New Iridacyclohexadienes and Iridabenzenes by [2+2+1] Cyclotrimerization of Alkynes and Facile Interconversion between Iridacyclohexadienes and Iridabenzenes

Chong Shik Chin* and Hyungeui Lee*[a]

Abstract: Iridabenzenes $[\mathrm{Ir}\{{=}\mathrm{CHCH}{=}\mathrm{CHCH}{=}\mathrm{C(CH_2R)}\}(\mathrm{CH_3CN})_2(\mathrm{PPh_3})_2]^{2+}$ (R = Ph **4a**, R = p-$\mathrm{C_6H_4CH_3}$ **4b**) are obtained from the reactions of $\mathrm{H^+}$ with iridacyclohexadienes $[\mathrm{Ir}\{{-}\mathrm{CH}{=}\mathrm{CHCH}{=}\mathrm{CHC}({=}\mathrm{CH}\text{-}p\text{-}\mathrm{C_6H_4R'})\}(\mathrm{CO})(\mathrm{PPh_3})_2]^+$ (R′ = H **3a**, R′ = $\mathrm{CH_3}$ **3b**), which are prepared from [2+2+1] cyclotrimerization of alkynes in the reactions of $[\mathrm{Ir}(\mathrm{CH_3CN})(\mathrm{CO})(\mathrm{PPh_3})_2]^+$ with HC≡CH and HC≡CR. Iridabenzenes **4** react with CO and $\mathrm{CH_3CN}$ in the presence of $\mathrm{NEt_3}$ to give iridacyclohexadienes $[\mathrm{Ir}\{{-}\mathrm{CH}{=}\mathrm{CHCH}{=}\mathrm{CHC}({=}\mathrm{CHR})\}(\mathrm{CO})_2(\mathrm{PPh_3})_2]^+$ (**6**) and $[\mathrm{Ir}\{{-}\mathrm{CH}{=}\mathrm{CHCH}{=}\mathrm{CHC}({=}\mathrm{CHR})\}(\mathrm{CH_3CN})_2(\mathrm{PPh_3})_2]^+$ (**7**), respectively. Iridacyclohexadienes **6** and **7** also convert to iridabenzenes **4** by the reactions with $\mathrm{H^+}$ in the presence of $\mathrm{CH_3CN}$. Alkynyl iridacyclohexadienes $[\mathrm{Ir}\{{-}\mathrm{CH}{=}\mathrm{CHCH}{=}\mathrm{CHC}({=}\mathrm{CH}\text{-}p\text{-}\mathrm{C_6H_4R'})\}({-}\mathrm{C{\equiv}CH})(\mathrm{PPh_3})_2]$ (**8**) undergo a cleavage of C≡C bond by $\mathrm{H^+/H_2O}$ to produce $[\mathrm{Ir}\{{-}\mathrm{CH}{=}\mathrm{CHCH}{=}\mathrm{CHC}({=}\mathrm{CH}\text{-}p\text{-}\mathrm{C_6H_4R'})\}({-}\mathrm{CH_3})(\mathrm{CO})(\mathrm{PPh_3})_2]$ (**10**) via facile inter-conversion between iridacyclohexadienes and iridabenzenes.

Keywords: alkynes · C–C coupling · diene ligands · iridium · metallacycles · vinylidene ligands

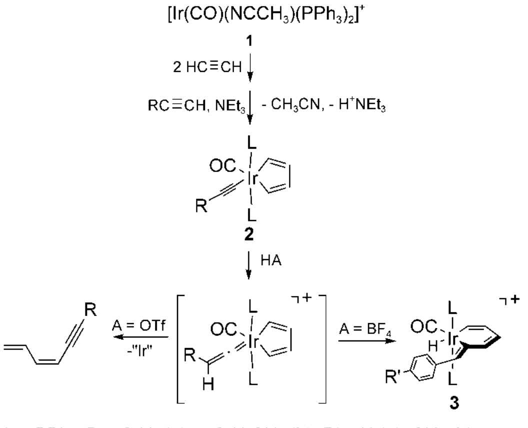
Introduction

Transition-metal-mediated reactions of alkynes have been extensively investigated, since they provide interesting compounds, such as metallacycles containing unsaturated five- and six-membered rings,[1–3] that are of great interest as the key intermediates for C–C bond forming reactions between alkynes.[2c,3,4] Among metallacycles, metallacyclopentadienes are well known as intermediates for cyclotrimerization of alkynes[3] and their reactions toward the alkynes have been studied extensively.[5] Unsaturated six-membered metallacycles, such as metallacyclohexadienes[6]and metallabenzenes,[7] have been also reported. While much attention has been recently paid to metallabenzenes, detailed investigation has been rarely carried out for their formation from the reactions of metals with alkynes and their reactivity.

We recently reported the proton-initiated reactions between the alkynyl and 1,3-butadiene-1,4-diyl ligands of $[\mathrm{Ir}({-}\mathrm{CH}{=}\mathrm{CHCH}{=}\mathrm{CH})(\mathrm{C{\equiv}CR})(\mathrm{CO})(\mathrm{PPh_3})_2]$ (**2**)[5d] to produce iridacyclohexadienes[2e]$[\mathrm{Ir}\{{-}\mathrm{CH}{=}\mathrm{CHCH}{=}\mathrm{CHC}({=}\mathrm{CH}\text{-}p\text{-}\mathrm{C_6H_4R'})\}(\mathrm{CO})(\mathrm{PPh_3})_2]\mathrm{BF_4}$ (**3**) and $\mathrm{RC{\equiv}CCH{=}CHCH{=}CH_2}$,[2c,e] respectively, from the reactions of **2** with $\mathrm{HBF_4}$ and HOTf (Scheme 1).

It has been unprecedented that iridacyclohexadienes[2e] have been isolated from the [2+2+1] cyclotrimerization between alkynes, although iridacycloheptatrienes,[8] iridium–aryls[5a] and iridium–fulvenes[5c] have been previously reported from cyclotrimerization of alkynes.

We now wish to report a new simple way of preparing iridabenzenes from iridacyclohexadienes and facile interconversion between iridacyclohexadienes and iridabenzenes.



L = PPh3; R = C6H5 (**a**), p-C6H4CH3 (**b**); R′ = H (**a**), CH3 (**b**)

Scheme 1. Trimerization of alkynes: formation of linear conjugated dienynes and iridacyclohexadienes.

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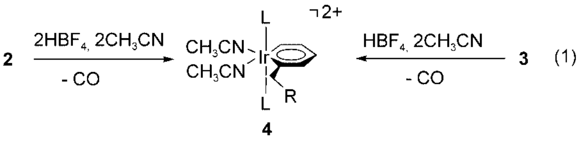
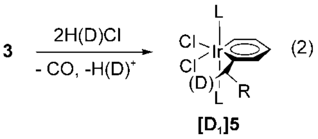
Results and Discussion

cis-Bis(acetonitrile)iridabenzenes **4** are obtained from the reactions of iridacyclopentadienes **2** with excess HBF_4 in the presence of CH_3CN [Eq. (1)], whereas the reactions of **2** with an excess of HBF_4 in the absence of CH_3CN give iridacyclohexadienes **3** (see Scheme 1). In the presence of CH_3CN, complexes **3** also react with HBF_4 to give iridabenzenes **4** [Eq. (1)].



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

The reactions of iridacyclohexadienes **3** with HCl and DCl give dichlolo-iridabenzenes, $[Ir\{=CH{-}CH{=}CH{-}CH{=}C(CH_2R)\}(Cl)_2(PPh_3)_2]$ (R = Ph **5a**, R = *p*-$C_6H_4CH_3$ **5b**) and $[Ir\{=CH{-}CH{=}CH{-}CH{=}C(CHDR)\}(Cl)_2(PPh_3)_2]$ (**[D$_1$]5**), respectively [Eq. (2)].



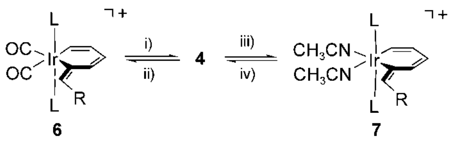
L = PPh_3, R = Ph (**a**), *p*-tolyl (**b**)

The formation of **[D$_1$]5** suggests that methylene carbon (=CH-*p*-C_6H_4R'; R' = H (**a**), CH_3 (**b**)) of aryl methenyl group in **3** is attacked by a proton.

Osmabenzene[7f] and osmabenzyne[9] are prepared from the reactions with alkynes, and, more recently, iridabenzene[7a] and iridanaphthalene[7a] have been obtained from the reactions of iridacycloheptatrienes[8] prepared from the [2+2+2] cyclotrimerization of alkynes. However, no report has been made previously on iridabenzenes formed from [2+2+1] cyclotrimerization of alkynes via iridacyclopentadienes.

Iridabenzenes **4** readily lose H^+ in the presence of a base such as CO and NEt_3 to produce the 18-electron iridacyclohexadienes **6** and **7** (Scheme 2), which are also obtained from the reactions of **3** with CO and CH_3CN, respectively.[2e,10]

Iridabenzenes **4** are regenerated from the reactions of **6** and **7** with acid (H^+) in the presence of CH_3CN (Scheme 2).



L = PPh_3, R = Ph (**a**), *p*-tolyl (**b**)

Scheme 2. i) $2CH_3CN$, $H^+/-2CO$; ii) $2CO/-2CH_3CN$, $-H^+$; iii) $NEt_3/-H^+NEt_3$; iv) H^+.

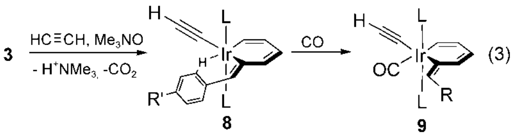
It is somewhat unusual that the two CO ligands of **6** are readily replaced by two CH_3CN (more labile ligand than CO in general) to give the iridabenzenes **4** (Scheme 2), and it may be mentioned that no evidence has been yet obtained for the formation of dicarbonyliridabenzenes $[Ir\{=CH{-}CH{=}CH{-}CH{=}C(CH_2R)\}(CO)_2(PPh_3)_2]^{2+}$.

This facile interconversion between iridacyclohexadienes (**6** and **7**) and iridabenzenes (**4**) (Scheme 2) supports the iridabenzene intermediates previously suggested (but not isolated) during the novel interconversion between iridacyclohexadienes (**3**→**6** under CO, **3**→**7** in CH_3CN).[2e,10]

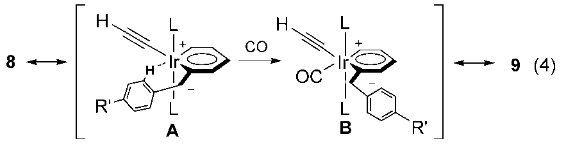
It may be said that this facile interconversion occurs due to the amphiprotic carbon ($Ir{-}CH({=}CH$-*p*-$C_6H_4R'){-}CH{=}CHCH{=}CH$) bound to the α-carbon of iridacyclohexadienes.

Other types of alkynyliridacyclohexadienes (**8** and **9**) have been prepared [Eq. (3)] in the hope that the same type of the C–C bond formation would occur to give new types of iridacycles as seen with **2** in Scheme 1.

The addition of CO to **8** may occur via iridabenzenes intermediates (**A** and **B**) [Eq. (4)].



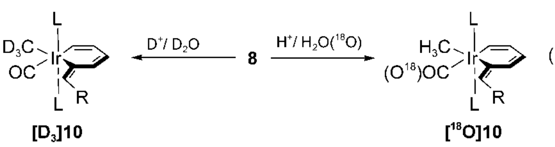
L = PPh_3, R = Ph (**a**), *p*-tolyl (**b**), R' = H (**a**), CH_3 (**b**)



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

Unlike the alkynyliridacyclopentadienes **2**, the alkynyl iridacyclohexadienes **8** and **9** do not undergo the proton-initiated C–C bond forming reaction between the alkynyl and 1,3-pentadiene-1,5-diyl ligands. Both **8** and **9** react with H^+ to produce iridabenzenes **4** and HC≡CH in the presence of excess CH_3CN and unknown complexes and HC≡CH in the absence of CH_3CN.

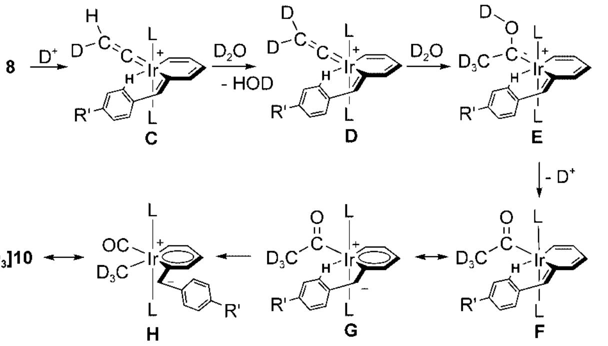
In the absence of CH_3CN, the reactions of **8** with H^+/H_2O afford the methylcarbonyliridacyclohexadienes **10** [Eq. (5)], whereas unknown compounds are obtained from reactions of **9** with aqueous H^+. These results are strikingly different from those of the other 16-electron carbonyliridacyclohexadienes **3**, which are not reactive with H^+ at all in the absence of CH_3CN.



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

The newly prepared complexes **4**, **5**, **8**, **9**, and **10** were unambiguously characterized by detailed spectral and elemental analysis data (see Experimental Section and Supporting Information).

Metal–vinylidenes (M=C=CHR) are frequently observed and suggested in the reactions of metal–alkynyls (M−C≡CR) with protons.[2,11,12] The α-carbon atom (M=*C*=CHR) of the vinylidene group is known to be so electrophilic that it readily interacts with a nucleophile.[12] A detailed mechanistic study for C≡C bond cleavage by water was previously reported.[12a,b] Isotopomers **[^{18}O]10** and **[D$_3$]10** are obtained from reactions of **8** with $H^+/H_2{}^{18}O$ and D^+/D_2O, respectively [Eq. (5)]. These results lead us to suggest the mechanism depicted in Scheme 3, which includes 1) the cleavage of C≡C bond of the alkynyl ligand with water by means of well-established pathways[12a,b] and 2) the alkyl group (CH_3) migration from the acyl ligand (CH_3CO-Ir) to the metal; this seems to be facilitated by the formation of iridabenzene intermediates **H** and **G**.



L = PPh$_3$, R' = H (**a**), CH$_3$ (**b**)

Scheme 3. Plausible reaction pathways for the cleavage of C≡C bond by means of facile interconversion between iridacyclohexadienes and iridabenzenes.

Conclusion

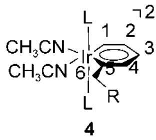
In conclusion, new iridacyclohexadienes and iridabenzenes have been prepared from reactions of alkynyl iridacyclopentadienes with H$^+$. Reversible interconversion between iridacyclohexadienes and iridabenzenes is feasible under the appropriate conditions. Alkynyliridacyclohexadienes, unlike alkynyliridacyclopentadienes, do not undergo the proton-initiated C−C bond forming reactions between the hydrocarbyl ligands, but undergo the alkyne abstraction reaction from the metal in the presence of H$^+$ (non-aqueous) and C≡C bond cleavage reaction of the alkynyl ligand in the presence of aqueous H$^+$.

Experimental Section

General: 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. $HBF_4 \cdot OEt_2$ (54 wt% in Et_2O), DCl, and $H_2{}^{18}O$ were purchased from Aldrich and [Ir{−CH=CHCH=CHC(=CH-*p*-C_6H_4R')}(CO)(PPh_3)$_2$]BF_4 (**3**) were prepared by the literature method.[2e]

Instruments: NMR spectra were recorded on a Varian 300 or 500 MHz spectrometer for ^{1}H, 125.7 MHz for ^{13}C, and 81 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205 spectrometer. Elemental analyses were carried out with a Carlo Erba EA1108 at the Organic Chemistry Center, Sogang University (Korea).

Preparation of [Ir{=CHCH=CHCH=C(CH$_2$R)}(CH$_3$CN)$_2$(PPh$_3$)$_2$][BF$_4$]$_2$ (R = Ph 4a, R = *p*-C$_6$H$_4$CH$_3$ 4b): A reaction mixture of **3a** (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 in the presence of CH_3CN (0.010 g, 0.24 mmol). Et_2O (30 mL) was added to precipitate light purple micro-crystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL) and dried under vacuum. The yield was 0.09 g and 95 % based on **4a**.



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Data for 4a: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 13.99$ (d, $J(H,H) = 6.9$ Hz, 1H; *H*1), 7.3–7.6 (m, 38H; P(C$_6$*H*$_5$)$_3$, Ph, *H*2, *H*3, *H*4), 3.93 (s, 2H; -C*H*$_2$Ph), 2.17, 1.97 ppm (s, 6H; C*H*$_3$CN); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -7.08$ ppm (s; *P*Ph$_3$). elemental analysis calcd (%) for $IrP_2C_{52}H_{47}N_2B_2F_8$: C 55.38, H 4.20, N 2.48; found: C 55.94, H 4.47, N 2.58.

Data for 4b: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 13.90$ (d, $J(H,H) = 7.5$ Hz, 1H; *H*1), 7.3–7.6 (m, 32H; P(C$_6$*H*$_5$)$_3$, *H*2, *H*3), 6.68–7.14 (AB quartet with $\delta\nu/J = 56.62$, $J(H_A,H_B) = 8.0$ Hz, 4H; *p*-C$_6$*H*$_4$CH$_3$), 6.88 (d, $J(H,H) = 8.0$ Hz, 1H; *H*4), 3.87 (s, 2H; -C*H*$_2$C$_6$H$_4$CH$_3$), 2.35 (s, 3H; -CH$_2$C$_6$H$_4$C*H*$_3$), 2.14, 1.93 ppm (s, 6H; C*H*$_3$CN); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 (C): $\delta = 238.40$ (br s; *C*5), 213.51 (br s; *C*1), 162.94, 131.12 (2 s; *C*2, *C*3), 131.90 (s; *C*4), 59.76 (s; -*C*H$_2$C$_6$H$_4$CH$_3$), 21.05 (s; -CH$_2$C$_6$H$_4$*C*H$_3$), 4.32, 3.10 (s; *C*H$_3$CN), 127.36, 126.58 (s; CH$_3$*C*N), 129.78, 129.28 (CH carbons of CH$_2$*C*$_6$H$_4$CH$_3$), 134.27, 132.52, 129.15, 124.56 ppm (P(*C*$_6$H$_5$)$_3$); HETCOR (^{1}H (500 MHz)→^{13}C (125.7 MHz)): $\delta = 13.90 \rightarrow 213.51$; $6.88 \rightarrow 131.90$; $3.87 \rightarrow 59.76$; $2.35 \rightarrow 21.05$; $2.14 \rightarrow 4.32$; $1.93 \rightarrow 3.10$ ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 7.01$ ppm (s; *P*Ph$_3$); IR (KBr): $\tilde{\nu} = 2321$ and 2291 (w, C≡N), 1064 cm^{-1} (s, due to non-coordinated $BF_4{}^-$); elemental analysis calcd (%) for $IrP_2B_2F_8C_{52}H_{47}N_2$: C 55.38, H 4.20, N 2.48; found: C 55.42, H 4.46, N 2.51.

Preparation of [Ir{=CHCH=CHCH=C(CH$_2$R)}(Cl)$_2$(PPh$_3$)$_2$] (R = Ph 5a, R = *p*-C$_6$H$_4$CH$_3$ 5b): A reaction mixture of **3a** (0.10 g, 0.1 mmol) in $CHCl_3$ (10 mL) and aqueous solution of HCl (0.25 mmol, 0.004 mL of H_2O containing 37 wt% HCl) was stirred at 25 °C for 3 h before excess HCl was removed by washing with H_2O. Addition of *n*-pentane (30 mL) resulted in purple microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL) and dried under vacuum. The yield was 0.094 g and 93 % based on **5a**.

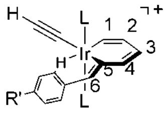
Data for 5a: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 13.95$ (d, $J(H,H) = 7.8$ Hz, 1H; *H*1), 7.2–7.7 (m, 30H; P(C$_6$*H*$_5$)$_3$), 7.48 (br t, $J(H,H) = 8.1$ Hz, 1H; *H*3), 6.99–7.07 (m, 3H; *m*-, *p*-protons of C$_6$*H*$_5$), 6.60 (d, $J(H,H) = 9.0$ Hz, 1H; *H*4), 6.48 (t, $J(H,H) = 7.8$ Hz, 1H; *H*2), 5.88 (d, $J(H,H) = 8.1$ Hz, 2H; *o*-protons of C$_6$*H*$_5$), 4.26 ppm (s, 2H; -C*H*$_2$C$_6$H$_5$); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -12.56$ ppm (s; *P*Ph$_3$); elemental analysis calcd (%) for $IrP_2C_{48}H_{41}Cl_2$: C 61.14, H 4.38; found: C 61.21, H 4.43.

Data for 5b: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 13.93$ (d, $J(H,H) = 7.5$ Hz, 1H; *H*1), 7.2–7.7 (m, 30H; P(C$_6$*H*$_5$)$_3$), 7.48 (br t, $J(H,H) = 7.0$ Hz, 1H; *H*3), 5.78–6.85 (AB quartet with $\delta\nu/J = 35.62$, $J(H_A,H_B) = 7.8$ Hz, 4H; *p*-C$_6$*H*$_4$CH$_3$), 6.63 (d, $J(H,H) = 9.0$ Hz, 1H; *H*4), 6.48 (t, $J(H,H) = 7.8$ Hz, 1H; *H*2), 4.24 (s, 2H; -C*H*$_2$C$_6$H$_4$CH$_3$), 2.26 ppm (s, 3H; -CH$_2$C$_6$H$_4$C*H*$_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 243.27$ (br s; *C*5), 223.85 (br s; *C*1), 157.08 (s; *C*3), 128.80 (s; *C*2), 128.26 (s; *C*4), 61.94 (s; -*C*H$_2$C$_6$H$_4$CH$_3$), 20.97 (s; -CH$_2$C$_6$H$_4$*C*H$_3$), 130.19, 125.64 (CH carbons of CH$_2$*C*$_6$H$_4$CH$_3$), 135.17, 130.52, 130.03, 127.40 ppm (P(*C*$_6$H$_5$)$_3$); ^{31}P{^{1}H}

NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -12.50$ ppm (s; *P*Ph_3); elemental analysis calcd (%) for $IrP_2C_{49}H_{43}Cl_2$: C 61.50, H 4.53; found: C 61.29, H 4.47.

Data for [D$_1$]5a: Reactions with deuterated acid, DCl were carried out in the same manner as described above for that of **5a**. ^1H NMR spectrum of the isotopomer **[D$_1$]5a** shows the decreased intensity of the signals due to [Ir{=CH–CH=CH–CH=C(CH**D**Ph)}(Cl)$_2$(PPh_3)$_2$] at $\delta = 4.26$ ppm.

Preparation of [Ir{–CH=CHCH=CHC(=CH-*p*-C_6H_4R')}(–C≡CH)(PPh_3)$_2$] (R′ = H 8a, R′ = CH_3 8b): A solution of **3a** (0.1 g, 0.1 mmol) and Me_3NO (0.019 g, 0.25 mmol) in $CHCl_3$ (10 mL) was stirred under HC≡CH (1 atm) at 25 °C for 30 min before the dark red solution turned dark orange. Excess Me_3NO and $[HNMe_3]BF_4$ were removed by extraction with H_2O (2 × 10 mL). Addition of *n*-hexane (10 mL) resulted in precipitation of dark orange microcrystals, which were collected by filtration, washed with *n*-hexane (3 × 10 mL), and dried under vacuum. The yield was 0.1 g or 96 % based on **8a**.



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Data for 8a: ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.2$–7.8 (m, 30H; P(C_6H_5)$_3$), 7.51 (m, 1H; *H1*), 7.00 (t, *J*(H,H) = 7.8 Hz, 2H; *m*-protons of C_6H_5), 6.55 (t, *J*(H,H) = 7.3 Hz, 1H; *p*-proton of C_6H_5), 6.30 (t, *J*(H,H) = 3.5 Hz, 1H; *H6*), 5.44 (ddt, *J*(H,H) = 6.8 Hz, *J*(H,H) = 6.8 Hz, *J*(H,H) = 3.2 Hz, 1H; *H2*), 5.19 (d, *J*(H,H) = 10.5 Hz, 1H; *H4*), 5.02 (dd, *J*(H,H) = 10.5 Hz, *J*(H,H) = 6.8 Hz, 1H; *H3*), 4.79 (br, 2H; agostic hydrogen atoms of C_6H_5), 2.48 ppm (t, *J*(H,P) = 1.75 Hz, 1H; C≡C*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 173.68$ (t, *J*(C,P) = 10.4 Hz; *C5*), 148.92 (s; *C7*), 141.38 (t, *J*(C,P) = 5.8 Hz; *C6*), 134.57 (brs; *C4*), 131.55 (t, *J*(C,P) = 11.3 Hz; *C1*), 130.95 (s; *m*-C C_6H_5), 125.70 (t, *J*(C,P) = 3.7 Hz; *C3*), 123.37 (s; *o*-C C_6H_5), 122.55 (s; *p*-C C_6H_5), 120.45 (t, *J*(C,P) = 5.2 Hz; *C2*), 107.16 (t, *J*(C,P) = 14.1 Hz; Ir–*C*≡CH), 104.78 ppm (s; Ir-C≡*C*H). HETCOR (^1H (500 MHz)→^{13}C (125.7 MHz)): $\delta = 7.51 \rightarrow 131.55$, $7.00 \rightarrow 130.95$, $6.55 \rightarrow 122.55$; $6.30 \rightarrow 141.38$; $5.44 \rightarrow 120.45$, $5.19 \rightarrow 134.57$, $5.02 \rightarrow 125.70$; $4.79 \rightarrow 123.37$, $2.48 \rightarrow 104.78$ ppm; ^{31}P NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 4.036$ ppm (s; *P*Ph_3); IR (KBr): $\tilde{\nu} = 1954$ cm^{-1} (m, C≡C); elemental analysis calcd (%) for $IrP_2C_{50}H_{41}$: C 67.02, H 4.61; found: C 67.10, H 4.63.

Data for 8b: ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.2$–7.7 (m, 30H; P(C_6H_5)$_3$), 7.50 (m, 1H; H_1), 6.78 (brd, *J*(H,H) = 7.5 Hz, 2H; *m*-protons of *p*-$C_6H_4CH_3$), 6.25 (t, *J*(H,P) = 3.5 Hz, 1H; *H6*), 5.43 (m, 1H; *H2*), 5.07 (d, *J*(H,H) = 10.0 Hz, 1H; *H4*), 4.93 (brt, *J*(H,H) = 6.5 Hz, 1H; *H3*), 4.76 (br, 2H; agostic *o*-protons of *p*-$C_6H_4CH_3$), 2.47 (t, *J*(H,P) = 1.5 Hz, 1H; C≡C*H*), 2.09 ppm (s, 3H; *p*-$C_6H_4CH_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 171.41$ (t, *J*(C,P) = 10.3 Hz; *C5*), 146.80 (s; *C7*), 140.75 (t, *J*(C,P) = 6.2 Hz; *C6*), 134.09 (brs; *C4*), 131.93 (s; *C9*), 130.68 (t, *J*(C,P) = 11.0 Hz; *C1*), 129.88 (s; *C10*), 125.22 (t, *J*(C,P) = 4.1 Hz; *C3*), 122.65 (s; *C8*), 120.63 (t, *J*(C,P) = 4.9 Hz; *C2*), 106.85 (t, *J*(C,P) = 14.1 Hz; Ir-*C*≡CH), 104.94 (s; Ir-C≡*C*H), 20.84 ppm (s; *p*-$C_6H_4CH_3$); HETCOR (^1H NMR (500 MHz)→^{13}C NMR (125.7 MHz)): $\delta = 7.50 \rightarrow 130.68$, $6.78 \rightarrow 131.93$, $6.25 \rightarrow 140.75$, $5.43 \rightarrow 120.63$, $5.07 \rightarrow 134.09$, $4.93 \rightarrow 125.22$, $4.76 \rightarrow 122.65$, $2.47 \rightarrow 104.94$, $2.09 \rightarrow 20.84$ ppm; ^{31}P NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = 3.176$ ppm (s; *P*Ph_3); IR (KBr): $\tilde{\nu} = 1950$ cm^{-1} (m, C≡C); elemental analysis calcd (%) for $IrP_2C_{51}H_{43}$: C 67.31, H 4.76; found: C 67.29, H 4.71.

Preparation of [Ir{–CH=CHCH=CHC(=CH-*p*-C_6H_4R')}(–C≡CH)(CO)(PPh_3)$_2$] (R′ = H 9a, R′ = CH_3 9b). A solution of **8a** (0.1 g, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred under CO (1 atm) at 25 °C for 1 h. *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 0.09 g and 97 % based on **9a**.

Data for 9a: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.52$ (br; *H1*), 6.98 (brs; *H6*), 6.27 (m; *H2*), 5.41 (d, *J*(H,H) = 10.5 Hz, 1H; *H4*), 5.30 (dd, *J*(H,H) = 10.5 Hz and 6.3 Hz; *H3*), 1.75 ppm (t; C≡C*H*); ^{31}P NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -13.15$ ppm (s; *P*Ph_3); IR (KBr): $\tilde{\nu} = 2014$ (s, C≡O), 1977 cm^{-1} (m, C≡C); elemental analysis calcd (%) for $IrP_2C_{51}H_{41}O$: C 66.29, H 4.47; found: C 66.38, H 4.39.

Data for 9b: ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.2$–7.8 (m, 31H; P(C_6H_5)$_3$, *H1*), 6.90 (brs, 1H; *H6*), 6.35–6.59 (AB quartet with $\delta\nu/J = 14.77$, *J*(H_A,H_B) = 7.75 Hz, 4H; *p*-$C_6H_4CH_3$), 6.25 (m, 1H; *H2*), 5.38 (d, *J*(H,H) = 10.0 Hz, 1H; *H4*), 5.28 (dd, *J*(H,H) = 10.0 Hz, *J*(H,H) = 6.5 Hz, 1H; *H3*), 2.19 (s, 3H; $C_6H_4CH_3$), 1.76 ppm (t, *J*(H,P) = 1.75 Hz, 1H; C≡C*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 173.60$ (t, *J*(C,P) = 6.73 Hz; Ir-*C*O), 144.64 (t, *J*(C,P) = 5.84 Hz; *C6*), 142.11, 134.95 (s, C_{ipso} of $C_6H_4CH_3$), 138.70 (t, *J*(C,P) = 11.31 Hz; *C5*), 137.36 (t, *J*(C,P) = 3.02 Hz; *C4*), 135.33 (t, *J*(C,P) = 5.22 Hz; *C1*), 129.70, 128.04 (2s, CH carbon atoms of $C_6H_4CH_3$), 127.56 (t, *J*(C,P) = 3.65 Hz; *C3*), 127.48 (t, *J*(C,P) = 4.84 Hz; *C2*), 96.12 (s; Ir-C≡*C*H), 80.63 (t, *J*(C,P) = 13.46 Hz; Ir-*C*≡CH), 21.35 ppm (s; $C_6H_4CH_3$); HETCOR (^1H (500 MHz)→^{13}C (125.7 MHz)): δ = ca. $7.3 \rightarrow 135.33$, $6.90 \rightarrow 144.64$, $6.25 \rightarrow 127.48$, $5.38 \rightarrow 137.36$, $5.28 \rightarrow 127.56$, $2.19 \rightarrow 21.35$, $1.76 \rightarrow 96.12$ ppm; ^{31}P NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -12.95$ ppm (s; *P*Ph_3); IR (KBr): $\tilde{\nu} = 2011$ (s, C≡O), 1993 cm^{-1} (m, C≡C); elemental analysis calcd (%) for $IrP_2C_{52}H_{43}O$: C 66.58, H 4.62; found: C 66.63, H 4.64.

Preparation of [Ir{–CH=CHCH=CHC(=CH-*p*-C_6H_4R')}(-CH_3)(CO)(PPh_3)$_2$] (R′ = H 10a, R′ = CH_3 10b): Aqueous HOTf (0.10 mL, 0.30 mmol of H_2O containing 35 wt % HOTf) was added to a solution of **8a** (0.1 g, 0.1 mmol) in $CHCl_3$ (15 mL) at 25 °C, and the reaction mixture was stirred for 30 min. Excess HOTf was removed by washing with H_2O. Addition of *n*-pentane (10 mL) to the $CHCl_3$ solution resulted in the beige microcrystals, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.08 g and 79 % based on **10a**.

Data for 10a: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.33$ (d, *J*(H,H) = 10.5 Hz, 1H; *H1*), 6.34 (m, 1H; *H2*), 5.95 (brs, 1H; *H6*), 5.77 (d, *J*(H,H) = 10.5 Hz, 1H; *H4*), 5.30 (dd, *J*(H,H) = 10.5, 6.3 Hz, 1H; *H3*), −0.31 ppm (t, *J*(H,P) = 5.0 Hz, 3H; Ir-C*H*$_3$); ^{31}P NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -5.99$ ppm (s; *P*Ph_3); IR (KBr): $\tilde{\nu} = 2009$ cm^{-1} (s, C≡O); elemental analysis calcd (%) for $IrP_2C_{50}H_{43}O$: C 65.70, H 4.74; found: C 65.00, H 4.66.

Data for [D$_3$]10a: ^1H NMR spectrum of the isotopomer **[D$_3$]10a** shows all the signals for **10a**, except for the disappearance of the resonance assigned to Ir-C*H*$_3$ of **10a**.

Data for 10b: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8.35$ (d, *J*(H,H) = 11.4 Hz, 1H; H1), 7.3–7.5 (m, 30H; P(C_6H_5)$_3$), 6.67–7.05 (AB quartet with $\delta\nu/J = 24.62$, *J*(H_A,H_B) = 7.5 Hz, 4H; *p*-$C_6H_4CH_3$), 6.34 (m, 1H; *H2*), 5.94 (s, 1H; *H6*), 5.78 (d, *J*(H,H) = 10.0 Hz, 1H; *H4*), 5.20 (dd, *J*(H,H) = 10.0 Hz, *J*(H,H) = 6.6 Hz, 1H; *H3*), 2.33 (s, 3H; *p*-$C_6H_4CH_3$), −0.338 ppm (t, *J*(H,P) = 4.95 Hz, 3H; Ir-C*H*$_3$); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 179.80$ (t, *J*(C,P) = 8.23 Hz; Ir-*C*O), 145.64 (t, *J*(C,P) = 14.3 Hz; *C5*), 142.01 (t, *J*(C,P) = 5.78 Hz; *C6*), 142.01, 131.90 (s; C_{ipso} of $C_6H_4CH_3$), 139.00 (t, *J*(C,P) = 10.7 Hz), 135.28 (t, *J*(C,P) = 5.15 Hz; *C1*, *C2*, *C3*, *C4*), 130.80 (t, *J*(C,P) = 3.33 Hz; *C1*, *C2*, *C3*, *C4*), 129.38, 127.98 (2s; CH carbon atoms of $C_6H_4CH_3$), 21.33 (s; $C_6H_4CH_3$), −19.22 ppm (t, J(C,P) = 6.7 Hz; Ir-*C*H_3); ^{31}P NMR (81 MHz, $CDCl_3$, 25 °C): $\delta = -6.37$ ppm (s; *P*Ph_3); IR (KBr): $\tilde{\nu} = 2003.5$ cm^{-1} (s, C≡O); elemental analysis calcd (%) for $IrP_2C_{51}H_{45}O$: C 66.00, H 4.89; found: C 66.42, H 4.96.

Data for [Ir{–CH=CHCH=CHC(=CH-*p*-$C_6H_4CH_3$)}(–CH_3)($C^{18}O$)(PPh_3)$_2$] ([^{18}O]10b): IR (KBr): $\tilde{\nu} = 1959.0$ cm^{-1} (s, C≡O).

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[10] Compounds **6** were prepared from the reactions of **3** with CO (1 atm) and compounds **7** were synthesized by the reactions of **3** with CH_3CN in the presence of Me_3NO. See Experimental Section in reference [2c].

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