.9; 6.02 → 127.0; 5.60 → 133.7; 5.36 → 130.8; 2.33 → 21.0; 1.77 and 1.72 → 3.1 and 2.7. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −7.49 (s, Ir*P*Ph$_3$). Anal. Calcd for $IrP_2N_2BF_4C_{53}H_{48}$: C, 60.40; H, 4.59; N, 2.66. Found: C, 60.48; H, 4.43; N, 2.59.

Reactions. Reactions of 7 and 8 with H(D)OTf: Formation of Dienynes RC≡CCH=CHCH=CH$_2$ (3) and RC≡CCH=C(CH$_2$)$_4$C=CH$_2$ (5, R = Ph (a), *p*-$C_6H_4CH_3$ (b), Cyclohex-1-enyl (c)). These reactions were carried out in the same manner as described below for **7a** with HOTf. Aqueous HOTf (0.32 mL, 0.90 mmol of H_2O containing 35 wt % HOTf) was added to a solution of **7** (0.3 g, 0.29 mmol) in $CHCl_3$ (15 mL) at 25 °C, and the reaction mixture was stirred for 5 h. Excess HOTf was removed by washing with H_2O. Addition of *n*-pentane (10 mL) to the $CHCl_3$ solution resulted in beige microcrystals of "Ir", which were removed by filtration. The filtrate was distilled at 25 °C under vacuum to less than 1.0 mL, and the residue was eluted with *n*-pentane on a column packed with silica gel to obtain cis-transoid CH_2=CHCH=CHC≡CPh (**3a**).



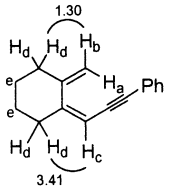
NOE measurement for **3a**

Cis-transoid CH$_2$=CHCH=CHC≡CPh (3a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.5 (m, C_6H_5, 5H), 7.04 (dt, J(H−H) = 17.0 Hz, J(H−H) = 11.0 Hz, H_c), 6.49 (t, J(H−H) = 11.0

Hz, H_d), 5.74 (d, J(H−H) = 11.0 Hz, H_e), 5.46 (d, J(H−H) = 17.0 Hz, H_b), 5.37 (d, J(H−H) = 11.0 Hz, H_a). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.3 (C_d), 134.1 (C_c), 120.4 (C_b), 109.9 (C_a), 123.3 and 119.8 (*C*≡*C*Ph), 131.5, 128.8, 128.3, and 128.2 (C_6H_5). HETCOR (^{1}H NMR (500 MHz) → ^{13}C NMR (126 MHz)): δ 7.04 → 134.1; 6.49 → 140.3; 5.74 → 109.9; 5.46 →120.4; 5.37 → 120.4. Electronic absorption: λ_{max} 300, 318 nm. MS: *m*/*z* 154 (M^+).

Cis-transoid CH$_2$=CHCH=CHC≡C-*p*-C$_6$H$_4$CH$_3$ (3b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4−7.5 (AB quartet with $\Delta\nu/J$ = 5.6, *p*-C_6H_4−CH_3, 4H), 7.04 (dt, J(H−H) = 16.1 Hz, J(H−H) = 10.5 Hz, H_c), 6.46 (t, J(H−H) = 10.5 Hz, H_d), 5.74 (d, J(H−H) = 10.5 Hz, H_e), 5.45 (d, J(H−H) = 16.1 Hz, H_b), 5.36 (d, J(H−H) = 10.5 Hz, H_a), 2.40 (s, CH_3). MS: *m*/*z* 168 (M^+).

Cis-transoid CH$_2$=CHCH=CHC≡CC(=CH(CH$_2$)$_3$CH$_2$) (3c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (dt, J(H−H) = 16.8 Hz, J(H−H) = 11.0 Hz, H_c), 6.38 (t, J(H−H) = 11.0 Hz, H_d), 6.17 (br s, C≡CC(=C*H*(CH$_2$)$_3$CH$_2$), 5.63 (d, J(H−H) = 11.0 Hz, H_e), 5.37 (d, J(H−H) = 17.0 Hz, H_b), 5.29 (d, J(H−H) = 11.0 Hz, H_a). MS: *m*/*z* 158 (M^+).



NOE measurement for **5a**

Cisoid CH$_2$=C(CH$_2$)$_4$C=CHC≡CPh (5a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.3−7.4 (m, C_6H_5, 5H), 5.53 (m, H_c), 5.42 (m, H_a), 5.14 (H_b), 2.32 (m, H_d, 4H), 1.69 (m, H_e, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.1 and 145.2 (both s, CH$_2$=*C*(CH$_2$)$_4$*C*=CHC≡CPh), 112.7 (C_a), 102.3 (C_c), 91.4 and 88.2 (*C*≡*C*), 36.8 and 36.0 (C_d), 26.93 and 26.90 (C_e). HETCOR (^{1}H NMR (500 MHz) → ^{13}C NMR (126 MHz)): δ 5.53 → 102.3; 5.42, 5.14 → 112.7; 2.32 → 36.8 and 36.0; 1.69 → 26.93 and 29.90. MS: *m*/*z* 208 (M^+).

Cisoid CH$_2$=C(CH$_2$)$_4$C=CHC≡C-*p*-C$_6$H$_4$CH$_3$ (5b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09−7.29 (AB quartet, *p*-$C_6H_4CH_3$, $\Delta\nu/J$ = 11.6, 4H), 5.52 (m, H_c), 5.42 (m, H_a), 5.14 (m, H_b), 2.34 (s, *p*-$C_6H_4CH_3$, 3H) 2.32 (m, H_d, 4H), 1.68 (m, H_e, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.5 and 145.2 (both s, CH$_2$=*C*(CH$_2$)$_4$*C*=CHC≡CPh), 112.7 (C_a), 102.4 (C_c), 91.6 and 87.6 (*C*≡*C*), 36.7 and 36.0 (C_d), 26.93 and 26.90 (C_e). MS: *m*/*z* 222 (M^+).

Cisoid CH$_2$=C(CH$_2$)$_4$C=CHC≡CC(=CH(CH$_2$)$_3$CH$_2$) (5c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03 (br s, C≡CC(=C*H*-(CH$_2$)$_3$CH$_2$), 5.41 (s, H_c), 5.32 (s, H_a), 5.07 (m, H_b). MS: *m*/*z* 212 (M^+).

Cis-transoid CHD=CHCH=CHC≡CPh (3a-*d*). The ^{1}H NMR spectrum of the isotopomer cis-transoid CHD=CHCH=CHC≡CPh shows a decreased intensity of the signals due to CH$_b$*D*=CHCH=CHC≡CPh and C*D*H$_a$=CHCH=CHC≡CPh at δ 5.46 and 5.37 (see Supporting Information). MS: *m*/*z* 155 (M^+).

Cisoid CHD=C(CH$_2$)$_4$C=CHC≡CPh (5a-*d*). The ^{1}H NMR spectrum of the isotopomer cis-transoid CHD=C(CH$_2$)$_4$CH=CHC≡CPh shows the decreased intensity of the signals due to CH$_b$D=C(CH$_2$)$_4$C=CHC≡CPh and CDH$_a$=C(CH$_2$)$_4$C=CHC≡CPh at δ 5.42 and 5.14 (see Supporting Information). MS: *m*/*z* 209 (M^+).

Reactions of Di- and Trinuclear Alkynyl Iridacyclopentadienes 9 and 10 with HOTf: Formation of Dienynes *p*-C$_6$H$_4$(C≡CCH=CHCH=CH$_2$)$_2$ (11), *p*-C$_6$H$_4$(C≡CCH=C(CH$_2$)$_4$C=CH$_2$)$_2$ (12), and *m*,*m*-C$_6$H$_3$(C≡CCH=CHCH=CH$_2$)$_3$ (13). These reactions were carried out in the same manner as described above for those of **3** with HOTf. The yields of yellow oils of **11**−**13** were ca. 85−93% based on **11**−**13** measured by ^{1}H NMR.

***p*-C$_6$H$_4$(C≡CCH=CHCH=CH$_2$)$_2$ (11).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (s, C_6H_4), 6.98 (dt, J(H−H) = 17.0, J(H−H) = 11.0 Hz, H_c), 6.47 (t, J(H−H) = 11.0 Hz, H_d), 5.70 (d, J(H−H) = 11.0 Hz, H_e), 5.44 (d, J(H−H) = 17.0 Hz, H_b), 5.35 (d, J(H−H) = 11.0 Hz, H_a). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.7 (C_d), 134.0 (C_c), 131.4 (C_a), 123.2 (C_6H_4), 120.8 (C_b), 109.6 (C_e), 95.4 and 88.4 (*C*≡*C*C_6H_4). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 7.41 → 131.4; 6.98 → 134.0; 6.47 → 140.7; 5.70 → 109.6; 5.44, 5.35 → 120.8. Electronic absorption: λ_{max} 242, 289, 340, 337 nm. MS: *m*/*z* 230 (M^+).

***p*-C$_6$H$_4$(C≡CCH=C(CH$_2$)$_4$C=CH$_2$)$_2$ (12).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (s, *p*-C_6H_4, 4H), 5.51 (br s, *p*-C_6H_4(C≡CC*H*=C(CH$_2$)$_4$C=CH$_2$)$_2$), 5.38 and 5.13 (both br s, *p*-C_6H_4-(−C≡CCH=C(CH$_2$)$_4$C=C*H*$_2$)$_2$, 4H), 2.31 and 1.68 (both m, *p*-C_6H_4(C≡CCH=C(C*H*$_2$)$_4$C=CH$_2$)$_2$, 16H). MS: *m*/*z* 338 (M^+).

***m*,*m*-C$_6$H$_3$(C≡CCH=CHCH=CH$_2$)$_3$ (13).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (s, C_6H_3), 6.97 (dt, J(H−H) = 17.0, J(H−H) = 11.0 Hz, H_c), 6.49 (t, J(H−H) = 11.0 Hz, H_d), 5.68 (d, J(H−H) = 11.0 Hz, H_e), 5.45 (d, J(H−H) = 17.0 Hz, H_b), 5.36 (d, J(H−H) = 11.0 Hz, H_a). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.1 (C_d), 134.0 (C_c), 133.7 (C_a), 124.1 (C_6H_4), 121.0 (C_b), 109.3 (C_e), 93.9 and 87.5 (*C*≡*C*). HETCOR (^{1}H (500 MHz) → ^{13}C (126 MHz)): δ 7.49 → 133.7; 6.97 → 134.0; 6.49 → 141.1; 5.68 → 109.3; 5.45, 5.36 → 121.0. Electronic absorption: λ_{max} = 305, 325 nm. MS (FD): *m*/*z* 306 (M^+).

Table 1. Details of Crystallographic Data Collection for 9a[a] and 17b[b]

	9a	17b
chem formula	$C_{92}H_{72}Ir_2O_2P_4$	$C_{50}H_{42}BF_4IrOP_2$
fw	1717.78	1637.89
temp, K	293(2)	293(2)
cryst dimens, mm	0.5 × 0.2 × 0.4	0.44 × 0.40 × 0.10
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
color of cryst	deep yellow	dark orange
a, Å	12.152(3)	17.698(2)
b, Å	18.888(3)	16.6739(19)
c, Å	18.289(3)	20.021(2)
α, deg.	90.00	90.00
β, deg.	106(2)	108.4(2)
γ, deg.	90.00	90.00
V, Å^3	4040.4(14)	5607.0(11)
Z	2	5
ρ_{calcd}, g cm^{-3}	1.412	2.425
μ, mm^{-1}	3.416	4.189
F(000)	1708	4020
radiation	Mo Kα	Mo Kα
wavelength, Å	0.7107	0.7107
$2\theta_{max}$, deg	40	50
hkl range	$0 \le h \le 11$	$-21 \le h \le 21$
	$0 \le k \le 18$	$-18 \le k \le 20$
	$-17 \le l \le 16$	$-24 \le l \le 24$
no. of rflns	3768	42 263
no. of unique data	3768	10 490
no. of obsd ($\|F_o\| > 2\sigma F_o$) data	2501	3849
no. of params	216	640
scan type	ω scan	ω scan
R1	0.111	0.0430
wR2	0.315	0.1052
GOF	1.223	0.947

[a] R1 = $[\sum|F_o| - |F_c|/|F_o|]$. wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w (F_o^2)^2]^{0.5}$; $w = 1/[\sigma^2F_o^2 + (0.1037P)^2 + 319.7255P]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] R1 = $[\sum|F_o| - |F_c|/|F_o|]$. wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w (F_o^2)^2]^{0.5}$; $w = 1/[\sigma^2F_o^2 + (0.0538P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Reactions of 2 with RC≡CH(D): Formation of Dienynes RC≡CCH═CHCH═CH_2 (3) and RC≡CCH═$C(CH_2)_4C$═CH_2 (5) and Cyclotrimers RC_6H_5 (4) and $RC_6H_3C_6H_8$ (6, 6-Aryl-1,2,3,4-tetrahydronaphthalene) (R = Ph, *p*-$C_6H_4CH_3$). These reactions were carried out in the same manner as described below for **2a** with PhC≡CH. A $CHCl_3$ (10 mL) solution of **2a** (0.30 g, 0.3 mmol) and PhC≡CH (0.1 mL, 0.9 mmol) was stirred at 50 °C for 18 h before pentane (20 mL) was added to precipitate beige microcrystals of "**Ir-A**", which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The ratio of PhC≡CCH═CHCH═CH_2 to $C_6H_5C_6H_5$ (biphenyl) was determined by GC.

Reaction of "Ir-A" with HC≡CH and HC≡$C(CH_2)_4C$≡CH. These reactions were carried out in the same manner as described below for the reaction of "**Ir-A**" with HC≡CH. The reaction mixture of "**Ir-A**" (0.1 g) and $NCCH_3$ (0.03 mL, 0.18 mmol) in $CHCl_3$ solution (10 mL) was stirred under HC≡CH (2 atm) for 24 h in a bomb reactor before *n*-pentane (20 mL) was added to precipitate beige microcrystals of **2a**, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.07 g (82%) based on [Ir(CH═CHCH═CH)(CO)($NCCH_3$)-(PPh_3)$_2$]OTf (**2a**).

X-ray Structure Determination of *p*-C_6H_4(C≡CIr(−CH═CHCH═CH)L_3)$_2$ (9a, L = (CO)(PPh_3)$_2$). Crystals of **9a** were grown by slow evaporation from CH_2Cl_2 solution. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation at 20 °C. All data were collected with the ω scan modes and corrected Lp effects and absorption. The structure of this compound was solved by Patterson's heavy-atom methods (SHELXS-97). In the least-squares refinement, six non-H atoms were refined anisotropically, all 92 C atoms were refined isotropically, and all hydrogen atoms were placed at their geometrically calculated positions with isotropic thermal parameters. Details of the crystallographic data collection are listed in Table 1. Bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters have been included in the Supporting Information.

X-ray Structure Determination of [Ir(−CH═CHCH═CHC(═CH-*p*-$C_6H_4CH_3$))(CO)(PPh_3)$_2$]BF_4 (17b). Crystals of **17b** were grown by slow evaporation from $CHCl_3$ solution. The crystal evaluation and data collection were performed on a Bruker CCD diffactometer with Mo Kα radiation. Preliminary orientation matrix and cell constants were determined from three series of ω scans at different starting angles. Each series consisted of 10 frames collected at intervals of 0.3° ω scans with an exposure time of 10 s per frame. The structure of this compound was solved by direct methods from the *E* map (SHELXS-97). Non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. Non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Details of the crystallographic data collection are listed in Table 1. Bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters have been included in the Supporting Information.

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Supporting Information Available: Tables of bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters for complexes **9a** and **17b** in CIF format and figures giving ^{1}H and ^{13}C NMR and HETCOR (^{1}H-^{13}C) spectra of complexes **8a**, **8b**, **9b**, **10, 17b**, **18b**, and **19b**, ^{1}H NOE spectra of **17b** and **19a**, FAB mass data of **9a** and **10**, ^{1}H NMR spectra and mass data of organic compounds **3a**, **5a**, **11**, and **13**, ^{1}H NOE of **3a** and **5a**, and ^{1}H NMR spectra of **3a-*d*** and **5a-*d***. This material is available free of charge via the Internet at http://pubs.acs.org.

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