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Synthesis of Cross-Conjugated Olefins from Alkynes: Regioselective C−C Bond Formation between Alkynes

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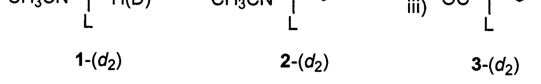
Reactions of *cis*-dihydrido complex $[Ir(H)_2(NCCH_3)_2(PPh_3)_2]^+$ (**1**) with $HC\equiv CH$ and $RC\equiv CH$ ($R = C_6H_5$, p-$C_6H_4CH_3$, cyclohex-1-enyl, $C(CH_3)=CH_2$, $C(CH_3)_3$) produce cross-conjugated hexatrienes ($RCH=C(CH=CH_2)_2$, R-**HEX**) and octatetraenes ($H_2C=CH-CR=CH-C(-CH=CH_2)=CHR$, R_2-**OCT**). Two molecules of $HC\equiv CH$ are inserted into Ir−H bonds of **1** to give *cis*-bis(ethenyl) complex $[Ir(CH=CH_2)_2(NCCH_3)_2(PPh_3)_2]^+$ (**2**), which reacts with $RC\equiv CD$ to produce both R-**HEX**-d_1 ($RCD=C(CH=CH_2)_2$) and R_2-**OCT**-d_2 ($H_2C=CH-CR=CD-C(-CH=CH_2)=CDR$). R-**HEX** are exclusively obtained from the reactions of $RC\equiv CH$ with $[Ir(CH=CH_2)_2(CO)_2(PPh_3)_2]^+$ (**3**). Alkynyl *cis*-bis(ethenyl) complexes $Ir(CH=CH_2)_2(C\equiv CR)(CO)(PPh_3)_2$ (**4**, $R = C_6H_5$ (**a**), p-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**)) react with D^+ to give η^4-R-**HEX**-d_1 complexes $[Ir(\eta^4\text{-}RC\boldsymbol{D}=C(CH=CH_2)_2)(CO)(PPh_3)_2]^+$ (**5**-d_1) from which R-**HEX**-d_1 are obtained in the presence of a base. Di- and trinuclear alkynyl−bis(alkenyl) complexes $[L_5Ir-C\equiv C$-p-C_6H_4-$C\equiv C-IrL_5]$ (**7**, $L_5 = (-CH=CH_2)_2(CO)(PPh_3)_2$) and $[L_5Ir-C\equiv C$-m,m-C_6H_3-$(C\equiv C-IrL_5)_2]$ (**8**, $L_5 = (-CH=CH_2)_2(CO)(PPh_3)_2$) react with H^+ to produce extended cross-conjugated olefins, p-C_6H_4-(**HEX**)$_2$ and m,m-C_6H_3-(**HEX**)$_3$, respectively, in high yields. Plausible reaction pathways involve alkenyl−vinylidene complexes that undergo the C−C bond formation reaction between the two hydrocarbyl ligands to produce the cross-conjugated olefins.

Introduction

Transition metal-mediated C−C bond formation between alkynes is probably the best way of synthesizing highly conjugated polyenes that are specially designed.[1] Those polyenes have attracted a great interest because of their utility toward organic synthesis and unique physical properties.[1−3] It is likely that metal−alkynyls, −alkenyls, and −vinylidenes are the intermediates that are formed during the oligomerization of alkynes to produce those polyenes.[1b−j] During the investigation on oligomerization between different alkynes, we observed cross-conjugated hexatrienes ($RCH=C(CH=CH_2)_2$, R-**HEX**) and octatetraenes ($H_2C=CH-CR=CH-C(-CH=CH_2)=CHR$, R_2-**OCT**) produced from reactions of $HC\equiv CH$ and $RC\equiv CH$ ($R = C_6H_5$, p-$C_6H_4CH_3$, cyclohex-1-enyl, $C(CH_3)=CH_2$, $C(CH_3)_3$) in the presence of *cis*-dihydrido−iridium(III) complex[4] $[Ir(H)_2(NCCH_3)_2(PPh_3)_2]^+$ (**1**). This prompted us to look into the details of the formation of those R-**HEX** and R_2-**OCT**, and the further utilization of these reactions. We now wish to report the derivatives of those R-**HEX** that are selectively and quantitatively produced from reactions of terminal alkynes with iridium complexes and suggest plausible mechanisms for the regioselective C−C bond formation between the alkenyl and alkynyl ligands to produce those R-**HEX** and R_2-**OCT**.

Results and Discussion

Two molecules of $HC\equiv CH$ are inserted into Ir−H(D) bonds of *cis*-dihydrido complex **1**-d_2 by a type of 1,2-addition to produce *cis*-bis(ethenyl) complex **2**-d_2 (eq 1) while unidentified iridium complexes are obtained from the reactions of **1** with $RC\equiv CH$.



1-(d_2) **2**-(d_2) **3**-(d_2)

$L = PPh_3$

i) $2HC\equiv CH$ ii) 2CO, $-2CH_3CN$

iii) $2CH_3CN, 2Me_3NO/ -2Me_3N, -2CO_2$

Both R-**HEX**-d_1 and R_2-**OCT**-d_2 are produced from the reactions of **2** with $RC\equiv CH(D)$ (eq 2, Table 1) while

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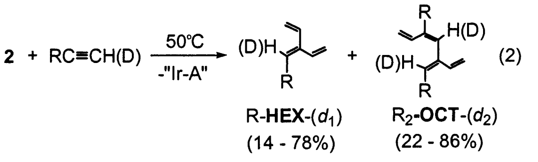
10.1021/om020410r CCC: $22.00

Table 1. Production of R-HEX ($RCH{=}C(CH{=}CH_2)_2$) and R_2-OCT ($H_2C{=}CH{-}CR{=}CH{-}C({-}CH{=}CH_2){=}CHR$) from Reactions of 2 ($[Ir(CH{=}CH_2)_2(NCCH_3)_2(PPh_3)_2]OTf$) and 3 ($[Ir(CH{=}CH_2)_2(CO)_2(PPh_3)_2]OTf$) with Alkynes ($HC{\equiv}CR$)

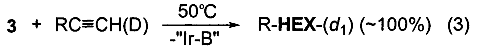
			product (%)[a]	
entry	Ir(III) complex	HC≡CR R	R-**HEX**	R_2-**OCT**
1	**2**	$C(CH_3){=}CH_2$	14	86
2	**2**	C_6H_5	59	41
3	**2**	p-$C_6H_4CH_3$	63	37
4	**2**	cyclohex-1-enyl	76	24
5	**2**	$C(CH_3)_3$	78	22
6	**3**	$C(CH_3){=}CH_2$	~100	
7	**3**	C_6H_5	~100	
8	**3**	p-$C_6H_4CH_3$	~100	
9	**3**	cyclohex-1-enyl	~100	
10	**3**	$C(CH_3)_3$	~100	

[a] Determined by GC of crude products.



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**)

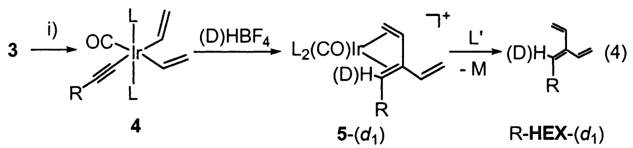
R-**HEX**-d_1 are exclusively obtained from the reactions of RC≡CH(D) with *cis*-dicarbonyl–*cis*-bis(ethenyl) complex **3** (eq 3, Table 1) that is prepared by the reaction of **2** with CO (eq 1). Relative yields of R-**HEX** to R_2-**OCT** vary with substituent R of RC≡CH (see Table 1). Different dimers (*cis*-PhCH=CH–C≡CPh (0.26 mmol), *trans*-PhCH=CH–C≡CPh (0.01 mmol), CH_2=CPh–C≡CPh (0.05 mmol)) of PhC≡CH are catalytically obtained after the production of Ph-**HEX** and Ph_2-**OCT** when an excess of PhC≡CH (3.0 mmol) is used in the reaction of **2** (0.1 mmol) at 50 °C for 48 h. Reaction of **3** (0.1 mmol) with excess PhC≡CH (3.0 mmol), however, produces *cis*-PhCH=CH–C≡CPh (0.5 mmol) exclusively and catalytically after the quantitative production of Ph-**HEX** under the same experimental conditions.



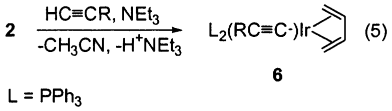
R = C_6H_5 (**a**), p-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**), $C(CH_3){=}CH_2$ (**d**), $C(CH_3)_3$ (**e**)

Isolated iridium complexes “Ir–A” in eq 2 and “Ir–B” in eq 3 have not been unequivocally identified while they seem to contain “$Ir(RC{\equiv}CH)_2(NCCH_3)_2(PPh_3)_2$” and “$Ir(RC{\equiv}CH)_2(CO)_2(PPh_3)_2$”, respectively, since reactions of “Ir–A” and “Ir–B” with H_2 give *cis*-dihydrido complexes **1** and $[Ir(H)_2(CO)_2(PPh_3)_2]^+$ (**1′**), respectively, in high yields and RCH=CH–CH=CHR.

During the investigation on the possible intermediates formed in the production of R-**HEX** and R_2-**OCT**, it has been found that reactions of **3** with RC≡CH in the presence of a base (Me_3NO) produce alkynyl–*cis*-bis(ethenyl) complexes **4** that readily react with H^+ to initiate the C–C bond formation between the two ethenyl and alkynyl groups to give η^4-R-**HEX** complexes **5** from which R-**HEX** are separated in the presence of a base (L′) (eq 4). No R_2-**OCT** has been observed at all in the reactions of **4** with H^+ even in the presence of excess RC≡CH. Alkynylation of **2**, unlike the reactions of **3** (eq 4), causes a C–C bond formation between the ethenyl groups to give η^4-butadiene complexes **6** exclusively (eq 5). Complexes **6** do not undergo further C–C bond formation between the alkynyl and butadiene groups even in the presence of H^+. η^4-Hexatriene (R-**HEX**) complexes have not been observed during the reactions of **2** or **3** with RC≡CH.

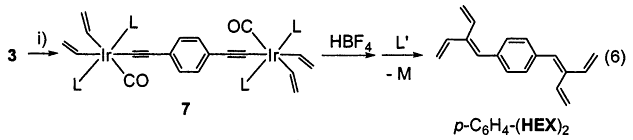


i) HC≡CR, Me_3NO/-CO_2, -H^+NMe_3
L = PPh_3, L′ = Cl^-, CH_3CN, PPh_3, M = $[IrL'(CO)L_2]^{0,+}$
R = C_6H_5 (**a**), p-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**)

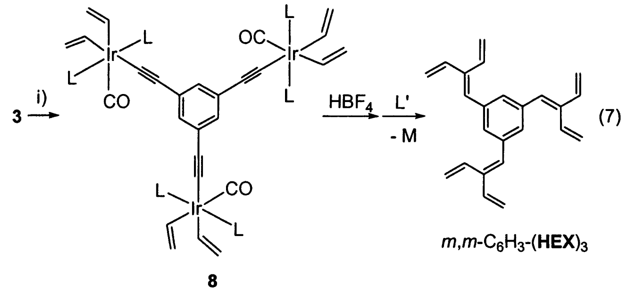


L = PPh_3
R = C_6H_5 (**a**), p-$C_6H_4CH_3$ (**b**)

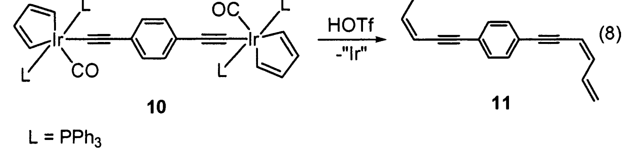
To see further C–C coupling between alkynyl and alkenyl groups to produce cross-conjugated olefins, di- and trinuclear alkynyl–bis(alkenyl) complexes **7** and **8** have been prepared in the same manner (see Experimental Section) and their reactions with H^+ have been found to produce extended cross-conjugated olefins, p-C_6H_4-$(\mathbf{HEX})_2$ and m,m-C_6H_3-$(\mathbf{HEX})_3$, respectively, in high yields (eqs 6 and 7). These results (eqs 6 and 7) are strikingly different from what we observed from reaction of similar binuclear alkynyl–bis(alkenyl) complex **10** with H^+ that gives the conjugated dienyne **11** (eq 8).[5]



i) p-$C_6H_4(C{\equiv}CH)_2$, Me_3NO/ -CO_2, -H^+NMe_3
L = PPh_3, L′ = Cl^-, CH_3CN, PPh_3, M = $[IrL'(CO)L_2]^{0,+}$



i) m,m-$C_6H_3(C{\equiv}CH)_3$, Me_3NO/ -CO_2, -H^+NMe_3
L = PPh_3, L′ = Cl^-, CH_3CN, PPh_3, M = $[IrL'(CO)L_2]^{0,+}$



L = PPh_3

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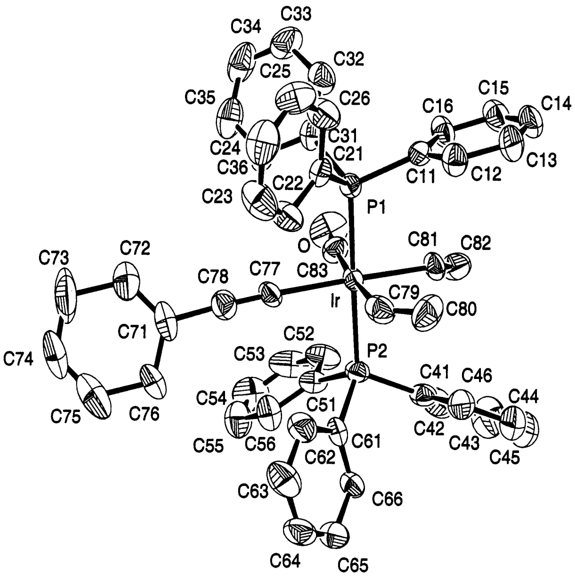
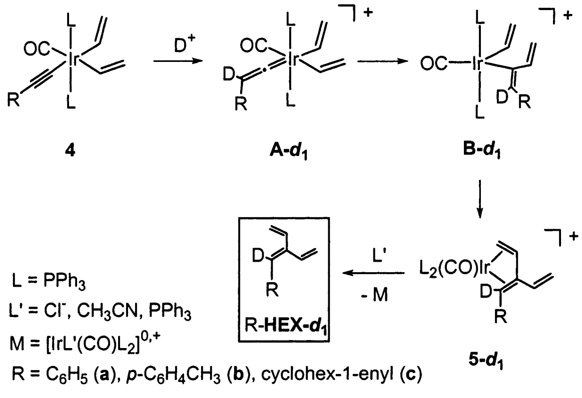


Figure 1. ORTEP drawing of $Ir(-CH{=}CH_2)_2(-C{\equiv}CC_6H_9)(CO)(PPh_3)_2$ (**4c**) with 50% thermal ellipsoids probability. Selected bond distances (Å): $Ir-C_{77} = 2.106(13)$; $Ir-C_{79} = 2.081(14)$; $Ir-C_{81} = 2.097(11)$; $Ir-C_{83} = 1.892(14)$; $C_{71}-C_{72} = 1.330(2)$; $C_{71}-C_{76} = 1.450(2)$; $C_{77}-C_{78} = 1.165(17)$; $C_{79}-C_{80} = 1.270(2)$; $C_{81}-C_{82} = 1.322(18)$; $C_{83}-O = 1.150(15)$. Selected bond angles (deg): $Ir-C_{77}-C_{78} = 176.6(11)$; $Ir-C_{79}-C_{80} = 138.4(12)$; $Ir-C_{81}-C_{82} = 129.9(11)$; $Ir-C_{83}-O = 173.6(12)$.

New iridium complexes (**2**−**8**) have been unambiguously characterized by detailed spectral and elemental analysis data, crystal structure determination by X-ray diffraction data analysis for **4c** (Figure 1), and FAB mass measurements for **7** and **8** (see Experimental Section and Supporting Information). The characterization is straightforward as similar compounds have been recently prepared in this laboratory.[6] Di- and trinuclear complexes with bridging benzene 1,4-diethynyl, p-C_6H_4-$(-C{\equiv}C-)_2$, and 1,3,5-triethynyl, m,m-$C_6H_3(-C{\equiv}C-)_3$, also have been recently reported.[7] Products of reactions of **4**, **7**, and **8** with H^+ also support the identification of these complexes as shown in eqs 4, 6, and 7.

The geometry of R-**HEX** in **5** is clearly determined by detailed spectral data analysis (see Experimental Section and Supporting Information) and also supported by the structure of isolated R-**HEX**. The ^{31}P NMR spectra of **5** show two signals (δ −5.94 to −7.76, 1.48 to 5.71) as does the very similar rhodium(I)−η^4-1,3-butadiene complex $(PPh_3)_2ClRh(\eta^4\text{-}H_2C{=}CH{-}C(Ph){=}CH_2)$, whose crystal structure shows the two PPh_3 being nonequivalent.[8] Cross-conjugated olefins, R-**HEX**, R-**HEX**-d_1, p-C_6H_4-(**HEX**)$_2$, m,m-C_6H_3-(**HEX**)$_3$, R_2-**OCT**, and R_2-**OCT**-d_2 have been unequivocally identified by detailed spectral data (see Experimental Section and Supporting Information). Those 18-electron iridium(III) complexes (**4**, **7**, **8**) containing three σ-bonded hydrocarbyl ligands are so stable that no reductive elimination of unsaturated hydrocarbons occurs even at elevated temperature.

Scheme 1



Metal−vinylidenes (M=C=CHR) are frequently observed and suggested in the reactions of metal−alkynyls with protons and of metals with terminal alkynes ($RC{\equiv}CH$).[9,10] The α-carbon ($M{=}C{=}CHR$) of the vinylidene group is known to be so electrophilic that it readily interacts with a neighboring hydrocarbyl ligand to form a new C−C bond.[10]

Scheme 1 is accordingly suggested for the formation of R-**HEX** from the reactions of **4** with proton (eq 4). While no vinylidene intermediate is detected even at low temperature during the reactions of **4** (eq 4), the formation of isotopomers **5**-d_1 and R-**HEX**-d_1 strongly supports the vinylidene complexes **A**-d_1 as the initial intermediates that undergo the C−C coupling reaction between the vinylidene and the *cis*-ethenyl groups to produce another intermediate **B**-d_1. These 16-electron Ir(III) complexes **B-d_1** then undergo the reductive C−C coupling reaction between the two hydrocarbyl ligands to give the stable 18-electron Ir(I) complexes **5**-d_1. Production of p-C_6H_4-(**HEX**)$_2$ (eq 6) and m,m-C_6H_3-(**HEX**)$_3$ (eq 7) may also be understood by reaction schemes similar to Scheme 1. A similar reaction pathway may also be applicable to the formation of R-**HEX** in reactions of **3** with $RC{\equiv}CH$ (eq 3).

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(6) Results will be reported elsewhere.

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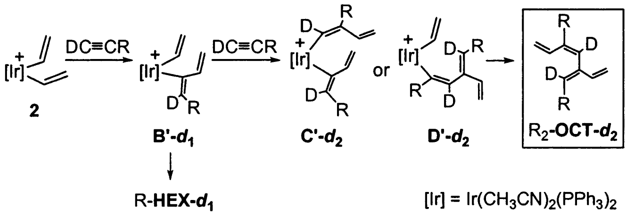
Scheme 2



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**)

Formation of the dienyne **11** (eq 8) is not explained simply by a reaction pathway similar to Scheme 1 and is currently under investigation.

Scheme 2 is proposed for the production of R-**HEX**-d_1 and R$_2$-**OCT**-d_2 in eq 2. The isotopomers **B′**-d_1 are the likely intermediates to give the observed isotopomers R-**HEX**-d_1 for the same reason discussed above with Scheme 1. Since the linear trienes $CH_2=CHCH=CRCH=CH_2$ have not been detected during the reactions of **2** with RC≡CH, it is less likely that the first RC≡C***D*** is added to **2** via a type of 1,2-addition to give $[(PPh_3)_2(CH_3CN)_2Ir(-C\boldsymbol{D}=CR-CH=CH_2)(-CH=CH_2)]^+$ which are therefore excluded in Scheme 2. The intermediates **B′**-d_1 then undergo the 1,2-insertion of another RC≡CD into one of the two Ir−C bonds to give **C′**-d_2 and/or **D′**-d_2 that finally eliminate R$_2$-**OCT**-d_2. The structure of R$_2$-**OCT** and positions of deuterium in R$_2$-**OCT**-d_2 strongly support the second RC≡CH insertion by a type of 1,2-addition (**B′** → **C′**, **D′**) rather than 1,1-addition via the vinylidene species (such as **A** → **B** in Scheme 1 or **2** → **B′** in Scheme 2). No direct evidence has been obtained yet to distinguish the two pathways via **C′** and **D′** for the formation of R$_2$-**OCT**.

It is noticed in Table 1 that the R-**HEX**/R$_2$-**OCT** is larger with bulkier R substituents. This may be understood by the steric effects of R experienced during the formation of R$_2$-**OCT**, which requires more space around the metal than the formation of R-**HEX** does.

The different reactivity of **2** and **3** toward RC≡CH (see eqs 2 and 3 and Table 1) could be due to the relative lability of CH_3CN in **2** and CO in **3**. The CH_3CN of **2** is readily replaced by CO whereas the CO of **3** seems to be even more strongly bound to the metal than PPh_3. It is likely that **B′** are far easier to interact with another RC≡CH because the CH_3CN ligands in **B′** are more labile than the PPh_3 ligands in **B″** ($[(PPh_3)_2(CO)_2Ir(-C(=CHR)CH=CH_2)(-CH=CH_2)]^+$) that are presumably suggested as the intermediates in reactions of **3** with RC≡CH. It is therefore expected for **B″** to give more cross-conjugated trienes R-**HEX** rather than to react with a second RC≡CH to give R$_2$-**OCT**. It may be said that replacing the labile CH_3CN ligands of **2** with relatively inert CO to produce **3** effectively increases the selectivity of the products (i.e., R-**HEX**/R$_2$-**OCT**).

Equations 2, 3, 6, and 7 are all stoichiometric reactions. Catalytic production of those cross-conjugated olefins seems quite feasible under the appropriate conditions since complexes **1** and **1′** are recovered in high yields from the reactions of “Ir−A” and “Ir−B” with H_2. It seems also possible that the method to form new C−C bonds described in this paper is further utilized to prepare more highly cross-conjugated olefins.

Experimental Section

General Information. A standard vacuum system and Schlenk type glass ware 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 and $HBF_4 \cdot OEt_2$ (54 wt % in Et_2O) were purchased from Aldrich and aqueous DBF_4 solution was prepared by mixing of HBF_4 (1 mL, 54 wt % in Et_2O) with D_2O (4 mL). 1,4-Diethynylbenzene,[11] 1,3,5-triethynylbenzene,[7b] and $[Ir(H)_2(NCCH_3)_2(PPh_3)_2]OTf$ (**1**)[4] were prepared by the literature method.

Instruments. NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer for ^1H, 75 or 125.7 MHz for ^{13}C, and 81 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205. Electronic absorption spectra were measured with a Hewlett-Packard HP8453 diode array spectrophotometer. Melting points were measured with an Electrothermal IA9000 series Digital Meting point apparatus. Elemental analyses were carried out with a Carlo Erba EA1108. Gas chromatography/mass spectra were measured with a Hewlett-Packard HP 5890A VG-trio 2000 at the Organic Chemistry Center, Sogang University. FAB mass measurements were carried out with a JMS-HX110/110A tandem mass spectrometer at the Korea Basic Science Institute.

Synthesis. (a) Preparation of $[Ir(-CH=CH_2)_2(NCCH_3)_2(PPh_3)_2]OTf$ (2). A 0.1-g (0.1 mmol) sample of **1** in CH_2Cl_2 (10 mL) was stirred under HC≡CH (1 atm) at 0 °C for 5 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 0.11 g and 98% based on $[Ir(-CH=CH_2)_2(NCCH_3)_2(PPh_3)_2]OTf$ (**2**). ^1H NMR (500 MHz, $CDCl_3$): δ 7.3−7.6 (m, 30H, $P(C_6H_5)_3$), 7.52 (ddt, 2H, $J(HH) = 18.0$ Hz, $J(HH) = 10.0$ Hz, $J(HP) = 3.8$ Hz, $Ir-CH=CH_2$), 5.68 (d, 2H, $J(HH) = 10.0$ Hz, $Ir-CH=CHH$), 4.61 (d, 2H, $J(HH) = 18.0$ Hz, $Ir-CH=CHH$), 1.72 (s, 6H, CH_3CN). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 125.1 (t, $J(CP) = 10.1$ Hz, $Ir-CH=CH_2$), 121.4 (t, $J(CP) = 4.0$ Hz, $Ir-CH=CH_2$), 119.5 (s, CH_3CN), 2.9 (s, CH_3CN), 134.8, 130.3, 128.7, and 127.7 ($P(C_6H_5)_3$). HETCOR (^1H (500 MHz) → ^{13}C (125.7 MHz)): δ 7.52 → 125.1; 4.61, 5.68 → 121.4; 1.72 → 2.9. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ −8.75 (s, PPh_3). IR (KBr, cm^{-1}): 2035 (w, $\nu_{C\equiv N}$), 1562 (m, $\nu_{C=C}$), 1271, 1152 and 1032 (s, due to uncoordinated OTf). Anal. Calcd for $IrF_3SO_3P_2C_{45}H_{42}N_2$: C, 53.94; H, 4.22; N, 2.79. Found: C, 53.84; H, 4.33; N, 2.72.

(b) Preparation of $[Ir(-CH=CHD)_2(NCCH_3)_2(PPh_3)_2]OTf$ (2-d_2). This compound was prepared in the same manner as described above for **2** by using **1**-d_2. ^1H NMR (500 MHz, $CDCl_3$): δ 7.3−7.6 (m, 30H, $P(C_6H_5)_3$), 7.52 (dt, 2H, $J(HH) = 10.0$ Hz, $J(HP) = 3.8$ Hz, $Ir-CH=CHD$), 5.68 (d, 2H, $J(HH) = 10.0$ Hz, $Ir-CH=CHD$), 1.72 (s, 6H, CH_3CN).

(c) Preparation of $[Ir(-CH=CH_2)_2(CO)_2(PPh_3)_2]OTf$ (3). A 0.1-g (0.1 mmol) sample of **2** in CH_2Cl_2 (10 mL) was stirred under CO (1 atm) at 25 °C for 3 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 0.96 g and 98% based on $[Ir(-CH=CH_2)_2(CO)_2(PPh_3)_2]OTf$ (**3**). ^1H NMR (500 MHz, $CDCl_3$): δ 7.5−7.7 (m, 30H, $P(C_6H_5)_3$), 6.59 (ddt, 2H, $J(HH) = 18.5$ Hz, $J(HH) = 10.5$ Hz, $J(HP) = 4.5$ Hz, $Ir-CH=CH_2$), 6.37 (d, 2H, $J(HH) = 10.5$ Hz, $Ir-CH=CHH$), 5.06 (d, 2H, $J(HH) = 18.5$ Hz, $Ir-CH=CHH$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 167.0 (t, $J(CP) = 5.8$ Hz, $Ir-CO$), 130.6 (t, $J(CP) = 4.5$ Hz, $Ir-CH=CH_2$), 129.6 (t, $J(CP) = 10.3$ Hz, $Ir-CH=CH_2$), 134.4, 132.2, 128.8 and 127.3 ($P(C_6H_5)_3$). HETCOR (^1H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.59 → 129.6; 5.06, 6.37 → 130.6. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ −17.40 (s, PPh_3). IR (KBr, cm^{-1}):

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

2121, 2086 (s, ν_{CO}), 1574 (m, $\nu_{\mathrm{C=C}}$), 1278, 1151 and 1032 (s, due to uncoordinated OTf). Anal. Calcd for $\mathrm{IrF_3SO_5P_2C_{43}H_{46}}$: C, 52.38; H, 4.70. Found: C, 52.51; H, 4.77.

(d) Preparation of $\mathbf{[Ir({-}CH{=}CHD)_2(CO)_2(PPh_3)_2]OTf}$ (3-*d*$_2$). This compound was prepared in the same manner as described above for **3** by using **2**-*d*$_2$. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.5−7.7 (m, 30H, $\mathrm{P(C_6\mathit{H}_5)_3}$), 6.59 (dt, 2H, *J*(HH) = 10.5 Hz, *J*(HP) = 4.5 Hz, $\mathrm{Ir{-}C\mathit{H}{=}CHD}$), 6.37 (d, 2H, *J*(HH) = 10.5 Hz, $\mathrm{Ir{-}CH{=}C\mathit{H}D}$).

(e) Preparation of $\mathbf{Ir({-}C{\equiv}CR)({-}CH{=}CH_2)_2(CO)(PPh_3)_2}$ (4, R = $\mathbf{C_6H_5}$ (a), *p*-$\mathbf{C_6H_4CH_3}$ (b), cyclohex-1-enyl (c)). These compounds were prepared by the same method as described below for **4a**. To a solution of **3** (0.1 g, 0.1 mmol) and $\mathrm{C_6H_5C{\equiv}CH}$ (0.012 g, 0.12 mmol) in $\mathrm{CHCl_3}$ (10 mL) was added $\mathrm{Me_3NO}$ (0.019 g, 0.25 mmol) and the reaction mixture was stirred at 25 °C under $\mathrm{N_2}$ for 30 min before the pale yellow solution turned light brown. Excess $\mathrm{Me_3NO}$ and $\mathrm{[HNMe_3]OTf}$ were removed by extraction with $\mathrm{H_2O}$ (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 0.074 g and 82% based on $\mathrm{Ir({-}C{\equiv}CC_6H_5)({-}CH{=}CH_2)_2(CO)(PPh_3)_2}$ (**4a**). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 6.9−7.8 (m, 36H, $\mathrm{P(C_6\mathit{H}_5)_3}$, $\mathrm{C{\equiv}CC_6\mathit{H}_5}$, and $\mathrm{Ir{-}C\mathit{H}{=}CH_2}$), 6.22 (ddt, 1H, *J*(HH) = 19.0 Hz, *J*(HH) = 11.0 Hz, *J*(HP) = 2.5 Hz, $\mathrm{Ir{-}C\mathit{H}{=}CH_2}$), 5.87 (ddt, *J*(HH) = 11.5 Hz, *J*(HH) = 2.5 Hz, *J*(HP) = 2.0 Hz) and 5.77 (ddt, *J*(HH) = 11.0 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 1.5 Hz) (2H, $\mathrm{Ir{-}CH{=}C\mathit{H}H}$), 5.19 (ddt, *J*(HH) = 19.0 Hz, *J*(HH) = 2.5 Hz, *J*(HP) = 2.0 Hz) and 4.92 (ddt, *J*(HH) = 19.0 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 1.5 Hz) (2H, $\mathrm{Ir{-}CH{=}CH\mathit{H}}$). ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3}$): δ 173.9 (t, *J*(CP) = 6.5 Hz, $\mathrm{Ir{-}\mathit{C}O}$), 143.0 (t, *J*(CP) = 8.9 Hz) and 135.2 (t, *J*(CP) = 12.8 Hz) ($\mathrm{Ir{-}\mathit{C}H{=}CH_2}$), 125.3 (t, *J*(CP) = 5.0 Hz) and 123.5 (br s) ($\mathrm{Ir{-}CH{=}\mathit{C}H_2}$), 112.0 (s, $\mathrm{Ir{-}C{\equiv}\mathit{C}}$), 89.6 (t, *J*(CP) = 12.5 Hz, $\mathrm{Ir{-}\mathit{C}{\equiv}C}$), 130.1 ($C_{\mathrm{ipso}}$ of $\mathrm{C_6H_5}$ carbons), 130.8, 127.5 and 124.4 (*C*H of $\mathrm{C_6H_5}$ carbons), 135.0, 131.3, 129.9 and 127.3 ($\mathrm{P(\mathit{C}_6H_5)_3}$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.22 → 143.0; 5.87, 5.19 → 125.3; 5.77, 4.92 → 123.5. ^{31}P{^{1}H} NMR (81 MHz, $\mathrm{CDCl_3}$): δ −12.44 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 2108 (m, $\nu_{\mathrm{C\equiv C}}$), 2045 (s, ν_{CO}). Anal. Calcd for $\mathrm{IrOP_2C_{49}H_{41}}$: C, 65.39; H, 4.59. Found: C, 65.01; H, 4.48.

$\mathrm{Ir({-}C{\equiv}C\text{-}\mathit{p}\text{-}C_6H_4CH_3)({-}CH{=}CH_2)_2(CO)(PPh_3)_2}$ (**4b**): ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.2−7.9 (m, 31H, $\mathrm{P(C_6\mathit{H}_5)_3}$ and $\mathrm{Ir{-}C\mathit{H}{=}CH_2}$), 6.7−7.0 (AB quartet with $\Delta\nu/J$ = 10.1, 4H, $J(\mathrm{H_AH_B})$ = 81.1 Hz, $\mathrm{Ir{-}C{\equiv}C\text{-}\mathit{p}\text{-}C_6\mathit{H}_4CH_3}$), 6.20 (ddt, 1H, *J*(HH) = 19.0 Hz, *J*(HH) = 11.5 Hz, *J*(HP) = 2.5 Hz, $\mathrm{Ir{-}C\mathit{H}{=}CH_2}$), 5.84 (ddt, *J*(HH) = 11.5 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 2.0 Hz) and 5.74 (ddt, *J*(HH) = 11.5 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 1.5 Hz) (2H, $\mathrm{Ir{-}CH{=}C\mathit{H}H}$), 5.17 (ddt, *J*(HH) = 18.5 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 2.0 Hz) and 4.90 (ddt, *J*(HH) = 19.0 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 1.5 Hz) (2H, $\mathrm{Ir{-}CH{=}CH\mathit{H}}$), 2.29 (s, $\mathrm{C\mathit{H}_3}$, 3H). ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3}$): δ 173.9 (t, *J*(CP) = 6.5 Hz, $\mathrm{Ir{-}\mathit{C}O}$), 143.0 (t, *J*(CP) = 8.9 Hz) and 135.3 (t, *J*(CP) = 5.0 Hz) ($\mathrm{Ir\text{-}\mathit{C}H{=}CH_2}$), 125.3 (t, *J*(CP) = 5.0 Hz) and 123.3 (br s) ($\mathrm{Ir{-}CH{=}\mathit{C}H_2}$), 111.8 (s, $\mathrm{Ir{-}C{\equiv}\mathit{C}}$), 87.5 (t, *J*(CP) = 13.1 Hz, $\mathrm{Ir{-}\mathit{C}{\equiv}C}$), 21.2 (s, $\mathrm{\mathit{p}\text{-}C_6H_4\mathit{C}H_3}$), 133.9 and 130.1 ($C_{\mathrm{ipso}}$ of $\mathrm{\mathit{p}\text{-}C_6H_4CH_3}$ carbons), 130.6 and 128.2 (*C*H of $\mathrm{\mathit{p}\text{-}C_6H_4CH_3}$ carbons), 135.0, 131.3, 130.0 and 127.3 ($\mathrm{P(\mathit{C}_6H_5)_3}$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.20 → 143.0; 5.84, 5.17 → 125.3; 5.74, 4.90 → 123.3; 2.29 → 21.2. ^{31}P{^{1}H} NMR (81 MHz, $\mathrm{CDCl_3}$): δ −12.38 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 2107 (m, $\nu_{\mathrm{C\equiv C}}$), 2027 (s, ν_{CO}). Anal. Calcd for $\mathrm{IrOP_2C_{50}H_{43}}$: C, 65.70; H, 4.74. Found: C, 65.94; H, 4.83.

$\mathrm{Ir({-}C{\equiv}C\text{-cyclohex-1-enyl})({-}CH{=}CH_2)_2(CO)(PPh_3)_2}$ (**4c**): ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.3−7.8 (m, 30H, $\mathrm{P(C_6\mathit{H}_5)_3}$), 7.24 (ddt, *J*(HH) = 19.0 Hz, *J*(HH) = 11.5 Hz, *J*(HP) = 4.5 Hz) and 6.17 (ddt, *J*(HH) = 19.0 Hz, *J*(HH) = 11.5 Hz, *J*(HP) = 2.0 Hz) (2H, $\mathrm{Ir{-}C\mathit{H}{=}CH_2}$), 5.85 (ddt, *J*(HH) = 11.3 Hz, *J*(HH)- = 3.0 Hz, *J*(HP) = 2.0 Hz) and 5.72 (ddt, *J*(HH) = 11.5 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 1.5 Hz) (2H, $\mathrm{Ir{-}CH{=}CH\mathit{H}}$), 5.38 (m, 1H, $\mathrm{Ir{-}C{\equiv}C{-}C{=}C\mathit{H}{-}(CH_2)_3CH_2}$), 5.18 (ddt, *J*(HH) = 19.0 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 2.0 Hz) and 4.90 (ddt, *J*(HH) = 19.0 Hz, *J*(HH) = 3.0 Hz, *J*(HP) = 1.5 Hz) (2H, $\mathrm{Ir{-}CH{=}CH\mathit{H}}$), 2.03, 1.79 and 1.52 (m, 8H, $\mathrm{Ir{-}C{\equiv}C{-}C{=}CH(C\mathit{H}_2)_3C\mathit{H}_2}$). ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3}$): δ 174.1 (t, *J*(CP) = 6.5 Hz, $\mathrm{Ir{-}\mathit{C}O}$), 143.5 (t, *J*(CP) = 8.9 Hz) and 135.6 (t, *J*(CP) = 12.5 Hz) ($\mathrm{Ir{-}\mathit{C}H{=}CH_2}$), 125.3 (s, $\mathrm{Ir{-}C{\equiv}C{-}\mathit{C}{=}CH{-}(CH_2)_3CH_2}$)), 126.3 (br s, $\mathrm{Ir{-}C{\equiv}C{-}C{=}\mathit{C}H(CH_2)_3CH_2}$), 125.2 (t, *J*(CP) = 4.9 Hz) and 123.1 (br s) ($\mathrm{Ir{-}CH{=}\mathit{C}H_2}$), 114.1 (s, $\mathrm{Ir{-}C{\equiv}\mathit{C}}$), 82.7 (t, *J*(CP) = 13.1 Hz, $\mathrm{Ir{-}\mathit{C}{\equiv}C}$), 30.3, 25.4, 22.8 and 22.2 (br s, $\mathrm{Ir{-}C{\equiv}C{-}C{=}CH(\mathit{C}H_2)_3\mathit{C}H_2}$), 127.2, 129.9, 131.4 and 135.0 ($\mathrm{P(\mathit{C}_6H_5)_3}$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 7.24 → 135.6; 6.17 → 143.5; 5.85, 5.18 → 125.2; 5.72, 4.90 → 123.1; 5.38 → 126.3; 2.03 → 25.4; 1.79 → 30.3; 1.52 → 22.2, 22.8. ^{31}P{^{1}H} NMR (81 MHz, $\mathrm{CDCl_3}$): δ −12.99 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 2097 (m, $\nu_{\mathrm{C\equiv C}}$), 2017 (s, ν_{CO}). Anal. Calcd for $\mathrm{IrOP_2C_{49}H_{45}}$: C, 65.10; H, 5.02. Found: C, 65.39; H, 5.09.

(f) Preparation of $\mathbf{Ir(\eta^4\text{-}CH_2{=}CH{-}CH{=}CH_2)({-}C{\equiv}CR)\text{-}(PPh_3)_2}$ (6, R = $\mathbf{C_6H_5}$ (a), *p*-$\mathbf{C_6H_4CH_3}$ (b)). To a solution of **2** (0.1 g, 0.1 mmol) and $\mathrm{C_6H_5C{\equiv}CH}$ (0.012 g, 0.12 mmol) in $\mathrm{CHCl_3}$ (10 mL) was added $\mathrm{NEt_3}$ (0.019 g, 0.25 mmol) and the reaction mixture was stirred at 25 °C under $\mathrm{N_2}$ for 6 h before the pale yellow solution turned light brown. Excess $\mathrm{NEt_3}$ and $\mathrm{[HNEt_3]OTf}$ were removed by extraction with $\mathrm{H_2O}$ (5 × 10 mL). Addition of *n*-pentane (10 mL) at −78 °C resulted in precipitation of beige microcrystals that were collected by filtration, washed with cold *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.078 g and 89% based on $\mathrm{Ir(\eta^4\text{-}CH_2{=}CH{-}CH{=}CH_2)({-}C{\equiv}CC_6H_5)(PPh_3)_2}$ (**6a**). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 6.8−7.6 (m, 35H, $\mathrm{P(C_6\mathit{H}_5)_3}$, $\mathrm{C_6\mathit{H}_5}$), 5.51 and 5.16 (m, 2H, $\mathrm{Ir\text{-}\eta^4\text{-}CH_2{=}C\mathit{H}C\mathit{H}{=}CH_2}$), 2.80 and 1.60 (m, 2H, $\mathrm{Ir\text{-}\eta^4\text{-}C\mathit{H}_{\mathit{syn}}H{=}CHCH{=}C\mathit{H}_{syn}H}$), −0.54 (m, 2H, $\mathrm{Ir\text{-}\eta^4\text{-}CH\mathit{H}_{anti}{=}CHCH{=}CH\mathit{H}_{anti}}$). ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3}$): δ 105.5 (s, $\mathrm{Ir{-}C{\equiv}\mathit{C}}$), 95.8 (t, *J*(CP) = 12.8 Hz, $\mathrm{Ir{-}\mathit{C}{\equiv}C}$), 88.7 (s) and 80.8 (t, *J*(CP) = 6.1 Hz) ($\mathrm{Ir\text{-}\eta^4\text{-}CH_2{=}\mathit{C}H\mathit{C}H{=}CH_2}$), 38.2 and 33.1 (s, $\mathrm{Ir\text{-}\eta^4\text{-}\mathit{C}H_2{=}CHCH{=}\mathit{C}H_2}$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 5.51 → 80.8; 5.16 → 88.7; 2.80, −0.54 → 38.2; 1.60, −0.54 → 33.1. ^{31}P{^{1}H} NMR (81 MHz, $\mathrm{CDCl_3}$): δ 6.46 (d, *J*(PP) = 17.9 Hz, *P*Ph$_3$), −7.41 (d, *J*(PP) = 17.9 Hz, *P*Ph$_3$). IR (KBr, cm^{-1}): 2102 (m, $\nu_{\mathrm{C\equiv C}}$). Anal. Calcd for $\mathrm{IrOP_2C_{48}H_{41}}$: C, 65.39; H, 4.59. Found: C, 65.32, H, 4.54.

$\mathrm{Ir(\eta^4\text{-}CH_2{=}CH{-}CH{=}CH_2)({-}C{\equiv}C\text{-}\mathit{p}\text{-}C_6H_4CH_3)(PPh_3)_2}$ (**6b**) ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 6.9−7.8 (m, 30H, $\mathrm{P(C_6\mathit{H}_5)_3}$), 6.5−6.8 (AB quartet with $\Delta\nu/J$ = 9.8, 4H, $J(\mathrm{H_AH_B})$ = 78.6 Hz, $\mathrm{C{\equiv}C\text{-}\mathit{p}\text{-}C_6\mathit{H}_4CH_3}$,), 5.34 and 5.03 (m, 2H, $\mathrm{Ir\text{-}\eta^4\text{-}CH_2{=}C\mathit{H}C\mathit{H}{=}CH_2}$), 2.65 and 1.42 (m, 2H, $\mathrm{Ir\text{-}\eta^4\text{-}C\mathit{H}_{\mathit{syn}}H{=}CHCH{=}C\mathit{H}_{\mathit{syn}}H}$), 2.29 (s, 3H, $\mathrm{C{\equiv}C\text{-}\mathit{p}\text{-}C_6H_4C\mathit{H}_3}$) −0.69 (m, 2H, $\mathrm{Ir\text{-}\eta^4\text{-}CH\mathit{H}_{\mathit{anti}}{=}CHCH{=}CH\mathit{H}_{\mathit{anti}}}$). ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3}$): δ 104.9 (s, $\mathrm{Ir{-}C{\equiv}\mathit{C}}$), 94.3 (t, *J*(CP) = 12.8 Hz, $\mathrm{Ir{-}\mathit{C}{\equiv}C}$), 87.6 (s) and 79.6 (t, *J*(CP) = 6.0 Hz) ($\mathrm{Ir\text{-}\eta^4\text{-}CH_2{=}\mathit{C}H\mathit{C}H{=}CH_2}$), 38.2 and 33.1 (s, $\mathrm{Ir\text{-}\eta^4\text{-}\mathit{C}H_2{=}CHCH{=}\mathit{C}H_2}$), 20.2 (s, $\mathrm{C{\equiv}C\text{-}\mathit{p}\text{-}C_6H_4\mathit{C}H_3}$). ^{31}P{^{1}H} NMR (81 MHz, $\mathrm{CDCl_3}$): δ 6.21 (d, *J*(PP) = 17.8 Hz, *P*Ph$_3$), −7.82 (d, *J*(PP) = 17.8 Hz, *P*Ph$_3$). IR (KBr, cm^{-1}): 2101 (m, $\nu_{\mathrm{C\equiv C}}$). Anal. Calcd for $\mathrm{IrOP_2C_{49}H_{43}}$: C, 66.42; H, 4.89. Found: C, 66.29; H, 4.78.

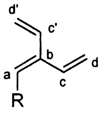
(g) Preparation of *p*-$\mathbf{C_6H_4({-}C{\equiv}C{-}IrL_5)_2}$ (7, $\mathbf{L_5 = ({-}CH{=}CH_2)_2(CO)(PPh_3)_2}$). To a solution of **3** (0.2 g, 0.2 mmol) and *p*-$\mathrm{C_6H_4({-}C{\equiv}CH)_2}$ (0.013 g, 0.11 mmol) in $\mathrm{CHCl_3}$ (10 mL) was added $\mathrm{Me_3NO}$ (0.038 g, 0.50 mmol) and the reaction mixture was kept at 25 °C under $\mathrm{N_2}$ for 2 h before excess $\mathrm{Me_3NO}$ and $\mathrm{[HNMe_3]OTf}$ were removed by extraction with $\mathrm{H_2O}$ (2 × 10 mL). Addition of *n*-pentane (20 mL) resulted in precipitation of beige microcrystals that were collected by filtration, washed with $\mathrm{CH_3OH}$ (3 × 10 mL), and dried under vacuum. The yield was 0.064 g and 74% based on *p*-$\mathrm{C_6H_4\text{-}(C{\equiv}C{-}IrL_5)_2}$ (**7**, $\mathrm{L_5 = ({-}CH{=}CH_2)_2(CO)(PPh_3)_2}$).^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.2−7.8 (m, 62H, $\mathrm{P(C_6\mathit{H}_5)_3}$ and $\mathrm{Ir{-}C\mathit{H}{=}CH_2}$), 6.63 (s, 4H, $\mathrm{Ir{-}C{\equiv}C{-}C_6\mathit{H}_4}$,), 6.18 (ddt, 2H, *J*(HH) = 19.0 Hz, *J*(HH) = 11.5 Hz,

J(HP) = 2.5 Hz, Ir–CH=CH$_2$), 5.83 (ddt, J(HH) = 11.5 Hz, J(HH) = 3.0 Hz, J(HP) = 2.0 Hz) and 5.72 (ddt, J(HH) = 11.5 Hz, J(HH) = 3.0 Hz, J(HP) = 1.5 Hz) (4H, Ir–CH=CHH), 5.16 (ddt, J(HH) = 18.5 Hz, J(HH) = 3.0 Hz, J(HP) = 2.0 Hz) and 4.89 (ddt, J(HH) = 19.0 Hz, J(HH) = 3.0 Hz, J(HP) = 1.5 Hz) (4H, Ir–CH=CHH). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ −12.55 (s, PPh$_3$). IR (KBr, cm^{-1}): 2109 (m, $\nu_{C\equiv C}$), 2026 (s, ν_{CO}). Anal. Calcd for Ir$_2$O$_2$P$_4$C$_{92}$H$_{76}$: C, 64.17; H, 4.45. Found: C, 63.65; H, 4.38. MS (FAB) m/z Calcd for [M + H]$^+$: 1722.9. Found: 1722.1 ([M + H]$^+$).

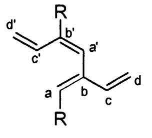
(h) Preparation of *m,m*-C$_6$H$_3$-(C≡C–IrL$_5$)$_3$ (8, L$_5$ = (–CH=CH$_2$)$_2$(CO)(PPh$_3$)$_2$). This compound was prepared in the same manner as described above for **7** by using 0.3 g (0.3 mmol) of **3**, 0.017 g (0.11 mmol) of *m,m*-C$_6$H$_3$-(–C≡CH)$_3$ and 0.057 g (0.75 mmol) of Me$_3$NO. The yield was 0.18 g and 71% based on *m,m*-C$_6$H$_3$-(C≡C–IrL$_5$)$_3$ (**8**, L$_5$ = (–CH=CH$_2$)$_2$(CO)-(PPh$_3$)$_2$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.2–7.8 (m, 93H, P(C$_6$$H_5$)$_3$ and Ir–CH=CH$_2$), 6.53 (s, 3H, Ir–C≡C–C$_6$$H_3$,), 6.17 (ddt, 3H, J(HH) = 19.0 Hz, J(HH) = 12.0 Hz, J(HP) = 2.0 Hz, Ir–CH=CH$_2$), 5.93 (dd, J(HH) = 11.5 Hz, J(HH) = 2.0 Hz) and 5.71 (dd, J(HH) = 12.0 Hz, J(HH) = 1.5 Hz) (6H, Ir–CH=CHH), 5.25 (dd, J(HH) = 18.0 Hz, J(HH) = 2.0 Hz) and 4.95 (ddt, J(HH) = 19.0 Hz, J(HH) = 1.5 Hz) (6H, Ir–CH=CHH). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 174.1 (t, J(CP) = 6.3 Hz, Ir–CO), 143.8 (t, J(CP) = 8.2 Hz) and 135.7 (t, J(CP) = 12.8 Hz) (Ir–CH=CH$_2$), 130.4 (s, CH carbon of (Ir–C≡C–)$_3$C$_6$H$_3$), 124.9 and 123.0 (br s, Ir–CH=CH$_2$), 112.9 (s, Ir–C≡C), 85.8 (t, J(CP) = 13.0 Hz, Ir–C≡C). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.35 → 130.4; 6.17 → 143.8; 5.93, 5.25 → 124.9; 5.71, 4.95 → 123.0. ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ −12.31 (s, PPh$_3$). IR (KBr, cm^{-1}): 2101 (m, $\nu_{C\equiv C}$), 2029 (s, ν_{CO}). Anal. Calcd for Ir$_3$O$_3$P$_6$C$_{135}$H$_{111}$: C, 68.95; H, 4.76. Found: C, 68.55; H, 4.69. MS (FAB) m/z Calcd for [M + H]$^+$: 2544.8. Found: 2545.6 ([M + H]$^+$).

Reactions. (a) Reactions of 2 and 3 with RC≡CH(D): Isolation of R-HEX and R$_2$-OCT (R = C$_6$H$_5$ (a), *p*-C$_6$H$_4$CH$_3$ (b), Cyclohex-1-enyl (c), C(CH$_3$)=CH$_2$ (d), C(CH$_3$)$_3$ (e)). These reactions were carried out in the same manner as described below for **2** with C$_6$H$_5$C≡CH. A CHCl$_3$ (10 mL) solution of **2** (0.30 g, 0.3 mmol) and C$_6$H$_5$C≡CH (0.12 g, 1.2 mmol) was stirred at 50 °C for 12 h before *n*-pentane (20 mL) was added to precipitate brown microcrystals of "Ir–A" 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 through a silica gel packed column to separate the pale yellow oil of C$_6$H$_5$-**HEX** and (C$_6$H$_5$)$_2$-**OCT**. The yields were 0.15 mmol (49%) based on C$_6$H$_5$-**HEX** and 0.09 mmol (30%) based on (C$_6$H$_5$)$_2$-**OCT** measured by ^{1}H NMR, respectively.

The reaction of **3** (0.30 g, 0.3 mmol) with C$_6$H$_5$C≡CH (0.092 g, 0.9 mmol) gave brown microcrystals of "Ir–B" which were removed by filtration and C$_6$H$_5$-**HEX** of which the yield was 0.26 mmol and 87% based on C$_6$H$_5$-**HEX** measured by ^{1}H NMR.



R-**HEX**



R$_2$-**OCT**

C$_6$H$_5$-**HEX**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.2–7.5 (m, 5H, C$_6$$H_5$), 6.68 (br s, 1H, H_a), 6.74 (dd, J(HH) = 17.7 Hz, J(HH) = 11.3 Hz) and 6.59 (dd, J(HH) = 17.3 Hz, J(HH) = 10.5 Hz) (2H, H_c and $H_{c'}$), 5.57 (dd, J(HH) = 17.3 Hz, J(HH) = 1.5 Hz) and 5.48 (dd, J(HH) = 17.7 Hz, J(HH) = 1.5 Hz) (2H, $H_{d-trans}$ and $H_{d'-trans}$), 5.38 (dd, J(HH) = 11.3 Hz, J(HH) = 1.5 Hz) and 5.24 (dd, J(HH) = 10.5 Hz, J(HH) = 1.5 Hz) (2H, H_{d-cis} and $H_{d'-cis}$). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 137.8 and 133.5 (s, C_c and $C_{c'}$), 129.5 (s, C_a), 118.3 and 116.1 (s, C_d and $C_{d'}$), 137.9 and 137.1 (C_b and C_{ipso} of C$_6$H$_5$ carbons), 129.7, 128.1 and 127.1 (CH of C$_6$H$_5$ carbons). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.68 → 129.5; 5.24, 5.57 → 116.1; 5.38, 5.48 → 118.3. Electronic absorption: λ_{max} = 294 nm. MS m/z 156 (M$^+$).

C$_6$H$_5$-**HEX**-d_1: ^{1}H NMR spectrum of the isotopomer C$_6$H$_5$-**HEX**-d_1 shows all the signals for C$_6$H$_5$-**HEX** except the resonance at δ 6.68 ppm assigned to H_a of C$_6$H$_5$-**HEX**. MS m/z 157 (M$^+$).

p-CH$_3$C$_6$H$_4$-**HEX**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.13–7.28 (AB quartet with $\Delta\nu/J$ = 4.8, 4H, J(H$_A$H$_B$) = 13.5 Hz, *p*-C$_6$$H_4$-CH$_3$), 6.62 (br s, 1H, H_a), 6.71 (dd, J(HH) = 17.7 Hz, J(HH) = 11.5 Hz) and 6.55 (dd, J(HH) = 17.3 Hz, J(HH) = 10.8 Hz) (2H, H_c and $H_{c'}$), 5.52 (dd, J(HH) = 17.3 Hz, J(HH) = 2.0 Hz) and 5.44 (dd, J(HH) = 17.7 Hz, J(HH) = 1.5 Hz) (2H, $H_{d-trans}$ and $H_{d'-trans}$), 5.34 (dd, J(HH) = 11.5 Hz, J(HH) =1.5 Hz) and 5.16 (dd, J(HH) = 10.8 Hz, J(HH) = 2.0 Hz) (2H, H_{d-cis} and $H_{d'-cis}$), 2.36 (s, 3H, *p*-C$_6$$H_4CH_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 138.0 and 133.6 (s, C_c and $C_{c'}$), 118.0 and 115.7 (s, C_d and $C_{d'}$), 129.6 (s, C_a), 21.2 (s, *p*-C$_6$H$_4$$CH_3$), 137.2, 137.0 and 134.2 (C_b and C_{ipso} of *p*-C$_6$H$_4$CH$_3$ carbons), 129.6 and 128.8 (CH of *p*-C$_6$H$_4$CH$_3$ carbons). MS m/z 170 (M$^+$).

Cyclohex-1-enyl-**HEX**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.75 (dd, J(HH) = 17.5 Hz, J(HH) = 11.1 Hz) and 6.48 (dd, J(HH) = 17.5 Hz, J(HH) = 10.7 Hz) (2H, H_c and $H_{c'}$), 6.03 (br s, 1H, H_a), 5.81 (m, 1H, $\overline{\mathrm{C{=}C}H\mathrm{{-}(CH_2)_3{-}C}}\mathrm{H_2}$), 5.41 (dd, J(HH) = 17.5 Hz, J(HH) = 1.7 Hz) and 5.31 (dd, J(HH) = 17.5 Hz, J(HH) = 1.7 Hz) (2H, $H_{d-trans}$ and $H_{d'-trans}$), 5.24 (dd, J(HH) = 11.1 Hz, J(HH) = 1.7 Hz,) and 5.11 (dd, J(HH) = 10.7 Hz, J(HH) = 1.7 Hz) (2H, H_{d-cis} and $H_{d'-cis}$), 0.8–1.2 (m, 8H, $\overline{\mathrm{C{=}CH{-}(C}H_2\mathrm{)_3{-}C}}H_2$). MS m/z 160 (M$^+$).

CH$_2$=(CH$_3$)C-**HEX**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.75 (dd, J(HH) = 17.8 Hz, J(HH) = 11.1 Hz) and 6.46 (dd, J(HH) = 17.3 Hz, J(HH) = 11.0 Hz) (2H, H_c and $H_{c'}$), 6.09 (br s, 1H, H_a), 5.44 (dd, J(HH) = 17.3 Hz, J(HH) = 1.8 Hz) and 5.34 (dd, J(HH) = 17.8 Hz, J(HH) = 1.8 Hz) (2H, $H_{d-trans}$ and $H_{d'-trans}$), 5.28 (dd, J(HH) = 11.1 Hz, J(HH) = 1.8 Hz) and 5.14 (dd, J(HH) = 11.0 Hz, J(HH) = 1.8 Hz) (2H, H_{d-cis} and $H_{d'-cis}$), 5.11 and 5.00 (s, 2H,C(CH$_3$)=CH_2), 1.93 (s, 3H, C(CH_3)=CH$_2$). MS m/z 120 (M$^+$).

(CH$_3$)$_3$C-**HEX**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.64 (ddd, J(HH) = 18.0 Hz, J(HH) = 11.3 Hz, J(HH) = 1.0 Hz) and 6.35 (ddd, J(HH) = 17.3 Hz, J(HH) = 10.5 Hz, J(HH) = 1.0 Hz) (2H, H_c and $H_{c'}$), 5.60 (br s, 1H, H_a), 5.27 (dd, J(HH) = 11.3 Hz, J(HH) = 2.0 Hz) and 4.98 (dd, J(HH) = 10.5 Hz, J(HH) = 1.8 Hz) (2H, H_{d-cis} and $H_{d'-cis}$), 5.24 (dd, J(HH) = 17.3 Hz, J(HH) = 1.8 Hz) and 5.18 (dd, J(HH) = 18.0 Hz, J(HH) = 2.0 Hz) (2H, $H_{d-trans}$ and $H_{d'-trans}$), 1.15 (s, 9H, C(CH_3)$_3$). MS m/z 136 (M$^+$).

(C$_6$H$_5$)$_2$-**OCT**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.1–7.6 (m, 10H, C$_6$$H_5$), 6.98 (dd, J(HH) = 17.4 Hz, J(HH) = 10.5 Hz) and 6.65 (dd, J(HH) = 17.1 Hz, J(HH) = 10.3 Hz) (2H, H_c and $H_{c'}$), 6.65 and 6.45 (br s, 2H, H_a and $H_{a'}$), 5.37 (dd, J(HH) = 17.4 Hz, J(HH) = 1.75 Hz) and 5.28 (dd, J(HH) = 17.1 Hz, J(HH) = 1.5 Hz) (2H, $H_{d-trans}$ and $H_{d'-trans}$), 5.20 (dd, J(HH) = 10.5 Hz, J(HH) = 1.75 Hz) and 5.16 (dd, J(HH) = 10.3 Hz, J(HH) = 1.5 Hz) (2H, H_{d-cis} and $H_{d'-cis}$). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 140.5 and 132.0 (s, C_c and $C_{c'}$), 132.0 and 131.8 (s, C_a and $C_{a'}$), 118.4 and 115.6 (s, C_d and $C_{d'}$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.98 → 132.0; 6.65 → 140.5; 6.65 → 131.8; 6.45 → 132.0; 5.37, 5.20 → 118.4; 5.28, 5.16 → 115.6. MS m/z 258 (M$^+$).

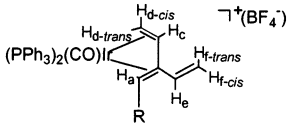
(C$_6$H$_5$)$_2$-**OCT**-d_2. ^{1}H NMR spectrum of the isotopomer (C$_6$H$_5$)$_2$-**OCT**-d_2 shows all the signals for (C$_6$H$_5$)$_2$-**OCT** except the resonance at δ 6.65 and 6.45 ppm assigned to H_a and $H_{a'}$ of (C$_6$H$_5$)$_2$-**OCT**. MS m/z 260 (M$^+$).

(*p*-CH$_3$-C$_6$H$_4$)$_2$-**OCT**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.1–7.6 (m, 8H, *p*-C$_6$$H_4CH_3$), 7.00 (dd, J(HH) = 16.8 Hz, J(HH) = 10.2 Hz) and 6.64 (dd, J(HH) = 17.1 Hz, J(HH) = 10.5 Hz) (2H, H_c and $H_{c'}$), 6.62 and 6.43 (br s, 2H, H_a and $H_{a'}$), 5.35 (d, *J*(HH) = 16.8 Hz) and 5.26 (d, *J*(HH) = 17.1 Hz) (2H, $H_{d-trans}$ and $H_{d'-trans}$), 5.18 (d, *J*(HH) = 10.2 Hz) and 5.13 (d, *J*(HH) = 10.5 Hz) (2H, H_{d-cis} and $H_{d'-cis}$), 2.40 and 2.31(s, 6H, $C_6H_5CH_3$). MS *m*/*z* 286 (M^+).

Detailed spectral data for (cyclohex-1-enyl)$_2$-**OCT**, (CH_2=(CH_3)C)$_2$-**OCT**, and ((CH_3)$_3$C)$_2$-**OCT** are not given here since we have not been able to obtain a large enough amount of these R_2-**OCT** in high purity to measure the detailed spectra. GC/mass spectra, however, unambiguously confirm (cyclohex-1-enyl)$_2$-**OCT** (*m*/*z* 266 (M^+)), (CH_2=(CH_3)C)$_2$-**OCT** (*m*/*z* 186 (M^+)), and ((CH_3)$_3$C)$_2$-**OCT** (*m*/*z* 218 (M^+)).

(b) Reactions of "Ir−A" and "Ir−B" with H_2. Both reactions were carried out in the same manner as described below for the reaction of "Ir−A" with H_2. A $CHCl_3$ (10 mL) solution of "Ir−A" (0.05 g) was stirred under H_2 (3 atm) at 25 °C for 24 h in a bomb reactor before *n*-pentane (10 mL) was added to precipitate beige microcrystals of $[Ir(H)_2(NCCH_3)_2(PPh_3)_2]OTf$ (**1**) which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.045 g. $[Ir(H)_2(CO)_2(PPh_3)_2]OTf$ (**1′**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4−7.7 (m, 30H, $P(C_6H_5)_3$), −9.91 (t, 2H, *J*(HP) = 14.4 Hz, Ir−*H*).^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.4 (t, *J*(CP) = 11.8 Hz, Ir−*C*O), 133.5, 132.7, 130.1 and 129.7 ($P(C_6H_5)_3$).^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ −16.3 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 2148 (w, ν_{Ir-H}), 2022, 2002 (s, ν_{CO}), 1270, 1151 and 1034 (s, due to uncoordinated OTf).

(c) Reactions of $Ir(-C{\equiv}CR)(-CH{=}CH_2)_2(CO)(PPh_3)_2$ (4, R = C_6H_5 (a), *p*-$CH_3C_6H_4$ (b), cyclohex-1-enyl (c)) with HBF_4: Formation of $[Ir(\eta^4$-R-HEX)(CO)$(PPh_3)_2]BF_4$ (5) and Detailed NMR Spectral Data Analysis for 5c. These reactions were carried out in the same manner as described below for the reaction of **4a**. A reaction mixture of **4a** (0.10 g, 0.1 mmol) and HBF_4 (8.4 μL, 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 beige microcrystals which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.092 g and 93% based on [Ir(η^4-C_6H_5-**HEX**)(CO)$(PPh_3)_2]BF_4$ (**5a**).



^{1}H NMR (500 MHz, $CDCl_3$): δ 6.8−7.5 (m, 36H, $P(C_6H_5)_3$, C_6H_5 and H_e), 5.87 (d, 1H, *J*(HH) = 17.5 Hz, $H_{f-trans}$), 5.74 (d, 1H, *J*(HH) = 11.0 Hz, H_{f-cis}), 5.61 (m, 1H, H_c), 2.44 (quartetlike, 1H, H_{d-cis}), 1.37 (dd, 1H, *J*(HP) = 11.3, 9.0 Hz, H_a), 0.29 (m, 1H, $H_{d-trans}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 172.5 (dd, *J*(CP) = 12.8 Hz, Ir−*C*O), 130.3 (br s, C_e), 124.7 (br s, C_f), 106.2 (br s, C_b), 85.5 (br s, C_c), 61.5 (d, *J*(CP) = 31.7 Hz, C_a), 39.3 (br s, C_d). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 5.87, 5.74 → 124.7; 5.61 → 85.5; 1.37 → 61.5; 2.44, 0.29 → 39.2. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 1.55 (d, *J*(PP) = 11.3 Hz, *P*Ph$_3$), −6.00 (d, *J*(PP) = 11.3 Hz, *P*Ph$_3$). IR (KBr, cm^{-1}): 2019 (s, ν_{CO}), 1057 (s, due to uncoordinated BF_4^-). Anal. Calcd for $IrBF_4OP_2C_{49}H_{42}$: C, 59.58; H, 4.29. Found: C, 59.87; H, 4.41.

[Ir(η^4-*p*-$C_6H_4CH_3$-**HEX**)(CO)$(PPh_3)_2]BF_4$ (**5b**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.8−7.5 (m, 34H, $P(C_6H_5)_3$ and *p*-$C_6H_4CH_3$), 6.83 (dd, 1H, *J*(HH) = 17.3 Hz, *J*(HH) = 10.7 Hz, H_e), 5.86 (d, 1H, *J*(HH) = 17.3 Hz, $H_{f-trans}$), 5.73 (d, 1H, *J*(HH) = 10.7 Hz, H_{f-cis}), 5.59 (m, 1H, H_c), 2.43 (quartetlike, 1H, H_{d-cis}), 2.37 (s, 3H, CH_3), 1.37 (dd, 1H, *J*(HP) = 11.0 and 8.8 Hz, H_a), δ 0.25 (m, 1H, $H_{d-trans}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 172.2 (d, *J*(CP) = 10.5 Hz, Ir−*C*O), 128.9 (br s, C_e), 124.5 (br s, C_f), 106.1 (br s, C_b), 85.5 (br s, C_c), 61.9 (d, *J*(CP) = 31.6 Hz, C_a), 39.3 (br s, C_d), 21.1 (s, *p*-$C_6H_4CH_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.83 → 128.9; 5.86, 5.73 → 124.5; 5.59 → 85.5; 2.37 → 21.1; 1.37 → 61.9; 2.43, 0.25 → 39.3. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 1.48 (d, *J*(PP) = 10.8 Hz, *P*Ph$_3$), −5.94 (d, *J*(PP) = 10.8 Hz, *P*Ph$_3$). IR (KBr, cm^{-1}): 2019 (s, ν_{CO}), 1062 (s, due to uncoordinated BF_4^-). Anal. Calcd for $IrBF_4OP_2C_{50}H_{44}$: C, 59.94; H, 4.43. Found: C, 60.26; H, 4.51.

[Ir(η^4-cyclohex-1-enyl-**HEX**)(CO)$(PPh_3)_2]BF_4$ (**5c**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.9−7.5 (m, 30H, $P(C_6H_5)_3$), 6.58 (dd, 1H, *J*(HH) = 17.5 Hz, *J*(HH) = 10.9 Hz, H_e), 5.96 (d, 1H, *J*(HH) = 17.5 Hz, $H_{f-trans}$), 5.77 (d, 1H, *J*(HH) = 10.9 Hz, H_{f-cis}), 5.62 (m, 1H, H_c), 5.17 (br s, 1H, Ir(η^4-($CH_2(CH_2)_3CH{=}C$)-**HEX**), 2.55 (quartetlike, 1H, H_{d-cis}), 1.4−2.0 (m, 8H, Ir(η^4-($CH_2(CH_2)_3CH{=}C$)-**HEX**), 0.61 (t, 1H, *J*(HP) = 9.5 Hz, *J*(HH) = 9.5 Hz, H_a), 0.04 (m, 1H, $H_{d-trans}$).^{13}C NMR (125.7 MHz, $CDCl_3$): δ 172.0 (d, *J*(CP) = 11.7 Hz, Ir−*C*O), 133.7 (d, *J*(CP) = 2.7 Hz, Ir(η^4-($CH_2(CH_2)_3CH{=}C$)-**HEX**)), 130.8 (d, *J*(CP) = 3.1 Hz, Ir(η^4-($CH_2(CH_2)_3CH{=}C$)-**HEX**)), 129.4 (d, *J*(CP) = 2.4 Hz, C_e), 123.3 (br s, C_f), 107.3 (t, *J*(CP) = 3.7 Hz, C_b), 84.2 (br s, C_c), 69.2 (d, *J*(CP) = 34.8 Hz, C_a), 38.5 (br s, C_d), 30.7 (d, *J*(CP) = 4.9 Hz, Ir(η^4-($CH_2(CH_2)_3-CH{=}C$)-**HEX**)), 25.6, 22.9, and 21.6 (s, Ir(η^4-($CH_2(CH_2)_3-CH{=}C$)-**HEX**)), 133.2, 133.1, 131.6, 131.4, 130.5, 130.1, 129.0 and 128.5 ($P(C_6H_5)_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 6.58 → 129.4; 5.96, 5.77 → 123.3; 5.62 → 84.2; 5.17 → 130.8; 0.61 → 69.2; 2.55, 0.04 → 38.5. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 5.71 (d, *J*(P−P) = 10.3 Hz, *P*Ph$_3$), −7.76 (d, *J*(P−P) = 10.3 Hz, *P*Ph$_3$). IR (KBr, cm^{-1}): 2011 (s, ν_{CO}), 1063 (s, due to uncoordinated BF_4^-). Anal. Calcd for $IrBF_4OP_2C_{49}H_{46}$: C, 59.34, H, 4.67. Found: C, 59.62; H, 4.74. ^{1}H NMR spectrum of **5c** shows the four terminal olefinic protons of the two $-CH{=}CH_2$ groups at δ 5.77 (H_{f-cis}), 5.96 ($H_{f-trans}$), 0.04 ($H_{d-trans}$), and 2.55 (H_{d-cis}). The large separation between the two groups (H_d at δ 0.04−2.55 and H_f at δ 5.77−5.96) strongly suggests that these two groups are very much different in interaction with the central metal suggesting one $-CH{=}CH_2$ group (H_{d-cis} and $H_{d-trans}$) being coordinated to the metal and the other (H_{f-cis} and $H_{f-trans}$) being free from the metal as shown by **5c**. The larger NOE enhancement between H_c and $H_{f-trans}$ (4.50%) and the smaller one between H_c and H_e (0.86%) on irradiation at H_c (δ 5.70) resonance of **5c** also strongly suggest a shorter distance between H_c and $H_{f-trans}$ than the one between H_c and H_e.

(d) Reactions of $Ir(-C{\equiv}CR)(-CH{=}CH_2)_2(CO)(PPh_3)_2$ (4, R = C_6H_5 (a), *p*-$CH_3C_6H_4$ (b), cyclohex-1-enyl (c)) with DBF_4: Formation of [Ir(η^4-R-HEX-*d_1*)(CO)$(PPh_3)_2]BF_4$ (5-*d_1*). Reactions with deutrated acid, DBF_4, were carried out in the same manner as described above for that of **4a**. ^{1}H NMR spectra of the isotopomer [Ir(η^4-R-**HEX**-d_1)(CO)$(PPh_3)_2]BF_4$ (**5**-d_1) show all the signals for **5** except the resonance assigned to H_a of **5**.

(e) Reactions of [Ir(η^4-R-HEX)(CO)$(PPh_3)_2]BF_4$ (5, R = C_6H_5 (a), *p*-$CH_3C_6H_4$ (b), cyclohex-1-enyl (c)) with Et_4NCl, CH_3CN, or PPh_3. These reactions were carried out in a similar manner as described below for the reaction of **5a** with Et_4NCl. A light brown solution of **5a** (0.1 mmol) and Et_4NCl (0.025 g, 0.15 mmol) in $CHCl_3$ (10 mL) was stirred at 25 °C under N_2 for 1 h before excess Et_4NCl was removed by extraction with H_2O (2 × 10 mL). Addition of *n*-pentane (30 mL) resulted in yellow microcrystals of $IrCl(CO)(PPh_3)_2$[12] which were removed by filtration. The filtrate was concentrated to less than 1.0 mL by distillation at 25 °C under vacuum and the residue was eluted through a silica gel column with *n*-hexane to obtain C_6H_5-**HEX**. The yield was 0.089 mmol and 89% based on C_6H_5-**HEX** measured by ^{1}H NMR.

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[12] (a) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100. (b) *Inorg. Synth.* **1968**, *11*, 101.

$IrCl(CO)(PPh_3)_2$, $[Ir(NCCH_3)(CO)(PPh_3)_2]BF_4$,[13] and $[Ir(CO)(PPh_3)_3]BF_4$[14] obtained from the reactions of **5** with Et_4NCl, CH_3CN, or PPh_3, respectively, have been identified by ^1H NMR and IR spectral measurements.

(f) Reactions of 7 and 8 with HBF_4 followed by Treatment with Et_4NCl, CH_3CN, or PPh_3: Isolation of *p*-C_6H_4-(HEX)$_2$ and *m,m*-C_6H_3-(HEX)$_3$. These reactions were carried out in the same manner as described above for those of **4** with HBF_4 and of **5** with Et_4NCl, CH_3CN, or PPh_3. The yields of light yellow microcrystals of *p*-C_6H_4-(**HEX**)$_2$ and yellow oil of *m,m*-C_6H_3-(**HEX**)$_3$ were ca. 79% based on *p*-C_6H_4-(**HEX**)$_2$ and ca. 81% based on *m,m*-C_6H_3-(**HEX**)$_3$ measured by ^1H NMR, respectively.

p-C_6H_4-(**HEX**)$_2$: ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 (s, 4H, C_6H_4), 6.62 (br s, 2H, H_a), 6.73 (dd, $J(HH) = 17.8$ Hz, $J(HH) = 11.0$ Hz) and 6.56 (dd, $J(HH) = 17.3$ Hz, $J(HH) = 10.8$ Hz) (4H, H_c and $H_{c'}$), 5.55 (dd, $J(HH) = 17.3$ Hz, $J(HH) = 1.5$ Hz) and 5.48 (dd, $J(HH) = 17.8$ Hz, $J(HH) = 1.5$ Hz) (4H, $H_{d-trans}$ and $H_{d'-trans}$), 5.39 (dd, $J(HH) = 11.0$ Hz, $J(HH) = 1.5$ Hz) and 5.22 (dd, $J(HH) = 10.8$ Hz, $J(HH) = 1.5$ Hz) (4H, H_{d-cis} and $H_{d'-cis}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 138.0 and 133.5 (s, C_c and $C_{c'}$), 129.2 (s, C_a), 118.6 and 116.1 (s, C_d and $C_{d'}$), 138.0 and 136.0 (C_b and C_{ipso} of C_6H_4 carbons), 129.5 (CH of C_6H_4 carbons). Mp 48−49 °C. Electronic absorption: $\lambda_{max} = 333$ nm. MS *m/z* 234 (M^+).

m,m-C_6H_3-(**HEX**)$_3$: ^1H NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 3H, C_6H_3), 6.62 (br s, 3H, H_a), 6.72 (dd, $J(HH) = 17.8$ Hz, $J(HH) = 11.5$ Hz) and 6.56 (dd, $J(HH) = 17.1$ Hz, $J(HH) = 10.5$ Hz) (6H, H_c and $H_{c'}$), 5.56 (dd, $J(HH) = 17.1$ Hz, $J(HH) = 1.5$ Hz) and 5.47 (dd, $J(HH) = 17.8$ Hz, $J(HH) = 1.5$ Hz) (6H, $H_{d-trans}$ and $H_{d'-trans}$), 5.39 (dd, $J(HH) = 11.5$ Hz, $J(HH) = 1.5$ Hz) and 5.23 (dd, $J(HH) = 10.5$ Hz, $J(HH) = 1.5$ Hz) (6H, H_{d-cis} and $H_{d'-cis}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 137.8 and 133.4 (s, C_c and $C_{c'}$), 129.8 (s, C_a), 118.6 and 116.3 (s, C_d and $C_{d'}$), 138.3 and 136.7 (C_b and C_{ipso} of C_6H_3 carbons), 129.2 (CH of C_6H_3 carbons). Electronic absorption: $\lambda_{max} = 303$ nm. MS *m/z* 312 (M^+).

X-ray Structure Determination of Ir(−C≡C-cyclohex-1-enyl)(−CH=CH$_2$)$_2$(CO)(PPh$_3$)$_2$ (4c). Crystals were grown from $CHCl_3$. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation at 20 °C. Accurate cell parameters were determined from the least-squares fit of 24 accurately centered reflections in each selected range. All data were collected with the *ω/2θ* scan modes, and corrected *Lp* effects and absorption. The structures of these compounds were solved by Patterson's heavy atom methods (SHELXS-97). Details of crystallographic data collection are listed in Table 2. Bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters have been included in the tables of Supporting Information. The non-hydrogen atom was refined by full-matrix least-squares techniques (SHELXL-97). All hydrogen atoms were placed at their geometrically calculated positions (d(CH) = 0.960 Å for methyl and 0.930 Å for aromatic) and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The final R_1 and wR_2 ($R_1 = [\sum|F_o| - |F_c|/|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$) values were 0.0486 and 0.1578.

Table 2. Details of Crystallographic Data Collection for 4c[a]

chemical formula	$C_{49}H_{45}IrOP_2$
fw	903.99
temp, K	293(2)
cryst size, mm^3	0.8 × 0.3 × 0.2
cryst system	monoclinic
space group	$P2_1/n$
color of crystal	yellow
a, Å	10.1830(10)
b, Å	18.715(2)
c, Å	21.413(4)
α, deg.	90.00
β, deg.	95.110(10)
γ, deg.	90.00
V, Å^3	4064.6(10)
Z	4
$\rho_{(calc)}$, g cm^{-1}	1.477
μ, mm^{-1}	3.400
F(000)	1816
radiation	Mo Kα
wavelength	0.7107
2θ max, deg	50
hkl range	$-10 \le h \le 10$ $-1 \le k \le 19$ $-22 \le l \le 22$
no. of reflcns	4949
no. of unique data	4319
no. of obsd ($\lvert F_o\rvert > 2\sigma F_o$) data	3849
no. of parameters	478
scan type	$\omega/2\theta$ scan
R_1	0.0486
wR_2	0.1578
GOF	1.132

[a] $R_1 = [\sum|F_o| - |F_c|/|F_o|]$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$, $w = 1/[\sigma^2F_o^2 + (0.0865P)^2 + 28.8775P]$, where $P = (F_o^2 + 2F_c^2)/3$.

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Supporting Information Available: Tables of bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters for complex **4c** in CIF format and ^1H NMR (for **2**, **2**-d_2, **4c**, **5c**, **6a**, **7**, **8**, C_6H_5-**HEX**, C_6H_5-**HEX**-d_1, $(C_6H_5)_2$-**OCT**, $(C_6H_5)_2$-**OCT**-d_2, *p*-C_6H_4-(**HEX**)$_2$, and *m,m*-C_6H_3-(**HEX**)$_3$), ^{13}C NMR (for **2**, **4c**, **5c**, and **6a**), ^1H NOE (for **5c**), ^1H,^{13}C-2D HETCOR (for **2**, **5c**, and **6a**), GC/mass (for C_6H_5-**HEX**, C_6H_5-**HEX**-d_1, $(C_6H_5)_2$-**OCT**, $(C_6H_5)_2$-**OCT**-d_2, *p*-C_6H_4-(**HEX**)$_2$, and *m,m*-C_6H_3-(**HEX**)$_3$), and FAB mass (for **7** and **8**) data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020410R

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