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Carbon−Carbon Bond Formation between Adjacent Alkenyl Ligands: η^3-Allyl Iridium(III) and η^4-Butadiene Iridium(I) Complexes from a *cis*-Bis(alkenyl) Iridium(III) Complex

Chong Shik Chin,* Hyungeui Lee, Soyoung Noh, Hyeyun Park, and Mieock Kim

Chemistry Department, Sogang University, Seoul 121-742, Korea

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A carbon−carbon bond is formed between the α-carbons of the alkenyl ligands of the *cis*-bis(ethenyl)iridium complex $[Ir(-CH{=}CH_2)_2(CH_3CN)_2(PPh_3)_2]^+$ (**2**) to produce the η^3-allyl complex $[Ir(\eta^3\text{-}CH_3CHCHCH_2)(NCCH_3)_2(PPh_3)_2]^{2+}$ (**4**) in the reaction of **2** with H^+, and η^4-butadiene complexes $Ir(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)(A)(PPh_3)_2$ (A = $-CH{=}CH\text{-}^+NEt_3$ (**6**), $-C{\equiv}CR$ (**7**)) in reactions of **2** with terminal alkynes ($RC{\equiv}CH$; R = H, Ph, and p-$C_6H_4CH_3$) in the presence of NEt_3. The deuterium labeling experiments suggest an initial attack of H^+ on the β-carbon of an ethenyl ligand to lead to the C−C bond formation between the α-carbons of the two alkenyl groups of **2** to produce **4**.

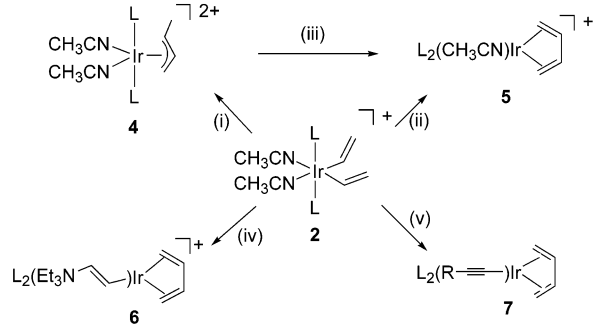
Introduction

Transition metal-mediated C−C bond formation between alkynes has been extensively investigated since it is probably the most useful transformation in synthetic chemistry.[1] It is likely that metal-hydrocarbyls such as metal-alkyls, -alkenyls, -alkynyls, -carbenes, and -vinylidenes are the intermediates formed during the C−C coupling.[1,2]

We have recently reported that some alkynyl-iridium complexes are utilized as precursors for the C−C bond formation to give polyenes such as di-, tri-, and tetraenes.[2] Iridium-alkynyls ($Ir-C_\alpha{\equiv}C_\beta-R$)[2] are readily protonated at the electrophilic β-carbon to give iridium-vinylidenes ($Ir{=}C_\alpha{=}C_\beta HR$) that undergo carbon−carbon coupling reactions with adjacent hydrocarbyl ligands (Ir-alkyl,[2a,d,e] Ir-alkenyl,[2a−c] and Ir-allyl[2a,f]) to produce those polyenes.

We now wish to report a proton-initiated C−C bond formation between *cis*-bis(alkenyl) ligands of iridium-alkenyls ($Ir-CH{=}CH_2$)[2b,3] to produce 2-butene and 1,3-butadiene via iridium-carbene ($Ir{=}CHCH_3$) intermediates.

Scheme 1



L = PPh_3, R= C_6H_5 (**a**), p-$C_6H_4CH_3$ (**b**)
(i) H^+, (ii) 60 °C, $-CH_3CN$, (iii) $-H^+$, $-CH_3CN$
(iv) $HC{\equiv}CH$, NEt_3/ $-2CH_3CN$,(v) $HC{\equiv}CR$, NEt_3/ $-2CH_3CN$, $-H^+NEt_3$

Results and Discussion

Reaction of the *cis*-bis(ethenyl) Ir(III) complex $[Ir(-CH{=}CH_2)_2(CH_3CN)_2(PPh_3)_2]^+$ (**2**)[2b,3] with H^+ readily gives the η^3-allyl complex $[Ir(\eta^3\text{-}CH_3CHCHCH_2)(CH_3CN)_2(PPh_3)_2]^{2+}$ (**4**), which slowly undergoes reductive deprotonation at room temperature to give the η^4-butadiene complex $[Ir(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)(CH_3CN)(PPh_3)_2]^+$ (**5**) (Scheme 1). Complex **5** is also obtained directly by heating **2** in $CHCl_3$ at 60 °C (Scheme 1). In the presence of NEt_3, complex **2** reacts with alkynes $HC{\equiv}CH$ and $RC{\equiv}CH$ (R = C_6H_5 and p-$C_6H_4CH_3$) to give the alkenyl η^4-butadiene complex $Ir(-CH{=}CH\text{-}^+NEt_3)(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)(PPh_3)_2$ (**6**) and alkynyl η^4-butadiene complexes $Ir(-C{\equiv}CR)(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)(PPh_3)_2$ (**7**, R = C_6H_5 (**a**), p-$C_6H_4CH_3$ (**b**)),[2b] respectively, in high yields (Scheme 1). These 18-electron Ir(I) complexes (**5**, **6**, and **7**) are very stable both in the solid state and in solution at 25 °C even in air for several

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(3) Iridium-alkenyls, *cis*-bis(ethenyl) Ir(III) complexes $[Ir(-CH{=}CH_2)_2L'_2(PPh_3)_2]^+$ (L′ = CH_3CN (**2**), CO (**3**)) have been prepared by the insertion of $HC{\equiv}CH$ into Ir−H bonds of the *cis*-dihydrido Ir(III) complex $[Ir(H)_2(NCCH_3)_2(PPh_3)_2]^+$ (**1**). See Experimental Section in ref 2b.

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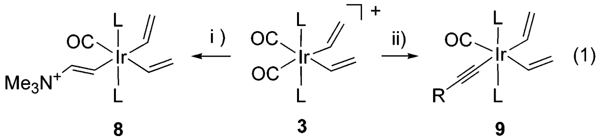
hours. Complex **4** reacts with H_2 to give 2-butene (mixture of *cis* and *trans*), butane, and *cis,cis*-$[\mathrm{Ir(H)_2(NCCH_3)_2(PPh_3)_2}]^+$ (**1**), while 1,3-butadiene is liberated from **7** by reactions with CO, which affords $\mathrm{Ir(C{\equiv}CR)(CO)(PPh_3)_2}$.

There are a few examples of proton-initiated C−C bond formation between adjacent alkenyl ligands to give η^3-allyl complexes[4] and of reductive C−C coupling between two *cis*-alkenyl ligands by thermal activation to give η^4-butadiene complexes.[5] Hardly does the conversion of η^3-butenyl complex to η^4-butadiene complex occur under normal conditions except one by photolysis.[6]

Neither the C−C coupling reaction between *cis*-ethenyl groups nor protonation has been observed for the *cis,cis*-dicarbonylbis(ethenyl) complex $[\mathrm{Ir({-}CH{=}CH_2)_2(CO)_2(PPh_3)_2}]^+$ (**3**)[2b,3] to give an η^4-butadiene or η^3-allyl complex. Instead, tris(alkenyl) Ir(III) complex **8** and alkynyl bis(alkenyl) Ir(III) complexes **9**[2b] are obtained from reaction with alkynes in high yields (eq 1). Both **8** and **9** are stable both in the solid state and in solution at 25 °C even in air for several hours. Attempts to observe C−C bond formation between the two *cis*-alkenyl ligands of **8** have been unsuccessful thus far, while complexes **9** undergo proton-initiated C−C coupling reaction between the alkynyl and two *cis*-alkenyl ligands to produce cross-conjugated hexatrienes ($\mathrm{RCH{=}C(CH{=}CH_2)_2}$, R-**HEX**).[2b]



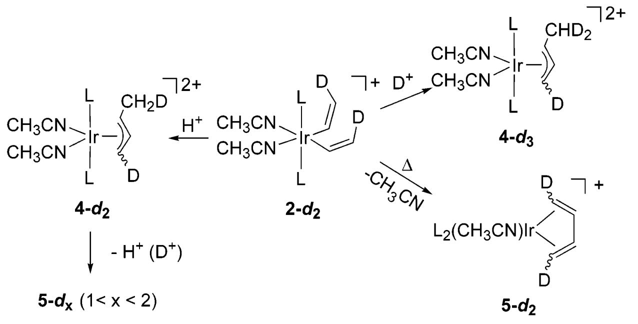
i) HC≡CH, Me_3NO/ $-CO_2$ ii) HC≡CR, Me_3NO/ $-CO_2$, $-H^+NMe_3$

L = PPh_3, R = C_6H_5 (**a**), *p*-$C_6H_4CH_3$ (**b**), cyclohex-1-enyl (**c**)

Newly prepared compounds **4**, **5**, **6**, and **8** have been unambiguously identified by detailed spectral (^{1}H, ^{13}C, ^{1}H, ^{1}H-2D COSY, ^{1}H, ^{13}C-2D HETCOR, and ^{31}P NMR) and elemental analysis data (see Experimental Section). Characterization of **4** is rather straightforward by comparing the spectral data with those for related allylic metal compounds.[4,7] The ^{13}C NMR spectrum of **4** shows all four carbons for the allyl ligand at 16.4−116.6 ppm (see Experimental Section).

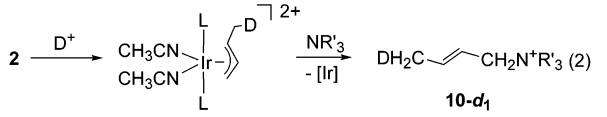
Assignments of ^{1}H NMR signals to $\mathrm{Ir\text{-}C}H_\alpha{=}\mathrm{C}H_\beta\text{-}{}^+\mathrm{NR_3}$ (R = Et (**6**), Me (**8**)) are also straightforward by comparing the data with those for the related well-characterized complexes containing $\mathrm{Ir\text{-}CH{=}CH\text{-}{}^+NR_3}$ and other related metal alkenyls.[2e,8] ^{13}C NMR spectra of **5** and **6** show the signals due to the inner carbons of the 1,3-butadiene of $\mathrm{Ir}(\eta^4\text{-}\mathrm{CH_2{=}}C\mathrm{H}C\mathrm{H{=}CH_2})$ at δ 72.1−89.1 and those due to the outer carbons of $\mathrm{Ir}(\eta^4\text{-}C\mathrm{H_2{=}CHCH{=}}C\mathrm{H_2})$ at δ 31.3−42.0. ^{31}P NMR spectra of these complexes show two signals at δ 5.6−15.3 and δ −7.1 to −8.0, respectively (see Experimental Section), as does the related η^4-1,3-butadiene complex $(\mathrm{PPh_3})_2\mathrm{ClRh}(\eta^4\text{-}\mathrm{CH_2{=}CHC(Ph){=}CH_2})$,[9] whose crystal structure shows the two PPh_3 being nonequivalent.

Scheme 2



L = PPh_3

To obtain more information on the reaction pathway for the proton-initiated C−C coupling reaction between the two *cis*-ethenyl ligands (**2** → **4**), deuterium labeling experiments (see eq 2 and Scheme 2) have been carried out. The d_1 isotopomer $[\mathrm{Ir}(\eta^3\text{-}\mathrm{CH_2DCHCHCH_2})(\mathrm{NCCH_3})_2(\mathrm{PPh_3})_2]^{2+}$ (**4-d_1**) is obtained from the reaction of **2** with D^+ and found to react with NR'_3 (NC_5H_5 (**a**), NEt_3 (**b**)) to produce *trans*-2-butenylammonium cations *trans*-$\mathrm{CH_2DCH{=}CHCH_2N^+R'_3}$ (**10-d_1**) (eq 2). This nucleophilic attack of NR'_3 on the terminal C_α carbon of the η^3-butenyl (η^3-$\mathrm{CH_3C_\gamma HC_\beta H}C_\alpha\mathrm{H_2}$) group of **4** is somewhat expected since allylic ligands are known to be readily attacked by nucleophiles to form C−C and C−heteroatom bonds.[7] Isolated metal complexes ([Ir] in eq 2) from the reactions of **2** with D^+ have not been fully characterized.



L = PPh_3

NR'_3 = NC_5H_5 (**a**), NEt_3 (**b**)

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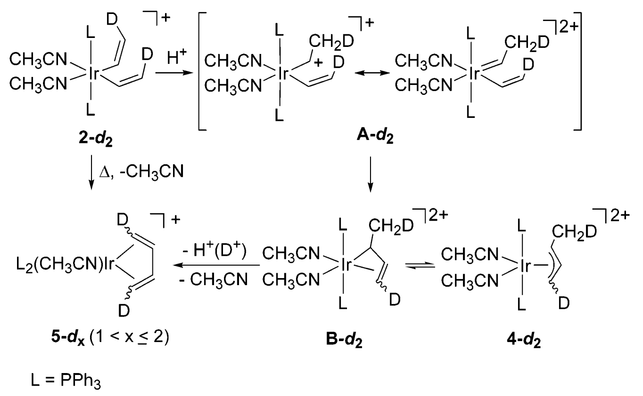
Scheme 3



Scheme 2 summarizes the reactions of $[\mathrm{Ir(CH{=}CHD)_2(CH_3CN)_2(PPh_3)_2}]^+$ (**2-*d*₂**)^{2b} (Scheme 2). Isotopomers **4-*d*₁**, **4-*d*₂** ($[\mathrm{Ir}(\eta^3\text{-}\mathrm{CH_2DCHCHCHD})(\mathrm{NCCH_3})_2(\mathrm{PPh_3})_2]^{2+}$), **4-*d*₃** ($[\mathrm{Ir}(\eta^3\text{-}\mathrm{CHD_2CHCHCHD})(\mathrm{NCCH_3})_2(\mathrm{PPh_3})_2]^{2+}$), **5-*d*₂** ($[\mathrm{Ir}(\eta^4\text{-}\mathrm{CHD{=}CHCH{=}CHD})(\mathrm{NCCH_3})(\mathrm{PPh_3})_2]^+$), **5-*d*ₓ** ($1 < x < 2$), **10**, and **10-*d*₁** have been unequivocally identified by ^{1}H NMR (**4-*d*₁**, **4-*d*₂**, **4-*d*₃**, **5-*d*₂**, and **5-*d*ₓ**) and mass spectral data (**10** and **10-*d*₁**) (see Experimental Section).

Metal-carbenes ($\mathrm{M^+{=}CHCH_2R}$) are frequently observed and suggested in reactions of metal-alkenyls ($\mathrm{M\text{-}CH{=}CHR}$) with the proton,[10] and the α-carbon ($\mathrm{M^+{=}}\mathit{C}\mathrm{HCH_2R}$) of the electrophilic alkylidene group readily interacts with the α-carbon of a neighboring hydrocarbyl ligand to form a new C−C bond.[4,11] Scheme 3 is accordingly suggested for the C−C bond formation between adjacent alkenyl groups of **2** (**2** → **4**). The formation of **4-*d*₂** from the reaction of **2-*d*₂** with H$^+$ suggests the attack of H$^+$ on the β-carbon of an alkenyl group to give the intermediate **A-*d*₂**, which undergoes a C−C coupling reaction between α-carbons of the carbene ($\mathrm{Ir{=}}\mathit{C}\mathrm{HCH_2D}$) and *cis*-ethenyl ($\mathrm{Ir\text{-}}\mathit{C}\mathrm{H{=}CHD}$) ligands to produce another intermediate, **B-*d*₂**. The complex **4-*d*₂** is then produced by the isomerization of complex **B-*d*₂**, which also slowly undergoes reductive deprotonation to produce the stable 18-electron Ir(I) complex **5-*d*ₓ** ($1 < x < 2$).

In conclusion, we have observed two different types of C−C bond forming reactions between the *cis* alkenyl groups of **2**: (i) proton-initiated C−C bond formation to produce η^3-allyl complexes via proton attack on the β-carbon of an ethenyl group and (ii) reductive C−C coupling to produce η^4-1,3-butadiene complexes.

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.

HOTf and DOTf were purchased from Aldrich. $[\mathrm{Ir(H)_2(NCCH_3)_2(PPh_3)_2}]$OTf (**1**),[12] $[\mathrm{Ir(-CH{=}CH_2)_2(NCCH_3)_2(PPh_3)_2}]$OTf (**2**),[2b] $[\mathrm{Ir(-CH{=}CHD)_2(NCCH_3)_2(PPh_3)_2}]$OTf (**2-*d*₂**),[2b] and $[\mathrm{Ir(-CH{=}CH_2)_2(CO)_2(PPh_3)_2}]$OTf (**3**)[2b] were prepared by literature methods.

Instrumentation. NMR spectra were recorded on a Varian 200 or 500 MHz spectrometer for ^{1}H, 125.7 MHz for ^{13}C, and 81 or 121.3 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205. Elemental analyses were carried out with a Carlo Erba EA1108 at the Organic Chemistry Research Center, Sogang University. FD mass measurements were carried out with a Micro Mass Co. Autospec-Q at the SK research center.

Synthesis of $[\mathrm{Ir}(\eta^3\text{-}\mathrm{CH_3\text{-}CHCHCH_2})(\mathrm{CH_3CN})_2(\mathrm{PPh_3})_2](\mathrm{OTf})_2$ (4). A reaction mixture of **2** (0.10 g, 0.1 mmol) and HOTf (11 μL, 0.12 mmol) in $\mathrm{CHCl_3}$ (10 mL) was stirred for 1 h at 25 °C before diethyl ether (30 mL) was added to precipitate beige microcrystals, which were collected by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum. The yield was 0.11 g and 95% based on $[\mathrm{Ir}(\eta^3\text{-}\mathrm{CH_3CHCHCH_2})(\mathrm{CH_3CN})_2(\mathrm{PPh_3})_2](\mathrm{OTf})_2$ (**4**). ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.2−7.6 (m, $\mathrm{P(C_6}\mathit{H}\mathrm{_5)_3}$, 30H), 5.82 (m, Ir-$\eta^3$-$\mathrm{CH_3CHC}\mathit{H}\mathrm{CH_2}$, 1H), 4.47 (m, Ir-$\eta^3$-$\mathrm{CH_3C}\mathit{H}\mathrm{CHCH_2}$, 1H), 4.30 and 3.37 (both br m, Ir-η^3-$\mathrm{CH_3CHCHC}\mathit{H}\mathrm{_2}$, 2H), 2.20 and 2.15 (both br s, $2\mathrm{C}\mathit{H}\mathrm{_3CN}$, 6H), 1.19 (quartet like, Ir-η^3-$\mathrm{C}\mathit{H}\mathrm{_3CHCHCH_2}$, 3H). ^{13}C NMR (125.7 MHz, $\mathrm{CDCl_3}$): δ 122.6 and 121.2 (s, $2\mathrm{CH_3}\mathit{C}\mathrm{N}$), 116.6 (s, Ir-$\eta^3$-$\mathrm{CH_3CH}\mathit{C}\mathrm{HCH_2}$), 84.2 (br s, Ir-$\eta^3$-$\mathrm{CH_3}\mathit{C}\mathrm{HCHCH_2}$), 62.5 (br s, Ir-$\eta^3$-$\mathrm{CH_3CHCH}\mathit{C}\mathrm{H_2}$), 16.4 (s, Ir-$\eta^3$-$\mathit{C}\mathrm{H_3CHCHCH_2}$), 4.7 (br s, $2\mathit{C}\mathrm{H_3CN}$), 133.4, 132.3, 129.4 and 127.8. ($\mathrm{P(}\mathit{C}\mathrm{_6H_5)_3}$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ 5.82 → 116.6; 4.47 → 84.2; 4.30, 3.37 → 62.5; 2.20, 2.15 → 4.7; 1.19 → 16.4. HOMOCOSY (^{1}H (500 MHz) → ^{1}H (500 MHz)): δ 5.82 → 4.47, 4.30, 3.37; 4.47 → 5.82, 1.19; 4.30 → 5.82; 3.37 → 5.82, 1.19; 1.19 → 4.47, 3.37. ^{31}P{^{1}H} NMR (81 MHz, $\mathrm{CDCl_3}$): δ −9.59 (s, *P*Ph$_3$). IR (KBr, cm^{-1}): 1261, 1158, and 1031 (s, OTf$^-$). Anal. Calcd for $\mathrm{Ir_1P_2O_6S_2F_6N_2C_{46}H_{43}}$: C, 47.95; N, 2.43; H, 3.76. Found: C, 47.96; N, 2.27; H, 3.70.

Synthesis of $[\mathrm{Ir}(\eta^3\text{-}\mathrm{CH_2DCHCHCH_2})(\mathrm{CH_3CN})_2(\mathrm{PPh_3})_2](\mathrm{OTf})_2$ (4-*d*₁). Reaction with deutrated acid, DOTf, was carried out in the same manner as described above for that of **2** with HOTf. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.2−7.6 (m, $\mathrm{P(C_6}\mathit{H}\mathrm{_5)_3}$, 30H), 5.82 (m, Ir-$\eta^3$-$\mathrm{CH_2D\text{-}CHC}\mathit{H}\mathrm{CH_2}$, 1H), 4.47 (m, Ir-$\eta^3$-$\mathrm{CH_2D{-}C}\mathit{H}\mathrm{CHCH_2}$, 1H), 4.30 and 3.37 (both br m, Ir-η^3-$\mathrm{CH_2DCHCHC}\mathit{H}\mathrm{_2}$, 2H), 2.20 and 2.15 (both br s, $2\mathrm{C}\mathit{H}\mathrm{_3CN}$, 6H), 1.19 (quartet like, Ir-η^3-$\mathrm{C}\mathit{H}\mathrm{_2DCHCHCH_2}$, 2H).

Synthesis of $[\mathrm{Ir}(\eta^3\text{-}\mathrm{CH_2DCHCHCHD})(\mathrm{CH_3CN})_2(\mathrm{PPh_3})_2](\mathrm{OTf})_2$ (4-*d*₂). Reaction of **2-*d*₂** with HOTf was carried out in the same manner as described above for that of **2** with HOTf. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.2−7.6 (m, $\mathrm{P(C_6}\mathit{H}\mathrm{_5)_3}$, 30H), 5.82 (br m, Ir-$\eta^3$-$\mathrm{CH_2DCHC}\mathit{H}\mathrm{CHD}$, 1H), 4.47 (m, Ir-$\eta^3$-$\mathrm{CH_2DC}\mathit{H}\mathrm{\text{-}CHCHD}$, 1H), 4.30 and 3.37 (both br m, Ir-η^3-$\mathrm{CH_2DCHCHC}\mathit{H}\mathrm{D}$, 1H), 2.20 and 2.15 (both br s, $2\mathrm{C}\mathit{H}\mathrm{_3CN}$, 6H), 1.19 (br s, Ir-$\eta^3$-$\mathrm{C}\mathit{H}\mathrm{_2DCHCHCHD}$, 2H).

Synthesis of $[\mathrm{Ir}(\eta^3\text{-}\mathrm{CHD_2CHCHCHD})(\mathrm{CH_3CN})_2(\mathrm{PPh_3})_2](\mathrm{OTf})_2$ (4-*d*₃). Reaction of **2-*d*₂** with DOTf was carried out in the same manner as described above for that of **2** with HOTf. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 7.2−7.6 (m, $\mathrm{P(C_6}\mathit{H}\mathrm{_5)_3}$, 30H), 5.82 (m, Ir-$\eta^3$-$\mathrm{CHD_2CHC}\mathit{H}\mathrm{CHD}$, 1H), 4.47 (m, Ir-$\eta^3$-$\mathrm{CHD_2C\text{-}}\mathit{H}\mathrm{CH\text{-}CHD}$, 1H), 4.30 and 3.37 (both br m, Ir-η^3-$\mathrm{CHD_2CHCHC}\mathit{H}\mathrm{D}$,

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1H), 2.20 and 2.15 (both br s, 2CH_3CN, 6H), 1.19 (br s, Ir-η^3-CHD$_2$CHCHCHD, 1H).

Synthesis of [Ir(η^4-CH$_2$=CHCH=CH$_2$)(CH$_3$CN)(PPh$_3$)$_2$]OTf (5). Method A. A CHCl$_3$ solution of **2** (0.1 g, 0.1 mmol) was heated at 60 °C for 48 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 0.082 g and 85% based on [Ir(η^4-CH$_2$=CHCH=CH$_2$)(CH$_3$CN)(PPh$_3$)$_2$]OTf (**5**).

Method B. A CHCl$_3$ solution of **4** (0.12 g, 0.1 mmol) was stirred at 25 °C for 48 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 0.064 g and 67% based on compound **5**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.0−7.8 (m, P(C$_6$$H_5$)$_3$, 30H), 6.15 and 5.15 (m, Ir-η^4-CH$_2$=CHCH=CH$_2$, 2H), 3.14 and 1.81 (m, Ir-η^4-CH$_{syn}$$H_{anti}$=CHCH=CH$_{syn}$$H_{anti}$, 2H), 2.03 (s, CH$_3$CN, 3H), −0.49 and −0.66 (m, Ir-η^4-CH_{syn}H$_{anti}$=CHCH=CH_{syn}H$_{anti}$, 2H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 120.2 (s, Ir-NCCH$_3$), 92.3 (t, J(C−P) = 4.4 Hz) and 85.5 (d, J(C−P) = 4.8 Hz) (Ir-η^4-CH$_2$=CHCH=CH$_2$), 41.2 (d, J(C−P) = 39.0 Hz) and 20.1 (d, J(C−P) = 27.3 Hz) (Ir-η^4-CH$_2$=CHCH=CH$_2$), 3.6 (s, Ir-NCCH$_3$). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ 15.2 (d, J(P−P) = 8.3 Hz), −8.0 (d, J(P−P) = 8.3 Hz). IR (KBr, cm^{-1}): 1274, 1095, and 1033 (s, OTf$^-$). Anal. Calcd for Ir$_1$P$_2$O$_3$S$_1$F$_3$N$_1$C$_{43}$H$_{39}$: C, 53.74; N, 1.46; H, 4.09. Found: C, 53.82; N, 1.39; H, 4.18.

Synthesis of [Ir(η^4-CHD=CHCH=CHD)(CH$_3$CN)(PPh$_3$)$_2$]OTf (5-d_2). Heating a CHCl$_3$ solution of **2-d_2** was carried out in the same manner as method A in the synthesis of complex **5**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.0−7.8 (m, P(C$_6$$H_5$)$_3$, 30H), 6.15 and 5.15 (m, Ir-η^4-CHD=CHCH=CHD, 2H), 3.14, 1.81, −0.49 and −0.66 (m, Ir-η^4-CHD=CHCH=CHD, 2H), 2.03 (s, CH$_3$CN, 3H).

Synthesis of [Ir(η^4-CHD=CHCH=CHD)(CH$_3$CN)(PPh$_3$)$_2$]OTf (5-d_x). Stirring a CHCl$_3$ solution of **4-d_2** was carried out in the same manner as method B in the synthesis of complex **5**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.0−7.8 (m, P(C$_6$$H_5$)$_3$, 30H), 6.15 and 5.15 (m, Ir-η^4-CHD=CHCH=CHD, 2H), 3.14, 1.81, −0.49, and −0.66 (m, Ir-η^4-CHD=CHCH=CHD, xH ($1 < x < 2$)), 2.03 (s, CH$_3$CN, 3H).

Synthesis of [Ir(−CH=CH-$^+$NEt$_3$)(η^4-CH$_2$=CHCH=CH$_2$)(PPh$_3$)$_2$]OTf (6). A CHCl$_3$ solution of **2** (0.1 g, 0.1 mmol) and NEt$_3$ (0.015 g, 0.15 mmol) was stirred under HC≡CH (1 atm) at 25 °C for 1 h before the pale yellow solution turned light brown. An excess of NEt$_3$ was removed by extraction with H$_2$O (5 × 10 mL). Addition of *n*-pentane (10 mL) resulted in precipitation of beige microcrystals, which were collected by filtration, washed with cold *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.103 g and 98% based on [Ir(−CH=CH-$^+$NEt$_3$)(η^4-CH$_2$=CHCH=CH$_2$)(PPh$_3$)$_2$]OTf (**6**). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.0−7.4 (m, P(C$_6$$H_5$)$_3$ and Ir-CH=CH-NEt$_3$, 31H), 5.39 and 5.20 (m, Ir-η^4-CH$_2$=CHCH=CH$_2$, 2H), 4.94 (d, J(H−H) = 15.0 Hz, Ir-CH=CH-NEt$_3$, 1H), 2.84 (q, J(H−H) = 7.0 Hz, Ir-CH=CH-N(CH_2CH$_3$)$_3$, 6H), 2.23, and 1.93 (m, Ir-η^4-CH$_{syn}$$H_{anti}$=CHCH=CH$_{syn}$$H_{anti}$, 2H), 0.84 (t, J(H−H) = 7.0 Hz, Ir-CH=CH-N(CH$_2$CH_3)$_3$, 9H), −0.63, and −0.75 (m, Ir-η^4-CH_{syn}H$_{anti}$=CHCH=CH_{syn}H$_{anti}$, 2H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 128.3 (d, J(C−P) = 4.1 Hz, Ir-CH=CH-$^+$NEt$_3$), 123.9 (dd, J(C−P) = 12.9 Hz, J(C−P) = 4.7 Hz, Ir-CH=CH-$^+$NEt$_3$), 88.9 (d, J(C−P) = 4.5 Hz) and 80.5 (dd, J(C−P) = 7.9 Hz, J(C−P) = 4.5 Hz) (Ir-η^4-CH$_2$=CHCH=CH$_2$), 53.0 (s, Ir-CH=CH-$^+$N(CH$_2$CH$_3$)$_3$), 42.0 and 31.3 (s, Ir-η^4-CH$_2$=CHCH=CH$_2$), 7.3 (s, Ir-CH=CH-$^+$N(CH$_2$$CH_3$)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ ca. 7.2 → 123.9; 5.39 → 80.5; 5.20 → 88.9; 4.94 → 128.3; 2.84 → 53.0; 2.23 → 42.0; 1.93 → 31.3; 0.84 → 7.3; −0.63 → 31.3; −0.75 → 42.0. ^{31}P{^{1}H} NMR (121.3 MHz, CDCl$_3$): δ 5.62 (d, J(P−P) = 19.4 Hz), −7.12 (d, J(P−P) = 19.4 Hz). IR (KBr, cm^{-1}): 1120, 1092, and 1011 (s, OTf$^-$). Anal. Calcd for Ir$_1$P$_2$O$_3$S$_1$F$_3$N$_1$C$_{49}$H$_{53}$: C, 56.20; N, 1.34; H, 5.10. Found: C, 56.26; N, 1.29; H, 5.14.

Synthesis of [Ir(−CH=CH-$^+$NMe$_3$)(−CH=CH$_2$)$_2$(CO)(PPh$_3$)$_2$]OTf (8). A solution of **3** (0.1 g, 0.1 mmol) and Me$_3$NO (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 pale yellow solution turned light brown. An excess of Me$_3$NO was removed by extraction with H$_2$O (10 mL). Addition of *n*-hexane (10 mL) resulted in precipitation of beige microcrystals, which were collected by filtration, washed with *n*-hexane (3 × 10 mL), and dried under vacuum. The yield was 0.09 g or 87% based on [Ir(−CH=CH-$^+$NMe$_3$)(−CH=CH$_2$)$_2$(CO)(PPh$_3$)$_2$]OTf (**8**). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.3−7.4 (m, P(C$_6$$H_5$)$_3$ and Ir-CH=CH$_2$, 31H), 6.93 (dd, J(H−H) = 19.0 Hz, J(H−H) = 11.5 Hz, Ir-CH=CH$_2$, 1H), 6.45 (d, J(H−H) = 15.3 Hz, Ir-CH=CH−N(CH$_3$)$_3$, 1H), 6.19 (d, J(H−H) = 11.0 Hz) and 5.95 (d, J(H−H) = 11.5 Hz) (Ir-CH=CH_{cis}H$_{trans}$, 2H), 5.38 (d, J(H−H) = 15.3 Hz, Ir-CH=CH-N(CH$_3$)$_3$, 1H), 5.04 (d, J(H−H) = 18.5 Hz) and 4.96 (d, J(H−H) = 19.0 Hz) (Ir−CH=CH$_{cis}$$H_{trans}$, 2H), 2.50 (s, N(C$H_3$)$_3$, 9H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 176.0 (t, Ir-CO, J(C−P) = 5.0 Hz), 137.5 (t, J(C−P) = 10.0 Hz) and 136.7 (t, J(C−P) = 13.3 Hz) (Ir-CH=CH$_2$), 135.2 (br s, Ir-CH=CH-N(CH$_3$)$_3$), 131.6 (t, J(C−P) = 4.5 Hz, Ir-CH=CH-N(CH$_3$)$_3$), 127.1 (br s) and 125.7 (t, J(C−P) = 4.5 Hz) (Ir-CH=CH$_2$), 52.6 (s, N(CH$_3$)$_3$), 127.8, 130.2, 130.6, 134.3 (P(C_6H$_5$)$_3$). HETCOR (^{1}H (500 MHz) → ^{13}C (125.7 MHz)): δ ca. 7.3 → 136.7; 6.93 → 137.5; 6.19, 5.04 → 127.1; 5.95, 4.96 → 125.7; 5.38 → 135.2; 2.50 → 52.6. ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): δ −16.39 (s, PPh$_3$). IR (KBr, cm^{-1}): 2027 (s, ν_{CO}), 1581 (m, $\nu_{C=C}$), 1264, 1159 and 1031 (s, OTf$^-$). Anal. Calcd for Ir$_1$N$_1$F$_3$S$_1$O$_4$P$_2$C$_{47}$H$_{47}$: C, 54.64; H, 4.59; N, 1.36. Found: C, 54.13; H, 4.49; N, 1.29.

Reaction of [Ir(η^3-CH$_3$CHCHCH$_2$)(CH$_3$CN)$_2$(PPh$_3$)$_2$](OTf)$_2$ (4) with H$_2$: Formation of CH$_3$CH=CHCH$_3$ (mixture of *cis* and *trans*), CH$_3$CH$_2$CH$_2$CH$_3$, and [Ir(H)$_2$(CH$_3$CN)$_2$(PPh$_3$)$_2$]OTf (1). A CDCl$_3$ (5 mL) solution of **4** (0.3 g, 0.26 mmol) was stirred under H$_2$ (1 atm) at 25 °C for 12 h in a bomb reactor before the reaction mixture was distilled under vacuum to collect 2-butene (mixture of *cis* and *trans*) and butane in the cold trap of a dry ice/isopropyl alcohol bath. A CDCl$_3$ solution of 2-butene and butane was measured by ^{1}H NMR. The residue in the bomb reactor was dissolved in CHCl$_3$ (10 mL). HOTf was removed by extraction with H$_2$O (2 × 10 mL) 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 0.24 g or 97% based on compound **1**.

Reactions of Ir(−C≡CR)(η^4-CH$_2$=CHCH=CH$_2$)(PPh$_3$)$_2$ (7, R = Ph (a), *p*-C$_6$H$_4$CH$_3$ (b)) with CO (1 atm): Formation of CH$_2$=CHCH=CH$_2$ and Ir(−C≡CR)(CO)(PPh$_3$)$_2$. A CDCl$_3$ (5 mL) solution of **7a** (0.3 g, 0.34 mmol) was stirred under CO (1 atm) at 25 °C for 1 h in a bomb reactor before the reaction mixture was distilled under vacuum to collect 1,3-butadiene in the cold trap of a dry ice/isopropyl alcohol bath. The 1,3-butadiene was measured by ^{1}H NMR. The residue in the bomb reactor was dissolved in CHCl$_3$ (5 mL), and *n*-pentane (10 mL) was added to precipitate yellow microcrystals of Ir(−C≡CPh)(CO)(PPh$_3$)$_2$, which were collected by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum. The yield was 0.28 g or 94% based on Ir(−C≡CPh)(CO)(PPh$_3$)$_2$. Compounds Ir(−C≡CR)(CO)(PPh$_3$)$_2$[13] (R = Ph, *p*-C$_6$H$_4$CH$_3$) have been identified by ^{1}H NMR and IR spectral measurements.

Reactions of [Ir(η^3-CH$_3$CHCHCH$_2$)(CH$_3$CN)$_2$(PPh$_3$)$_2$](OTf)$_2$ (4) with NR′$_3$ (NR′$_3$ = NC$_5$H$_5$ (a), NEt$_3$ (b)): Formation of [*trans*-CH$_3$CH=CHCH$_2$NR′$_3$]OTf (10). These reactions were carried out in the same manner as described below for **4** with NC$_5$H$_5$. A light brown solution of **4** (0.35 g, 0.30 mmol) and NC$_5$H$_5$ (0.023 g, 0.30 mmol) in CHCl$_3$ (10 mL) was

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stirred at 25 °C under N_2 for 1 h before H_2O (5 mL) was added to the reaction mixture. The unidentified metal complexes were removed by extraction with $CHCl_3$ (3 × 10 mL), and a colorless oil was obtained from the distillation of the layer of H_2O at 50 °C under vacuum. The yield was 0.29 mmol and 97% based on [*trans*-$CH_3CH{=}CHCH_2NC_5H_5$]OTf (**10a**) measured by ^1H NMR.

[*trans*-$CH_3CH{=}CHCH_2NC_5H_5$]OTf (10a). ^1H NMR (500 MHz, $CDCl_3$): δ 8.03 − 8.93 (m, NC_5H_5, 5H), 6.19 (m, $CH_3CH{=}CH\text{-}CH_2{}^+NC_5H_5$, 1H), 5.74 (m, $CH_3CH{=}CHCH_2{}^+NC_5H_5$, 1H), 5.22 (d, J(H−H) = 7.0 Hz, $CH_3CH{=}CH\text{-}CH_2\text{-}{}^+NC_5H_5$, 2H) 1.80 (d, J(H−H) = 6.5 Hz, $CH_3CH{=}CHCH_2{}^+NC_5H_5$, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 145.4, 144.3, and 128.4 (s, NC_5H_5), 138.2 (s, $CH_3CH{=}CHCH_2{}^+NC_5H_5$), 122.2 (s, $CH_3CH{=}CHCH_2{}^+NC_5H_5$), 63.7 (s, $CH_3CH{=}CHCH_2{}^+NC_5H_5$), 17.9 (s, $CH_3CH{=}CHCH_2{}^+NC_5H_5$). HETCOR ($^1H$ (500 MHz) → ^{13}C (125.7 MHz)): δ 6.19 → 138.2; 5.74 → 122.2; 5.22 → 63.7; 1.80 → 17.9. IR (KBr, cm^{-1}): 1262, 1163, and 1033 (s, OTf^-). MS (FD): m/z 134 (M − OTf). No NOE enhancement are observed between olefinic protons ($CH_3CH{=}CHCH_2{}^+NC_5H_5$).

[*trans*-$CH_3CH{=}CHCH_2{-}NEt_3$]OTf (10b). ^1H NMR (200 MHz, $CDCl_3$): δ 6.13 (m, $CH_3CH{=}CHCH_2{}^+NEt$, 1H), 5.48 (m, $CH_3CH{=}CHCH_2{}^+NEt$, 1H), 3.72 (d, J(H−H) = 7.4 Hz, $CH_3CH{=}CHCH_2{}^+NEt_3$, 2H), 3.20 (q, J(H−H) = 7.4 Hz, $N(CH_2CH_3)_3$, 2H), 1.80 (d, J = 7.4 Hz, $CH_3CH{=}CHCH_2{}^+NEt_3$, 3H), 1.30 (t, J(H−H) = 7.4 Hz, $N(CH_2CH_3)_3$, 3H). MS (FD): m/z 156 (M − OTf).

Reaction of [Ir(η^3-$CH_2DCHCHCH_2$)($CH_3CN)_2(PPh_3)_2$]($OTf)_2$ (4-d_1) with NR'_3 ($NR'_3 = NC_5H_5$ (a), NEt_3 (b)). These reactions were carried out in the same manner as described above for the reactions of **4** with NC_5H_5.

[*trans*-$CH_2DCH{=}CHCH_2NC_5H_5$]OTf (10a-d_1). ^1H NMR (500 MHz, $CDCl_3$): δ 8.00−8.83 (m, NC_5H_5, 5H), 6.14 (m, $CH_2DCH{=}CHCH_2{}^+NC_5H_5$, 1H), 5.70 (m, $CH_2DCH{=}CHCH_2{}^+NC_5H_5$, 1H), 5.17 (d, J(H−H) = 7.0 Hz, $CH_2DCH{=}CHCH_2{}^+NC_5H_5$, 2H) 1.77 (d, J(H−H) = 6.5 Hz, $CH_2DCH{=}CHCH_2{}^+NC_5H_5$, 2H). MS (FD): m/z 135 (M − OTf).

[*trans*-$CH_2DCH{=}CHCH_2NEt_3$]OTf (10b-d_1). ^1H NMR (200 MHz, $CDCl_3$): δ 6.13 (m, $CH_2DCH{=}CHCH_2{}^+NEt_3$, 1H), 5.48 (m, $CH_2DCH{=}CHCH_2{}^+NEt_3$, 1H), 3.72 (d, J(H−H) = 7.4 Hz, $CH_2DCH{=}CHCH_2{}^+NEt_3$, 2H), 3.20 (q, J(H−H) = 7.4 Hz, $N(CH_2CH_3)_3$, 2H), 1.80 (d, J(H−H) = 7.4 Hz, $CH_2DCH{=}CHCH_2{}^+NEt_3$, 2H), 1.30 (t, J(H−H) = 7.4 Hz, $N(CH_2CH_3)_3$, 3H). MS (FD): m/z 157 (M − OTf).

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Supporting Information Available: ^1H NMR (for **4**, **4-d_1**, **4-d_2**, **5**, **6**, **8**, **10a**, and **10a-d_1**), ^{13}C NMR (for **4**, **5**, **6**, **8**, and **10a**), ^1H, ^{13}C-2D HETCOR (for **4**, **6**, **8** and **10a**), and ^{31}P NMR (for **5** and **6**) data. This material is available free of charge via the Internet at http://pubs.acs.org.

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