Synthesis and Characterization of the Allenylidene Compounds [Ir(diene)(C=C=CPh$_2$)(PR$_3$)]BF$_4$ (diene = 1,5-Cyclooctadiene, PR$_3$ = PCy$_3$; diene = Tetrafluorobenzobarrelene, PR$_3$ = PCy$_3$, P^{i}Pr$_3$): The First Mixed-Ligand Complexes of the Type [Ir(diene)L(PR$_3$)]$^+$ Containing an Unsaturated η^1-Carbon Ligand

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*Summary: The square-planar methoxy compounds Ir(OMe)(diene)(PR$_3$) (diene = COD, PR$_3$ = PCy$_3$ (**1**); diene = TFB, PR$_3$ = PCy3 (**2**), P^{i}Pr$_3$ (**3**)) react with 1,1-diphenyl-2-propyn-1-ol to give the hydroxyalkynyl complexes Ir{C≡CC(OH)Ph$_2$}(diene)(PR$_3$) (diene = COD, PR$_3$ = PCy$_3$ (**4**); diene = TFB, PR$_3$ = PCy$_3$ (**5**), P^{i}Pr$_3$ (**6**)), which by reaction with HBF$_4$·OEt$_2$ afford the corresponding allenylidene derivatives [Ir(diene)(C=C=CPh$_2$)(PR$_3$)]BF$_4$ (diene = COD, PR$_3$ = PCy$_3$ (**7**); diene = TFB, PR$_3$ = PCy$_3$ (**8**), P^{i}Pr$_3$ (**9**)).*

Introduction

Shapley, Schrock and Osborn[1] characterized the cationic rhodium and iridium complexes with the general formula [M(diene)L$_a$]$^+$ (a = 2, 3), which were found to be active catalysts for the hydrogenation of olefins,[2] dienes,[3] internal alkynes,[4] and ketones.[5] For the olefin hydrogenation, better results were obtained from the mixed-ligand complexes [Ir(COD)L(PR$_3$)]$^+$ (L = N-donor molecule), which in dichloromethane catalyze the reduction of tri- and tetrasubstituted olefins as well as tetrasubstituted prochiral amido alkenes.[6] It was Crabtree who first showed that an equimolecular mixture of [Ir(COD)(PPh$_3$)$_2$]PF$_6$ and [Ir(COD)(py)$_2$]PF$_6$ in dichloromethane at room temperature rapidly rearranges to give the mixed-ligand complex [Ir(COD)(py)(PPh$_3$)]PF$_6$ in high yield.[7] Since then, a large family of [Ir(diene)L(PR$_3$)]$^+$ compounds with L = N-, As-, Sb-, O-, and S-donor molecules have been reported.[8] However, complexes of this type containing unsaturated η^1-carbon ligands are not known.

Recently, we have reported that the reactions of the dimers [Ir(μ-OMe)(diene)]$_2$ (diene = 1,5-cyclooctadiene (COD), tetrafluorobenzobarrelene (TFB)) with bulky phosphines afford the square-planar complexes Ir(OMe)(diene)(PR$_3$).[9] The methoxide ligand of these compounds can be easily displaced by anions from molecules containing relatively acidic protons, such as alcohols, benzophenone imine,[9] propanethiol, and terminal alkynes,[10] to give alkoxide, azavinylidene, thiopropoxide, and alkynyl complexes, respectively. The alkynol 1,1-diphenyl-2-propyn-1-ol contains two relatively acidic protons, the H−C(sp) and H−OC hydrogen atoms. Therefore, at first glance, the reactions of Ir(OMe)(diene)(PR$_3$) with this alkynol could afford alkynyl or alternatively alkoxide derivatives. This prompted us to investigate the reactivity of the above-mentioned methoxide complexes toward 1,1-diphenyl-2-propyn-1-ol. In this note we report the selective formation of Ir{C≡CC(OH)Ph$_2$}(diene)(PR$_3$) by reaction of Ir(OMe)(diene)(PR$_3$) with 1,1-diphenyl-2-propyn-1-ol. In addition, we prove that these compounds are useful starting materials to prepare the allenylidene derivatives [Ir(diene)(C=C=CPh$_2$)(PR$_3$)]$^+$, which are the first mixed-ligand complexes of type [Ir(COD)L(PR$_3$)]$^+$ containing an unsaturated η^1-carbon ligand.

Results and Discussion

The reactions of the complexes Ir(OMe)(diene)(PR$_3$) (**1**−**3**; Scheme 1) with 1,1-diphenyl-2-propyn-1-ol were

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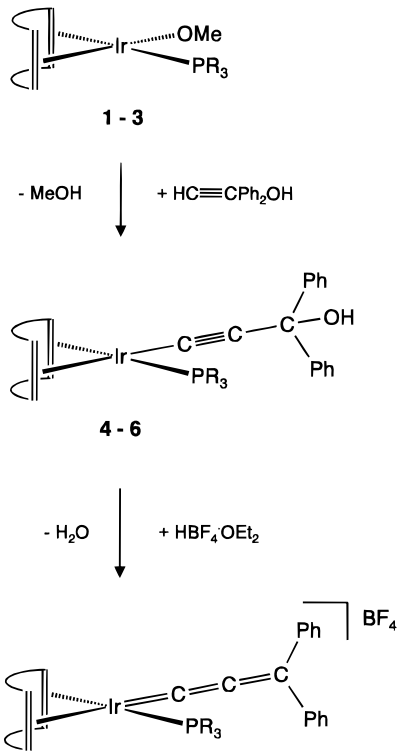
Scheme 1

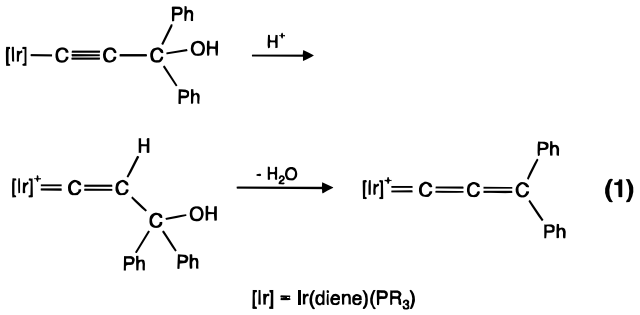


Complex	diene	PR_3
1, 4, 7	COD	PCy_3
2, 5, 8	TFB	PCy_3
3, 6, 9	TFB	P^iPr_3

carried out at room temperature in pentane or methanol as solvent. The reaction products, Ir{C≡CC(OH)Ph_2}(diene)(PR_3) (**4**−**6**), were isolated as red solids in high yield (70−80%) and characterized by elemental analysis, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy.

The presence of the η^1-carbon ligand in **4**−**6** is mainly supported by the IR and ^{13}C{^{1}H} NMR spectra. The IR spectra in Nujol show the ν(O−H) absorption between 3437 and 3450 cm^{-1} and the ν(C≡C) band at about 2080 cm^{-1}. In the ^{13}C{^{1}H} NMR spectra the signals corresponding to the α-carbon atoms of the alkynyl groups appear between 119 and 120 ppm as doublets with P−C coupling constants between 13.5 and 12.0 Hz, while those due to the β-carbon atoms are observed as singlets at about 148 ppm. In agreement with the square-planar structure proposed for these compounds in Scheme 1, the ^{13}C{^{1}H} NMR spectra also contain two resonances due to the olefinic carbon atoms of the dienes. In the spectrum of the 1,5-cyclooctadiene complex **4,** the olefinic carbon atoms disposed *trans* to the phosphine ligand give at 82.89 ppm a doublet with a P−C coupling constant of 12.8 Hz, while the olefinic carbon atoms disposed *trans* to the alkynyl group display a singlet at 67.20 ppm. In the spectra of the tetrafluorobenzobarrelene compounds **5** and **6** the signals corresponding to the olefinic carbon atoms disposed *trans* to the phosphine ligands appear at 62.74 (**5**) and 63.36 (**6**) ppm as doublets with a P−C coupling constant for both compounds of 12.1 Hz, and the carbon atoms of the carbon−carbon double bond disposed *trans* to the alkynyl group give rise to singlets at 148.69 (**5**) and 148.47 (**6**) ppm. In accordance with the ^{13}C{^{1}H} NMR spectra, the ^{1}H NMR spectra show two resonances corresponding to the vinylic protons of the dienes at 4.80 and 3.59 (**4**), 3.96 and 2.48 (**5**), and 4.01 and 2.34 (**6**) ppm. The resonance of the O*H* proton of **4** appears at 2.58 ppm, while those of **5** and **6** are observed at about 2.80 ppm. The ^{31}P{^{1}H} NMR spectra show singlets at 19.9 (**4**), 23.4 (**5**), and 35.4 (**6**) ppm.

The addition of 1 equiv of HBF_4·OEt_2 to diethyl ether solutions of **4**−**6** affords dark solids, from which the allenylidene complexes **7**−**9** (Scheme 1) were isolated as violet (**7**) or red (**8** and **9**) microcrystals in nearly quantitative yield. From a mechanistic point of view these compounds could be a consequence of the direct protonation of the −OH group of the alkynyl ligand or alternatively the result of the spontaneous dehydration of hydroxyvinylidene intermediates, which should be generated by electrophilic attack of the proton of the acid to the β-carbon atom of the alkynyl ligands of the starting complexes (eq 1). In this context, it should be



mentioned that (i) the addition of electrophiles to metal alkynyl compounds is a general method to prepare vinylidene compounds[11] and (ii) the dehydration of hydroxyvinylidene complexes to yield allenylidene derivatives is a well-known process.[12]

The most interesting feature of the IR spectra of **7**−**9** is the presence of the strong vibrations of the allene ligands, which are observed between 1948 and 1958 cm^{-1}. In addition, the spectra exhibit at about 1050 cm^{-1} the absorption due to the $[BF_4]^-$ anion with T_d symmetry, indicating that, although the metallic center of **7**−**9** is coordinatively unsaturated, the anion is not

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coordinated to the iridium metal. In the $^{13}C\{^1H\}$ NMR spectra the resonances due to the α-carbon atoms of the allenylidene ligands appear between 272 and 277 ppm as doublets with P−C coupling constants between 9 and 13 Hz, while the *β*- and *γ*-carbon atoms are observed as singlets at about 183 and 162 ppm, respectively. In agreement with the square-planar structure proposed for these compounds in Scheme 1, the spectra contain two olefinic resonances. The carbon atoms of the C−C double bonds disposed *trans* to the phosphine ligands give, between 88 and 68 ppm, doublets with P−C coupling constants between 9 and 16 Hz, while the resonances corresponding to the carbon atoms of the C−C double bonds disposed *trans* to the η^1-carbon ligand are observed between 93 and 73 ppm as singlets. In accordance with the $^{13}C\{^1H\}$ NMR spectra the 1H NMR spectra of **7** and **9** show two signals for the vinylic protons of the diolefins at 5.29 and 4.83 (**7**) and 4.63 and 4.50 (**9**) ppm. In the ^1H NMR spectrum of **8** the vinylic protons of the tetrafluororobenzobarrelene ligand display a broad resonance centered at 4.46 ppm. The $^{31}P\{^1H\}$ NMR spectrum of the three compounds show singlets at 45.0 (**7**), 32.9 (**8**), and 45.0 (**9**) ppm.

In conclusion, the methoxide group of complexes Ir(OR)(diene)(PR_3) (**1**−**3**) selectively reacts with the C(sp)−H hydrogen atom of 1,1-diphenyl-2-propyn-1-ol to afford methanol and the corresponding alkynyl derivatives Ir{C≡CC(OH)Ph_2}(diene)(PR_3) (**4**−**6**), which are useful starting materials to prepare the allenylidene complexes [Ir(diene)(C=C=CPh_2)(PR_3)]$^+$ (**7**−**9**). These compounds are the first examples of cationic allenylidene derivatives of Ir(I). It should be mentioned that Werner[13] has recently prepared neutral complexes of the type IrCl(C=C=CHR)(P^iPr_3)$_2$.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. 1,1-Diphenyl-2-propyn-1-ol was recrystallized from *n*-pentane. The starting complexes Ir(OMe)(diene)(PR_3) (diene = COD, PR_3 = PCy_3 (**1**);[9a] diene = TFB, PR_3 = PCy_3 (**2**)[9b] were prepared by published methods. Elemental analyses were performed with a Perkin-Elmer 240 XL microanalyzer. NMR spectra were recorded on Varian Unity 300 or Bruker AXR 300 instruments. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ ($^{13}C\{^1H\}$, ^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Infrared spectra were obtained from a Perkin-Elmer 783 instrument as Nujol mulls on polyethylene sheets or in solution using NaCl cells.

Preparation of Ir(TFB)(OMe)(P^iPr_3) (3). This compound was prepared using the procedure described for **2**. A 0.25 g (0.28 mmol) portion of [Ir(*μ*-OMe)TFB]$_2$ was dissolved in methanol, and 0.1 mL (0.6 mmol) of P^iPr_3 was added. An orange solid was obtained. Yield: 0.22 g (65%). Anal. Calcd for $C_{22}H_{30}F_4IrOP$: C, 43.34; H, 4.96. Found: C, 43.02; H, 5.18. IR (Nujol, cm^{-1}): *ν*(C−O) 1037. ^1H NMR (300 MHz, C_6D_6, 20 °C): *δ* 5.16 (br, 2 H, C*H*); 4.05 (s, 3 H, OCH_3); 3.55 (br, 2 H, =C*H*); 1.98 (m, 3 H, PC*H*); 1.41 (br, 2 H, =C*H*); 1.06 (dd, J_{H-H} = 7.5 Hz, J_{P-H} = 13.5 Hz, 18 H, PCH_3). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6, 20 °C): *δ* 30.41 (s).

Preparation of Ir(COD)(C≡CCPh_2OH)(PCy_3) (4). A solution of 0.225 g (0.37 mmol) of **1** in 10 mL of *n*-pentane was stirred for 1 h with 0.084 g (0.405 mmol) of 1,1-diphenyl-2-propyn-1-ol, yielding a clear, intensely red solution. Reducing the solvent to ca. 3 mL caused precipitation of a red solid. The solvent was decanted, and the solid was washed several times with pentane and dried in vacuo. Yield: 0.201 g (70%). Anal. Calcd for $C_{41}H_{56}IrOP$: C, 62.49; H, 7.16. Found: C, 62.26; H, 6.98. IR (Nujol, cm^{-1}): *ν*(OH) 3437; *ν*(C≡C) 2079; *ν*(Ph) 1598; *ν*(C−O) 1037. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): *δ* 7.63−7.13 (m, 10 H, Ph); 4.80 (br, 2 H, =C*H*); 3.59 (br, 2 H, =C*H*); 2.58 (s, 1 H, O*H*); 2.11−1.04 (41 H, C_6H_{11}, C_8H_{12}). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 20 °C): *δ* 148.83 (s, C_β); 128.23 (s, Ph); 128.0 (s, Ph); 127.68 (s, Ph); 120.05 (d, J_{P-C} = 13.5 Hz, C_α); 82.89 (d, J_{P-C} = 12.8 Hz, =*C*H); 75.32 (s, C*γ*), 67.20 (s, =*C*H); 34.70 (s, *C*H_2, C_8H_{12}); 34.38 (s, *C*H_2, C_8H_{12}); 32.79 (d, J_{P-C} = 30.2 Hz, C_6H_{11}); 30.73 (s, C_6H_{11}); 27.81 (d, J_{P-C} = 10.6 Hz, C_6H_{11}); 26.84 (s, C_6H_{11}). $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$, 20 °C): *δ* 19.88 (s).

Preparation of Ir(TFB)(C≡CCPh_2OH)(PCy_3) (5). The complex was prepared according to the preparation of compound **4**. A solution of 0.217 g (0.29 mmol) of **2** in 10 mL of methanol was treated with 0.074 g (0.35 mmol) of 1,1-diphenyl-2-propyn-1-ol to yield an intensively red solution, from which an intensively red solid was obtained. Yield: 0.215 g (82%). Anal. Calcd for $C_{45}H_{50}F_4IrOP$: C, 59.65; H, 5.56. Found: C, 59.30; H, 5.69. IR (Nujol, cm^{-1}): *ν*(OH) 3450; *ν*(C≡C) 2085; *ν*(Ph) 1598; *ν*(C−O) 1037. ^1H NMR (300 MHz, C_6D_6, 20 °C): *δ* 7.05−7.98 (m, 10 H, Ph); 5.21 (br, 2 H, C*H*); 3.96 (br, 2 H, =C*H*); 2.79 (s, ^1H, O*H*); 2.48 (br, 2 H, =C*H*); 1.96−1.03 (m, 33 H, C_6H_{11}). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 20 °C): *δ* 148.69 (s, C_β); 127.32 (Ph); 126.99 (Ph); 119.30 (d, J_{P-C} = 12.07 Hz, C_α); 75.61 (s, C_γ); 62.74 (d, J_{P-C} = 12.07 Hz, =*C*H); 45.60 (s, =*C*H); 40.82 (s, *C*H); 35.41 (d, J_{P-C} = 26.4 Hz, C_6H_{11}); 30.43 (s, C_6H_{11}); 27.75 (d, J_{P-C} = 10.6 Hz, C_6H_{11}); 26.68 (s, C_6H_{11}). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6, 20 °C): *δ* 23.43 (s).

Preparation of Ir(TFB)(C≡CCPh_2OH)(P^iPr_3) (6). The complex was prepared using the procedure described for **4**. A solution of 0.206 g (0.34 mmol) of **3** in 10 mL of *n*-pentane was treated with 0.077 g (0.37 mmol) of 1,1-diphenyl-2-propyn-1-ol to yield an intensively red suspension, from which a red solid was isolated. Yield: 0.198 g (75%). Anal. Calcd for $C_{36}H_{38}F_4IrOP$: C, 55.02; H, 4.87. Found: C, 55.52; H, 4.82. IR (Nujol, cm^{-1}): *ν*(OH) 3439; *ν*(C≡C) 2085; *ν*(Ph) 1597; *ν*(C−O) 1037. ^1H NMR (300 MHz, C_6D_6, 20 °C): *δ* 7.03−7.91 (m, 10 H, Ph); 5.17 (br, 2 H, C*H*); 4.01 (br, 2 H, =C*H*); 2.81 (s, 1H, O*H*); 2.34 (br, 2 H, =C*H*); 1.93 (m, 3 H, PC*H*); 1.00 (dd, J_{H-H} = 7.15 Hz, J_{P-H} = 13.64 Hz, 18 H, PCH_3). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 20 °C): *δ* 148.47 (s, C_β); 129.85 (s, Ph); 127.17 (s, Ph); 126.90 (s, Ph); 120.46 (d, J_{P-C} = 12.07 Hz, C_α); 75.57 (s, C_γ); 63.36 (d, J_{P-C} = 12.07 Hz, =*C*H); 45.96 (s, =*C*H); 40.85 (s, *C*H); 25.37 (d, J_{P-C} = 26.63 Hz, P*C*H); 19.8 (s, *C*H_3, P^iPr_3). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6, 20 °C): *δ* 35.43 (s).

Preparation of [Ir(COD)(C=C=CPh_2)(PCy_3)]BF_4 (7). A solution of **4** (0.1 g, 0.13 mmol) in 10 mL of diethyl ether was treated with HBF_4·OEt_2 (0.14 mmol, 20 *μ*L). The solution turned immediately dark violet, and a solid precipitated from the solution. The mixture was stirred for 0.5 h, and the volume of the solution was reduced to ca. 3 mL. The solvent was decanted and the solid washed several times with diethyl ether and dried under vacuum. Recrystallization from dichloromethane/diethyl ether gave dark violet microcrystals. Yield: 102 mg (94). Anal. Calcd for $C_{41}H_{55}BF_4IrP$: C, 57.40; H, 6.46. Found: C, 56.95; H, 6.06. IR (Nujol, cm^{-1}): *ν*(C=C=C) 1948; *ν*(BF_4) 1057. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): *δ* 8.01−7.51 (m, 10 H, Ph); 5.29 (br, 2 H, =C*H*); 4.83 (br, 2 H, =C*H*); 2.85−2.41 (m, 8 H, CH_2); 2.01−1.03 (m, 33 H, C_6H_{11}). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 20 °C): *δ* 272.4 (d, J_{P-C} = 10.5 Hz, C_α); 188.84 (s, C_β); 161.78 (s, C_γ); 144.34 (s, Ph); 134.13 (s, Ph); 131.28 (s, Ph); 130.45 (s, Ph); 93.35 (s, =*C*H); 87.70 (d, J_{P-C} = 9.05 Hz, =*C*H); 36.66 (d, J_{P-C} = 25.6 Hz, C_6H_{11}); 32.47 (s, *C*H_2, C_8H_{12}); 30.80 (s, C_6H_{11}); 30.58 (s, *C*H_2, C_8H_{12}); 27.46 (d, J_{P-C} = 11.3 Hz, C_6H_{11}); 26.13 (s, C6H11). $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$, 20 °C): *δ* 25.72 (s).

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Preparation of [Ir(TFB)(C═C═CPh$_2$)(PCy$_3$)]BF$_4$ (8). This compound was prepared according to the preparation of **7**. A solution of **5** (0.1 g, 0.11 mmol) in 10 mL of diethyl ether was treated with HBF$_4$·OEt$_2$ (0.12 mmol, 18 μL). The solution turned immediately dark orange-black, and a solid precipitated from the solution. Recrystallization from dichloromethane/diethyl ether gave dark red microcrystals. Yield: 99 mg (92%). Anal. Calcd for $C_{45}H_{49}BF_8IrP$: C, 55.39; H, 5.06. Found: C, 55.27; H, 4.87. IR (Nujol, cm^{-1}): ν(C═C═C) 1948; ν(BF$_4$) 1058. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.98−7.55 (m, 10 H, Ph); 5.91 (br, 2 H, C*H*); 4.46 (br, 4 H, =C*H*); 1.89−1.08 (m, 33 H, C_6H_{11}). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 20 °C): δ 277.0 (d, J_{P-C} = 9 Hz, C$_\alpha$); 183.85 (s, C$_\beta$); 162.59 (s, C$_\gamma$); 141.93 (s, Ph); 135.41 (s, Ph); 133.0 (s, Ph); 130.54 (s, Ph); 73.54 (s, =*C*H); 68.10 (d, J_{P-C} = 9 Hz, =*C*H); 41.71 (s, *C*H); 36.94 (d, J_{P-C} = 27.0 Hz, C_6H_{11}); 30.76 (s, C_6H_{11}); 27.78 (d, J_{P-C} = 11.3 Hz, C_6H_{11}); 26.43 (s, C_6H_{11}). ^{31}P{^{1}H} NMR (121.45 MHz, CD_2Cl_2, 20 °C): δ 32.89 (s).

Preparation of [Ir(TFB)(C═C═CPh$_2$)(P^{i}Pr$_3$)]BF4 (9). The complex was prepared according to the preparation of **7**. A solution of **6** (0.093 g, 0.12 mmol) in 10 mL of diethyl ether was treated with HBF4·OEt$_2$ (0.14 mmol, 20 μL). The complex was isolated as dark red microcrystals. Yield: 91.3 mg (89%). Anal. Calcd for $C_{36}H_{37}BF_8IrP$: C, 50.53; H, 4.36. Found: C, 49.95; H, 4.39. IR (Nujol, cm^{-1}): ν(C═C═C) 1936; ν(BF$_4$) 1058. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ 7.94−7.57 (m, 10 H, Ph); 5.93 (br, 2 H, C*H*); 4.63 (br, 2 H, =C*H*); 4.50 (br, 2 H, =C*H*); 2.23 (m, 3 H, PC*H*); 1.39 (dd, J_{H-H} = 7.14 Hz, J_{P-H} = 14.83 Hz, 18 H, PCH_3). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 20 °C): δ 275.6 (d, J_{P-C} = 12.8 Hz, C$_\alpha$); 183.47 (s, C$_\beta$); 162.88 (s, C$_\gamma$); 141.92 (Ph); 139.31 (Ph); 135.48 (Ph), 133.18 (Ph); 73.84 (s, =*C*H); 68.6 (d, J_{P-C} = 16.6 Hz, =*C*H); 41.81 (s, *C*H); 27.45 (d, J_{P-C} = 27.9 Hz, P*C*H); 19.7 (s, *C*H3, P^{i}Pr$_3$). ^{31}P{^{1}H} NMR (121.45 MHz, CD_2Cl_2, 20 °C): δ 45.01 (s).

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