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Reactions of Iridium(III) Compounds with Alkynes in the Presence of Triethylamine: The First Example of $M{-}CH{=}CH{-}^{+}NR_3$

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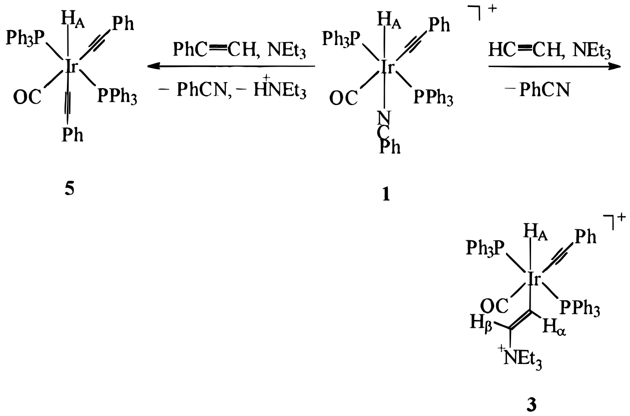
Summary: Reactions of the iridium(III) compounds $[Ir(H)(-C{\equiv}CPh)(PhCN)L_3]^+$ ***(1)*** *and* $[\overline{Ir{-}CH{=}CHCH{=}CH})(PhCN)L_3]^+$ ***(2)*** *(*$L_3 = (CO)(PPh_3)_2$*) with* $HC{\equiv}CH$ *in the presence of* NEt_3 *produce the acetylene-inserted products* $[Ir(H)(-C{\equiv}CPh)(-CH{=}CH{-}^{+}NEt_3)L_3]^+$ ***(3)*** *and* $[\overline{Ir{-}CH{=}CHCH{=}CH})(-CH{=}CH{-}^{+}NEt_3)L_3]^+$ ***(4)***, *while those with* $HC{\equiv}CPh$ *give the alkynyl complexes* $Ir(H)(-C{\equiv}CPh)_2L_3$ ***(5)*** *and* $\overline{Ir{-}CH{=}CHCH{=}CH})(-C{\equiv}CPh)L_3$ ***(6).***

Introduction

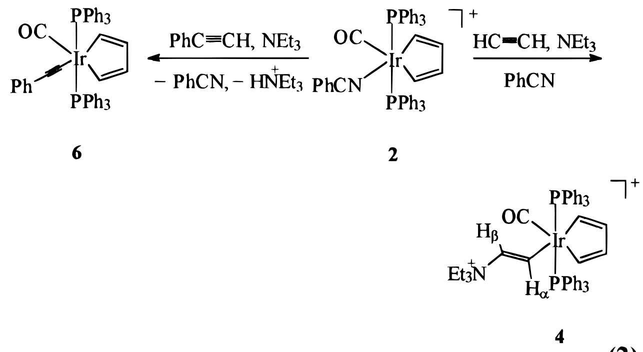
While reactions of terminal alkynes ($HC{\equiv}CR$) with transition metals in the presence of bases (py, PF_6^-, Et_2NH, OAc^-, CO_3^{2-}) mostly give metal alkynyls ($M{-}C{\equiv}C{-}R$),[1] alkyne insertion products $M{-}CH{=}CR{-}^{+}AR'_3$ (A = P, As), are also obtained from the reactions of alkynes with metals in the presence of AR'_3.[2] To the best of our knowledge, there has been no report on reactions of coordinated alkynes with amines. We now wish to report reactions of some iridium(III) complexes with acetylene in the presence of an amine to produce a new type of complex ($Ir{-}CH{=}CH{-}^{+}NEt_3$) containing acetylene inserted between iridium and triethylamine.

Results and Discussion

Reactions in the Presence of Triethylamine. The alkyne adducts $[Ir(H)(-C{\equiv}CPh)(PhCN)(CO)(PPh_3)_2]ClO_4$ ($\mathbf{1}(ClO_4)$)[3] and $[\overline{Ir{-}CH{=}CHCH{=}CH})(PhCN)(CO)(PPh_3)_2]ClO_4$ ($\mathbf{2}(ClO_4)$)[2a] react with acetylene in the presence of NEt_3 to give the products **3** and **4**, respectively, which contain a $-CH{=}CH-$ group inserted between iridium and NEt_3 ($Ir{-}CH{=}CH{-}^{+}NEt_3$), while reactions of **1** and **2** with phenylacetylene produce the phenylethynyl ($Ir{-}C{\equiv}CPh$) complexes **5** and **6** (see eqs 1 and 2). Small amounts (less than 10%) of the ethynyl compounds $Ir(H)(-C{\equiv}CH)(-C{\equiv}CPh)(CO)(PPh_3)_2$ **(5a)** and $\overline{Ir{-}CH{=}CHCH{=}CH})(-C{\equiv}CH)(CO)(PPh_3)_2$ **(6a)** are also produced in the reactions of **1** and **2** with $HC{\equiv}CH$, whereas no alkyne insertion products have been obtained from the reactions of $PhC{\equiv}CH$. All of the iridium(III) complexes **3**−**6** newly prepared in this study are stable both in the solid state and in solution at 25 °C, even in air for several hours, and have been characterized by X-ray crystal structural analysis (for **4**); see Figure 1), spectral measurements (^1H, ^{13}C, and ^{31}P NMR and IR), and elemental analysis (see Experimental Section).



(1)



(2)

α-Protons of metal-bound alkenyl groups have been observed in a wide range (*e.g.*, δ 7.7 ppm[4] to δ 12.5 ppm[5]) of ^1H NMR spectra. The α-proton ($Ir{-}CH_\alpha{=}CH_\beta{-}$

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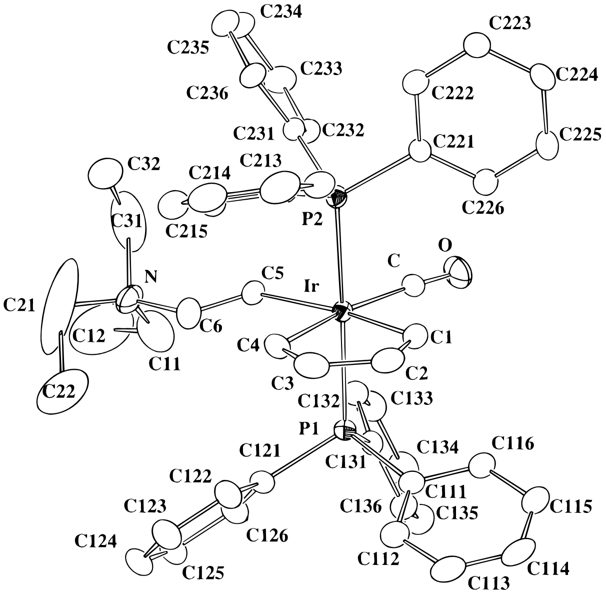

Figure 1. ORTEP drawing of **4** (30% probability ellipsoids). The anion (ClO_4^-) and solvent ($(CH_3CH_2)_2O$) were omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ir−C = 1.920(6), Ir−C1 = 2.114(6), Ir−C4 = 2.094(6), Ir−C5 = 2.149(5), Ir−P1 = 2.3575(15), Ir−P2 = 2.3585(15), C−O = 1.132(7), C1−C2 = 1.322(9), C2−C3 = 1.449(10), C3−C4 = 1.358(9), C5−C6 = 1.288(9), C6−N = 1.533(8), N−C11 = 1.671(13), N−C21 = 1.429(12), N−C31 = 1.516(14); C−Ir−C4 = 171.6(2), C−Ir−C1 = 94.9(2), C4−Ir−C1 = 77.0(3), C−Ir−C5 = 96.2(2), C4−Ir−C5 = 91.9(2), C1−Ir−C5 = 168.9(2), C−Ir−P1 = 91.9(2), C4−Ir−P1 = 86.2(2), C1−Ir−P1 = 89.6(2), C5−Ir−P1 = 89.5(2), C−Ir−P2 = 92.8(2), C4−Ir−P2 = 88.7(2), C1−Ir−P2 = 87.4(2), C5−Ir−P2 = 92.5(2), P1−Ir−P2 = 174.58(5), O−C−Ir = 176.1(5), C2−C1−Ir = 115.9(5), C1−C2−C3 = 116.0(6), C3−C4−Ir = 115.3(5), C6−C5−Ir = 129.0(5), C5−C6−N = 124.5(6), C21−N−C6 = 113.5(9), C6−N−C31 = 111.7(7), C6−N−C11 = 107.8(5).

$^+NEt_3$) of **3** is seen at δ 7.27 ppm, while that of **4** seems to be obscured by the protons of the PPh_3 at δ 7.0−8.0 ppm. The β-protons ($Ir{-}CH_\alpha{=}CH_\beta{-}^+NEt_3$) are clearly seen at δ 5.24 (for **3**) and 4.80 ppm (for **4**). The observed coupling constants (13−16 Hz) between H_α and H_β of **3** and **4** unambiguously suggest that these two protons are *trans* to each other, as shown in eqs 1 and 2, which is confirmed by X-ray crystal analysis (see Figure 1). Hydride (Ir−*H*) signals are frequently useful for the characterization of those iridium compounds investigated in this study and related ones: the hydrides *trans* to carbon are seen at δ −7 to −14 ppm, while those *trans* to nitrogen are measured at δ −16 to −20 ppm.[6] Accordingly, those triplets at δ −9.96 and −10.01 ppm observed for **3** and **5** are assigned due to the hydrides *trans* to carbons of newly inserted alkynes, since the hydride *trans* to CO is seen at δ −8.8 ppm for related compounds.[7] Small coupling constants (J_{H-P} = 13.7 Hz for **5** and 14.4 Hz for **3**) also confirm the structures of **3** and **5**, where the hydride is *cis* to both phosphorus atoms.[6] Assigning ^{13}C NMR signals for **3**−**6** is mostly straightforward: α- and β-carbons of $Ir{-}C_\alpha H{=}C_\beta H{-}^+NEt_3$ (for **3** and **4**) and $Ir{-}C_\alpha{\equiv}C_\beta{-}Ph$ (for **3**, **5**, and **6**) have been identified by comparing the spectral data (chemical shifts, multiplicities, and coupling constants J_{P-C}) for **3**−**6** with each other and with those reported values for the related compounds.[1g,2a,4,8] It seems certain that the ^{13}C NMR and ^{31}P NMR data (see Experimental Section) agree well with the structures of **3**−**6** shown in eqs 1 and 2. Infrared spectral data (see Experimental Section) also provide evidence for a newly added alkynyl group (Ir−C≡CPh) in **5** and **6**. The medium-intensity ν(C≡C) bands are newly seen at 2109−2098 cm^{-1} for **5** and **6**. The weak ν(Ir−H) band observed for **3** is not resolved in the spectrum of **5**, probably due to a stronger ν(C≡C) band at *ca.* 2100 cm^{-1}.

It has been suggested that the alkyne insertion between the metal−phosphorus bond (to produce $M{-}CH{=}CR{-}^+PR'_3$) occurs *via* nucleophilic attack of phosphine (PR'_3) on the coordinated alkyne (HC≡CR).[5,9,10] While alkyne insertion between the transition-metal−nitrogen bond has not been reported thus far, alkene (*e.g.*, HC=CH) insertion into the M−N bond is known to give $M{-}CHCH{-}^+NR_3$ species (NR_3 = $HNMe_2$, py), which are presumably obtained by the attack of $NHMe_2$ on coordinated HC=CH.[11] It may then be said that the acetylene insertion between Ir and NEt_3 to form $Ir{-}CH{=}CH{-}^+NEt_3$ in eqs 1 and 2 also occurs through the attack of NEt_3 on the coordinated HC≡CH in place of the labile PhCN of **1** and **2**.

It is somewhat unexpected not to see the insertion of HC≡CPh between iridium and NEt_3 in the reactions of eqs 1 and 2, since the insertion of HC≡CPh between iridium and NEt_3 should not cause much steric hindrance. In fact, the HC≡CPh insertion products $Ir(H)(-C{\equiv}CPh)(-CH{=}CPh{-}^+PPh_3)L_3$ and $\overline{Ir{-}CH{=}CHCH{=}CH})(-CH{=}CH{-}^+PPh_3)L_3$ (L_3 = $(CO)(PPh_3)_2$) are known to be stable.[2a] Then, the fact that phenylethynyl complexes **5** and **6** are the only products from the reactions of HC≡CPh, whereas from the reactions of HC≡CH the insertion products **3** and **4** are mainly obtained, may be understood in terms of the acetylenic hydrogen of HC≡CPh being more acidic than that of HC≡CH.

In the presence of other amines such as NMe_3 and $N(n\text{-}Pr)_3$, reactions of **1** and **2** with HC≡CH also give the HC≡CH insertion products $[Ir(H)(-C{\equiv}CPh)(-CH{=}CH{-}^+NR_3)L_3]^+$ and $[\overline{Ir{-}CH{=}CHCH{=}CH})(-CH{=}CH{-}^+NR_3)L_3]^+$ (L_3 = $(CO)(PPh_3)_2$, R = Me, *n*-Pr), which are identified by ^1H NMR and IR spectral data.

It should be mentioned that reactions of **1** and **2** with alkynes in the presence of primary and secondary amines give unknown products, whereas vinyl amido complexes have been previously reported from the reactions of primary amines with π-alkyne metal complexes.[12]

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(6) References 2a and 3, and references therein. Unpublished results for related compounds.

(7) Unpublished results.

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Experimental Section

Caution! Extensive precautions must be taken, since perchlorate salts are potentially explosive. All reactions were carried out under nitrogen with the use of standard Schlenk techniques. NMR spectra were recorded on either Varian Gemini 200 or/and 300 spectrometers (^{1}H, 200/300 MHz; ^{13}C, 50.3, 75.5 MHz; ^{31}P, 121.7 MHz). IR spectra were obtained on a Shimadzu IR-440 spectrophotometer. Elemental analyses were carried out at Organic Chemistry Reaction Center, Sogang University, Mapoku Seoul, Korea. $\mathrm{[Ir(H)(-C{\equiv}CPh)(PhCN)(CO)(PPh_3)_2]ClO_4}$ (**1**($\mathrm{ClO_4}$)) $\mathrm{[\overline{Ir-CH{=}CHCH{=}C}H)(PhCN)(CO)(PPh_3)_2ClO_4}$ (**2**($\mathrm{ClO_4}$)) were prepared by literature methods.[2a]

Syntheses. Acetylene-inserted compounds (**3** and **4**) and alkynyl compounds (**5** and **6**) were prepared in the same manner as described below for **3** and **5**, respectively.

$\mathbf{[Ir(H)(-C{\equiv}CPh)(-CH{=}CH-{}^{+}NEt_3)(CO)(PPh_3)_2]ClO_4}$ (3(ClO$_4$)). A pale yellow-brown solution of **1** (0.11 g, 0.1 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was stirred under $\mathrm{HC{\equiv}CH}$ (1 atm) in the presence of $\mathrm{NEt_3}$ (0.11 mmol) at 25 °C for 30 min, during which time the solution turned slightly darker. A 10 mL portion of water was added to the reaction mixture, and excess $\mathrm{NEt_3}$ and $\mathrm{NHEt_3^+}$ in the aqueous layer were separated from **3** in the $\mathrm{CH_2Cl_2}$ layer. Addition of *n*-hexane (25 mL) to the $\mathrm{CH_2Cl_2}$ solution resulted in precipitation of beige microcrystals of **3**, which were collected by filtration, washed with cold hexane (2 × 10 mL), and dried under vacuum. The yield was 0.092 g (86%). ^{1}H NMR ($\mathrm{CDCl_3}$, 25 °C): δ −9.96 (t, 1H, $J_{\mathrm{P-H}} = 14.4$ Hz, Ir−*H*), 0.72 (t, 9H, $J_{\mathrm{H-H}} = 6.8$ Hz, $^{+}\mathrm{N(CH_2C}H_3)_3$), 2.88 (q, 6H, $^{+}\mathrm{N(C}H_2\mathrm{CH_3)_3}$), 7.27 (d, 1H, $J_{\mathrm{H}_\alpha-\mathrm{H}_\beta} = 16.0$ Hz, $\mathrm{Ir-C}H_\alpha\mathrm{-CH}_\beta-$), 5.24 (d, 1H, $J_{\mathrm{H}_\alpha-\mathrm{H}_\beta} = 16.0$ Hz, $\mathrm{Ir-CH_\alpha{=}C}H_\beta$–). ^{13}C{^{31}P} NMR ($\mathrm{CDCl_3}$, 25 °C): δ 6.8 (s, $^{+}\mathrm{N(CH_2}C\mathrm{H_3)_3}$), 53.2 (s, $^{+}\mathrm{N(}C\mathrm{H_2CH_3)_3}$), 84.7 (t, $J_{\mathrm{P-C}} = 18.6$ Hz, $\mathrm{Ir-}C{\equiv}\mathrm{CPh}$), 110.4 (s, $\mathrm{Ir-}C\mathrm{Ph}$), 129.5 (t, $J_{\mathrm{P-C}} = 7.8$ Hz, $\mathrm{Ir-}C\mathrm{H{=}CH-{}^{+}N}$), 134.8 (s, $\mathrm{Ir-CH{=}}C\mathrm{H-{}^{+}N}$), 172.8 (t, $J_{\mathrm{P-C}} = 7.1$ Hz, *C*O). ^{31}P NMR ($\mathrm{CDCl_3}$, 25 °C): δ −2.1 (s). IR (Nujol): ν_{max}/cm^{-1} 2007 s (CO), 2115 w (Ir−H), 1100 s,br (noncoordinated tetrahedral $\mathrm{ClO_4}$). Anal. Calcd for $\mathrm{IrP_2C_{53}H_{53}NClO_4}$: C, 59.29; H, 4.98; N, 1.31. Found: C, 60.02; H, 4.85; N, 1.45.

$\mathbf{[\overline{Ir-CH{=}CHCH{=}C}H)(-CH{=}CH-{}^{+}NEt_3)(CO)(PPh_3)_2]ClO_4}$ (4(ClO$_4$)). This compound was prepared in the same manner as described for **3**. A 0.10 g (0.10 mmol) portion of **2** was used, and the yield was 0.082 g (80%). ^{1}H NMR ($\mathrm{CDCl_3}$, 25 °C): δ 0.80 (t, 9H, $J_{\mathrm{H-H}} = 7.0$ Hz, $^{+}\mathrm{N(CH_2C}H_3)_3$), 2.62 (q, 6H, $\mathrm{N(C}H_2\mathrm{CH_3)_3}$), 4.80 (d, 1H, $J_{\mathrm{H}_\alpha-\mathrm{H}_\beta} = 16.1$ Hz, $\mathrm{Ir-CH_\alpha{=}C}H_\beta\mathrm{-{}^{+}N}$), 5.90, 5.96, 6.81, 7.21 [4 × m, 1H, $\mathrm{Ir(C_4}H_4)$]. ^{13}C{^{31}P} NMR ($\mathrm{CDCl_3}$, 25 °C): δ 7.4 (s, $^{+}\mathrm{N(CH_2}C\mathrm{H_3)_3}$), 53.4 (s, $^{+}\mathrm{N(}C\mathrm{H_2CH_3)_3}$), 128.5 (t, $J_{\mathrm{P-C}} = 5.3$ Hz, $\mathrm{Ir-CH{=}}C\mathrm{H-{}^{+}N}$), 144.7 (t, $J_{\mathrm{P-C}} = 8.2$ Hz, $\mathrm{Ir-}C\mathrm{H{=}CH-{}^{+}N}$), 137.9 [br, α-*C* of $\mathrm{Ir(C_4H_4)}$], 143.8, 146.0 (2 × s, *β*-*C* of $\mathrm{Ir(C_4H_4)}$], 153.6 [t, $J_{\mathrm{P-C}} = 11.6$ Hz, α-*C* of $\mathrm{Ir(C_4H_4)}$], 175.8 (t, $J_{\mathrm{P-C}} = 8.7$ Hz, Ir−*C*O). ^{31}P NMR ($\mathrm{CDCl_3}$, 25 °C): δ 1.32 (s). IR (Nujol): ν_{max}/cm^{-1} 1998 s (CO). Single crystals of **4** were obtained by liquid diffusion of diethyl ether into a solution of **4** in $\mathrm{CHCl_3}$. Crystallographic data for **[4]ClO$_4$**$\cdot{}^{1}/_{2}\mathrm{(CH_3CH_2)_2O}$: $\mathrm{C_{51}H_{56}NO_{5.5}P_2ClIr}$, $M_{\mathrm{r}} = 1060.56$, triclinic, $P\bar{1}$; $a = 11.043(3)$ Å, $b = 12.337(3)$ Å, $c = 17.919(3)$ Å, $\alpha = 84.12(2)°$, $\beta = 82.61(2)°$, $\gamma = 76.19(2)°$, $Z = 2$, $D_{\mathrm{calcd}} = 1.502$ g cm^{-3}, $F(000) = 1074$. Reflections were collected at 20 °C with Mo Kα (0.710 73 Å) radiation, and the structure was solved using SHELXL-93 by full-matrix least squares: number of parameters 505, $R1 = 0.0364$, wR2 $= 0.0900$, GOF $= 1.046$.

$\mathbf{Ir(H)(-C{\equiv}CPh)_2(CO)(PPh_3)_2}$ (5). The reaction mixture of **1** (0.11 g, 0.10 mmol) and $\mathrm{PhC{\equiv}CH}$ (11 mg, 0.11 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was stirred in the presence of $\mathrm{NEt_3}$ (0.11 mmol) under nitrogen for 10 min at 0 °C. A 10 mL portion of water was added to the reaction mixture, and excess $\mathrm{NEt_3}$ and $\mathrm{HNEt_3^+}$ in the aqueous layer were separated from **5** in the $\mathrm{CH_2Cl_2}$ layer. Cold hexane (25 mL) was added to the $\mathrm{CH_2Cl_2}$ solution on a dry ice/2-propanol bath to precipitate beige microcrystals of **5**, which were collected by filtration, washed with cold hexane (2 × 10 mL), and dried under vacuum. The yield was 0.065 g (69%). ^{1}H NMR ($\mathrm{CDCl_3}$, 25 °C): δ −10.01 (t, 1H, $J_{\mathrm{P-H}} = 13.7$ Hz, Ir−*H*). ^{13}C{^{31}P} NMR ($\mathrm{CDCl_3}$, 25 °C): δ 82.6 (br, $\mathrm{Ir-}C{\equiv}\mathrm{CPh}$), 109.1, 108.7 (2 × s, $\mathrm{Ir-C{\equiv}}C\mathrm{Ph}$), 171.0 (t, $J_{\mathrm{P-C}} = 7.8$ Hz, *C*O). ^{31}P NMR ($\mathrm{CDCl_3}$, 25 °C): δ −3.58 (s). IR (Nujol): ν_{max}/cm^{-1} 2022 s (CO), 2108 m (C≡C). Anal. Calcd for $\mathrm{IrP_2C_{53}H_{41}O}$: C, 67.14; H, 4.36. Found: C, 67.01; H, 4.27.

$\mathbf{\overline{Ir-CH{=}CHCH{=}C}H)(-C{\equiv}CPh)(CO)(PPh_3)_2}$ (6). This compound was prepared in the same manner as described above for **5a**, except that the reaction temperature and time were 25 °C and 30 min. A 0.10 g (0.10 mmol) portion of **2** was used, and the yield was 0.085 g (95%). ^{1}H NMR ($\mathrm{CDCl_3}$, 25 °C): δ 5.70, 6.16, 6.87 [3 × m, 3H, $\mathrm{Ir(C_4}H_4)$], 6.68−7.10 (m, 6H, 1H of $\mathrm{Ir(C_4}H_4)$ + 5H of $\mathrm{C{\equiv}C-C_6}H_5$], 7.2−7.85 (m, 30H, $\mathrm{P-C_6}H_5$). ^{13}C{^{31}P} NMR ($\mathrm{CDCl_3}$, 25 °C): δ 88.6 (t, $J_{\mathrm{P-C}} = 15.1$ Hz, $\mathrm{Ir-}C{\equiv}\mathrm{CPh}$), 113.4 (s, $\mathrm{Ir-C{\equiv}}C\mathrm{Ph}$), 127.9, 144.2, 147.6, 149.8 [4 × t, $\mathrm{Ir(}C_4\mathrm{H_4)}$], 174.5 (t, $J_{\mathrm{P-C}} = 8.0$ Hz, Ir−*C*O). ^{31}P NMR ($\mathrm{CDCl_3}$, 25 °C): δ −2.32 (s). IR (Nujol): ν_{max}/cm^{-1} 1998 s (CO), 2098 m (C≡C). Anal. Calcd for $\mathrm{IrP_2C_{49}H_{41}O}$: C, 65.54; H, 4.38. Found: C, 66.01; H, 4.29.

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Supporting Information Available: Text giving details of the X-ray structure determination, a figure showing the unit cell packing, and tables of crystal data, positional and thermal parameters, and bond distances and angles for **4** (11 pages). Ordering information is given on any current masthead page.

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