Synthesis of Unsaturated Six-Membered Iridacycles from (Pentadienyl)iridium Precursors[1]

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Received September 22, 1992

Summary: An iridacyclohexene complex, [$CH_2CH(Me)CH{=}C(Me)CH_2Ir(PMe_3)_4]^+O_3SCF_3^-$ (4), and its iridacyclohexadiene analogue, [$CH{=}C(Me)CH{=}C(Me)CH_2Ir(PMe_3)_4]^+O_3SCF_3^-$ (6), have been synthesized and spectroscopically characterized. These novel unsaturated six-membered metallacycles are obtained via synthetic routes that utilize pentadienide as the source of ring carbon atoms.

Although the chemistry of four- and five-membered metallacycles is now fairly well developed,[2] comparatively little effort has been directed toward metallacycles with six atoms. Platinacyclohexanes,[3] titanacyclohexanes,[4] nickelacyclohexanes,[5] and osmacyclohexanes[6] have been reported but unsaturated six-membered metallacycles are quite rare. Noteworthy are the metallacyclohexadienes of Hughes[7] and the dibenzometallacyclohexadienes of Allison[8] and Pringle.[9]

During the past several years, we have been developing a new approach to the construction of unsaturated six-membered metallacycles, using pentadienide as the source of ring carbon atoms.[1] We have already shown that this approach can be successfully employed in the synthesis of "metallabenzenes", a fascinating subclass of six-membered metallacycles.[10] In this paper, we describe the application of our methodology to the synthesis of metallacyclohexene and metallacyclohexadiene complexes. These species are obtained in high yield from (pentadienyl)metal precursors.

Results and Discussion

As we reported earlier,[11] treatment of $ClIr(PMe_3)_3$ with potassium 2,4-dimethylpentadienide produces an equilibrium mixture of (1,2,5-η-2,4-dimethylpentadienyl)Ir(PMe_3)$_3$ (1, Scheme I) and *fac*-$CH{=}C(Me)CH{=}C(Me)CH_2Ir(PMe_3)_3(H)$ (2, Scheme I). Interconversion between 1 and 2 probably involves the intermediacy of 16e (η^1-2,4-dimethylpentadienyl)Ir(PMe_3)$_3$ (A, Scheme I) or the related 18e agostic species (B).[12] The iridium center in this intermediate can either coordinate the terminal double bond of the pentadienyl (producing 1) or oxidatively add across the vinylic C—H bond (producing 2). In benzene at 20 °C, the equilibrium mixture slightly favors the metallacycle (2:1 = 1.5:1). However, the position of the equilibrium can be pushed further toward the metallacycle by refluxing the mixture for a short time in polar solvents (e.g., acetone) and can be pushed toward the 1,2,5-η-pentadienyl complex by refluxing in nonpolar solvents (e.g., pentane). These isomerically-enriched solutions yield spectroscopically pure crystalline samples of 2 and 1, respectively, upon workup.

Treatment of compound 1 with triflic acid ($H^+O_3SCF_3^-$) cleanly produces the 1,3,4,5-η-pentenediyl complex [$CH_2CH(Me)CH{=}C(Me)CH_2Ir(PMe_3)_3]^+O_3SCF_3^-$ (3, Scheme I). This reaction probably proceeds by initial proton attack at the electron-rich iridium center, followed by rapid hydrogen migration to C2 of the pentadienyl ligand. Consistent with this mechanism is the X-ray crystal structure of 3, which shows that the hydrogen atom on C2 resides endo to the metal center (vide infra).

If D^+ ($D^+O_2CCF_3^-$) is substituted for H^+, and the reaction is run at low temperature, ^2H NMR monitoring shows deuterium incorporation *only* in the H2 site at −30 °C. However, upon warming of the sample to room temperature, deuterium is observed to distribute evenly among the five possible sites on C1, C2, and C5. The key intermediate in this scrambling process is believed to be [(1,2,5-η-2,4-dimethylpentadienyl)Ir(PMe_3)$_3$D]$^+$ (C, Scheme II), from which the deuterium can migrate to C2, C1, or C5. Migration to either C1 or C5 would lead to a short-lived [(η^4-2,4-dimethylpentadiene)Ir(PMe_3)$_3$]$^+$ species (D, Scheme II). Hydrogen atom migration back to the iridium center (E, Scheme II) and then to C2 would yield the observed deuterium-scrambled products.

An ORTEP drawing of the solid-state structure of 3 is shown in Figure 1. Important distances and angles are

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[1] Metallacyclohexadiene and Metallabenzene Chemistry. 9. Previous papers in this series include: (a) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics*, in press. (b) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* 1992, *11*, 2740. (c) Bleeke, J. R.; Bass, L. A.; Xie, Y.-F.; Chiang, M. Y. *J. Am. Chem. Soc.* 1992, *114*, 4213. (d) Bleeke, J. R.; Xie, Y.-F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* 1991, *113*, 4703. (e) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* 1991, *10*, 19. (f) Bleeke, J. R.; Peng, W.-J.; Xie, Y.-F.; Chiang, M. Y. *Organometallics* 1990, *9*, 1113. (g) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. Y. *J. Am. Chem. Soc.* 1989, *111*, 4118. (h) Bleeke, J. R.; Peng, W.-J. *Organometallics* 1987, *6*, 1576.

[2] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, Chapter 9 (see also references cited therein).

[3] (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* 1976, *98*, 6521. (b) Alcock, N. W.; Bryars, K. H.; Pringle, P. G. *J. Organomet. Chem.* 1990, *386*, 399.

[4] McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* 1976, *98*, 6529.

[5] Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* 1978, *100*, 7418.

[6] Lindner, E.; Jansen, R.-M.; Hiller, W.; Fawzi, R. *Chem. Ber.* 1989, *122*, 1403.

[7] (a) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* 1986, 1694. (b) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* 1987, *6*, 1578.

[8] Mike, C. A.; Nelson, T.; Graham, J.; Cordes, A. W.; Allison, N. T. *Organometallics* 1988, *7*, 2573.

[9] Alcock, N. W.; Bryars, K. H.; Pringle, P. G. *J. Chem. Soc., Dalton Trans.* 1990, 1433.

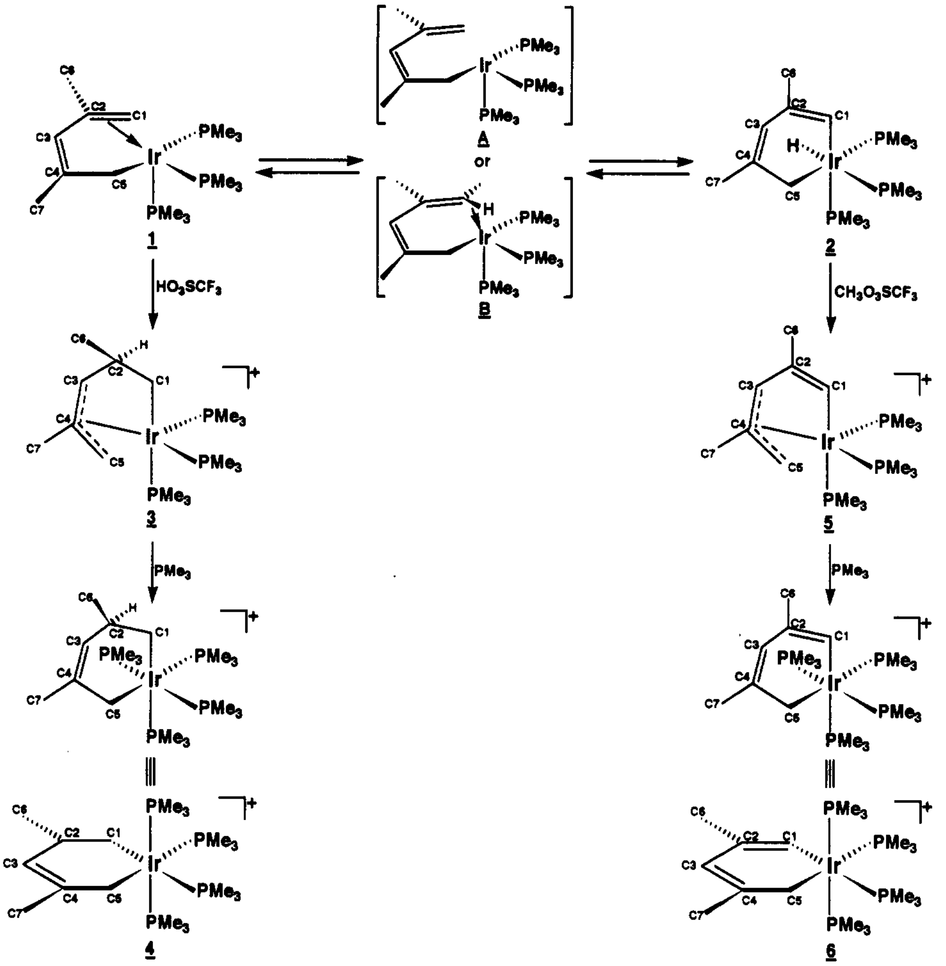
[10] Bleeke, J. R. *Acc. Chem. Res.* 1991, *24*, 271.

[11] Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, T. W., Jr.; Haile, T.; Beatty, A. M.; Xie, Y.-F. *Organometallics* 1991, *10*, 2391.

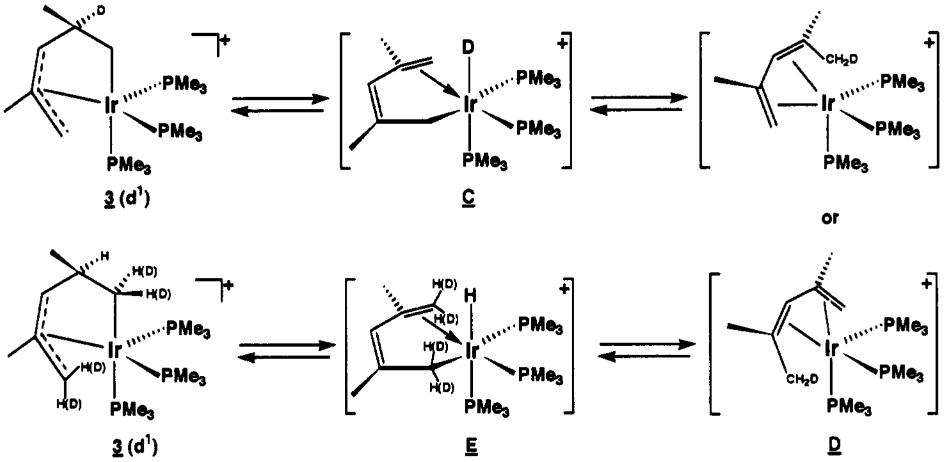
[12] Bergman has shown that (η^5-pentamethylcyclopentadienyl)Ir(PMe_3), an iridium fragment which is isoelectronic with (η^1-2,4-dimethylpentadienyl)Ir(PMe_3)$_3$, activates ethylene C–H bonds by first coordinating them through a C–H σ bond. See: Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* 1988, *110*, 5732.

0276-7333/93/2312-0970$04.00/0

Scheme I



Scheme II



listed in the caption to Figure 1, while atomic coordinates are given in Table I. The compound adopts an essentially octahedral geometry, in which the pentenediyl ligand occupies three mutually-cis sites and the PMe$_3$ ligands occupy the other three sites. The iridium center bonds strongly to C1 (Ir–C1 = 2.120(16) Å) and more weakly to the π-allyl portion (C3 → C5) of the pentenediyl ligand (average Ir–C$_{\pi\text{-allyl}}$ distance = 2.25 Å). As mentioned above, the methyl group on C2 (methyl carbon C6) is oriented exo to the metal center. Hence, C2 and C6 lie 0.79 and 2.32 Å, respectively, above the C1/C3/C4/C5 plane,[13] while Ir lies 1.65 Å below it. Perhaps the most interesting feature of the structure is the relatively large difference in lengths between allyl bonds C3–C4 (1.355(26) Å) and C4–C5 (1.431(26) Å), indicating that the allyl moiety is *not* fully delocalized; it retains considerable double-bond character between C3 and C4.

In the $^{13}C\{^1H\}$ NMR spectrum of 3, σ-bonded carbon C1 resonates farthest upfield at δ −8.4 and exhibits strong trans phosphine coupling (J_{C-P} = 64.0 Hz). The π-allyl carbons of the pentenediyl ligand, C3, C4, and C5, resonate at δ 60.5, 123.6, and 41.0, respectively, and C5 is coupled

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[13] The four metal-bound carbon atoms, C1, C3, C4, and C5, are coplanar to within 0.03 Å (mean deviation = 0.018 Å).

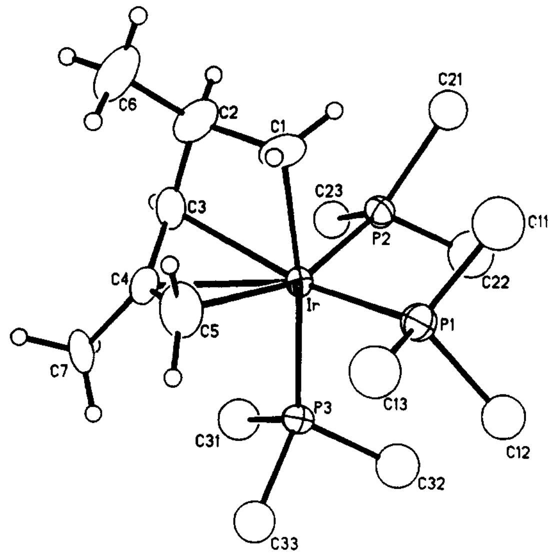

Figure 1. ORTEP drawing of the cation in $\mathrm{CH_2CH(Me)CH{=}C(Me)CH_2Ir(PMe_3)_3]^+O_3SCF_3^-}$ (**3**). Selected bond distances (Å): Ir–P1, 2.282(4); Ir–P2, 2.313(4); Ir–P3, 2.379(4); Ir–C1, 2.120(16); Ir–C3, 2.248(16); Ir–C4, 2.268(14); Ir–C5, 2.236(17); C1–C2, 1.481(23); C2–C3, 1.553(29); C2–C6, 1.561(27); C3–C4, 1.355(26); C4–C5, 1.431(26); C4–C7, 1.522(28). Selected bond angles (deg): Ir–C1–C2, 99.3(11); C1–C2–C3, 102.6(14); C1–C2–C6, 115.9(17); C6–C2–C3, 116.4(17); C2–C3–C4, 118.3(17); C3–C4–C5, 119.8(18); C3-C4-C7, 122.1(17); C7–C4–C5, 118.1(16); C4–C5–Ir, 72.7(9); C5–Ir–C1, 75.2(8); C1–Ir–C3, 65.6(7); C3–Ir–C5, 65.0(7).

Table I. Atomic Coordinates (×10^4) with Estimated Standard Deviations for Non-Hydrogen Atoms in $\mathrm{[CH_2CH(Me)CH{=}C(Me)CH_2Ir(PEt_3)_3]^+O_3SCF_3^-}$ (3)^a

atom	x	y	z
Ir	1683(1)	2565(1)	2168(1)
P1	−92(5)	4195(3)	2396(3)
P2	2160(4)	2416(3)	3734(3)
P3	−199(4)	1096(3)	2526(3)
C1	3483(18)	3764(15)	1684(16)
C2	4822(20)	2881(17)	1292(16)
C3	4011(20)	1688(19)	1350(12)
C4	3017(16)	1589(15)	767(11)
C5	2157(26)	2638(18)	501(12)
C6	5934(24)	3217(24)	260(15)
C7	2744(24)	382(19)	398(15)
C11	483(47)	5419(35)	2959(32)
C12	−2091(41)	4092(31)	3160(27)
C13	−497(50)	4740(36)	1211(32)
C21	2874(54)	3846(40)	4158(31)
C22	668(33)	2492(25)	4853(22)
C23	2779(51)	866(39)	4120(33)
C31	490(25)	−476(19)	2705(16)
C32	−1854(28)	1177(22)	3663(18)
C33	−1327(23)	986(17)	1603(15)
S	3823(7)	2027(5)	7218(5)
O1	4285(25)	962(15)	7742(16)
O2	3066(29)	2878(20)	8012(15)
O3	3120(36)	2006(30)	6388(17)
C70	5584(25)	2862(26)	6831(24)
F1	5244(31)	3617(25)	6102(22)
F2	6361(63)	2784(47)	7564(36)
F3	6382(36)	2133(26)	6069(24)

^{a} The carbon atoms bonded to P1 and P2 exhibited 2-fold rotational disorder. Only one set of disordered atoms is included in this atom list.

to phosphorus with a coupling constant of 36.0 Hz. Saturated carbon C2 appears at δ 38.4. In the ^{31}P{^{1}H} NMR spectrum of **3**, the three inequivalent phosphine ligands give rise to three distinct resonances.

As shown in Scheme I, treatment of compound **3** with PMe$_3$ in acetone leads to $\eta^3 \rightarrow \eta^1$ isomerization of the π-allyl portion of the pentenediyl ligand and production of the iridacyclohexene complex $\mathrm{[CH_2CH(Me)CH{=}C(Me)CH_2Ir(PMe_3)_4]^+O_3SCF_3^-}$ (**4**). This reaction is relatively slow, requiring approximately 24 h at room temperature to reach completion. A comparison of the ^{13}C{^{1}H} NMR spectrum of **4** with that of precursor **3** shows that C5 has shifted substantially upfield (to δ −0.1 from δ 41.0 in **3**) and exhibits stronger phosphorus coupling (J = 66.0 Hz vs 36.0 Hz in **3**), as expected for a σ-bound carbon. Ring carbons C3 and C4, which are no longer coordinated to the iridium center, are shifted downfield to δ 131.2 and 138.4, while the positions of C1 and C2 remain relatively stationary. The phosphine ligands in **4** are all inequivalent and give rise to four separate signals in the ^{31}P{^{1}H} NMR spectrum. However, the coupling between the two trans diaxial phosphines ($J_{\mathrm{P-P}}$ = 365 Hz) exceeds their chemical shift difference, leading to a second-order splitting pattern.

As shown in the right-hand column of Scheme I, the iridacyclohexa*diene* analogue of **4** (compound **6**) can be obtained using a closely related approach.[14] Treatment of *fac*-$\mathrm{CH{=}C(Me)CH{=}C(Me)CH_2Ir(PMe_3)_3(H)}$ (**2**) with methyl triflate results in removal of the hydride ligand (as methane)[15] and coordination of ring double bond C3—C4 to the iridium center, generating the 1,3,4,5-η-pentadienediyl complex $\mathrm{[CH{=}C(Me)CH{=}C(Me)CH_2Ir(PMe_3)_3]^+O_3SCF_3^-}$ (**5**).[16] In the ^{13}C{^{1}H} NMR spectrum of **5**, σ-bonded carbon C1 appears at δ 117.4 and exhibits strong trans phosphine coupling ($J_{\mathrm{C-P}}$ = 82.2 Hz), while olefin carbon C2 gives rise to the farthest downfield signal at δ 136.7. π-Allylic carbons C3, C4, and C5 appear at δ 73.7, 123.1, and 32.6, respectively, and C5 couples to phosphorus with a coupling constant of 38.9 Hz. The ^{31}P{^{1}H} NMR spectrum of **5** displays three well-resolved resonances for the three inequivalent PMe$_3$ ligands.

Treatment of **5** with PMe$_3$ in acetone leads to $\eta^3 \rightarrow \eta^1$ isomerization of the π-allyl portion of the 1,3,4,5-η-pentadienediyl ligand and production of the iridacyclohexadiene complex $\mathrm{[CH{=}C(Me)CH{=}C(Me)CH_2Ir(PMe_3)_4]^+O_3SCF_3^-}$ (**6**, Scheme I). Unlike the reaction of **3** with PMe$_3$ (vide supra), this reaction occurs rapidly, reaching completion within 10 min at room temperature. The faster rate reflects the greater strain within the pentadienediyl ligand in **5** vs the pentenediyl ligand in **3**. A comparison of the ^{13}C{^{1}H} NMR spectrum of **6** with that of precursor **5** shows that C5 has shifted substantially

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[14] This sequence parallels chemistry that we previously reported in the tris(PEt$_3$) system.[1f,h]

[15] Methane was detected by gas chromatography. GC analysis conditions: column, Porapak Q; carrier gas, helium; carrier flow, 30 mm/s; oven temperature, 50 °C; injector temperature, 100 °C.

[16] We reported earlier[1h] that the tris(PEt$_3$) analogue of **5**, $\mathrm{CH{=}C(Me)CH{=}C(Me)CH_2Ir(PEt_3)_3}$, undergoes a carbon–carbon coupling reaction at room temperature in acetone solvent, ultimately producing [(η^5-1,3-dimethylcyclopentadienyl)Ir(PEt$_3$)$_2$(H)]$^+$O$_3$SCF$_3$$^-$. In sharp contrast, compound **5** is stable indefinitely under these conditions. Since the coupling reaction probably requires initial loss of phosphine, the stability of **5** can be attributed to its relatively uncongested coordination environment, unlike the sterically crowded tris(PEt$_3$) system.

upfield (to δ 3.4) and $J_{\text{C5–P}}$ has increased (to 65.0 Hz), while C3 and C4 have moved downfield (to δ 128.8 and 131.0). The positions of C1 and C2 have remained essentially unchanged. Unlike compound 4, compound 6 possesses mirror-plane symmetry in solution. Hence, in the ^{31}P{^{1}H} NMR spectrum, the two trans diaxial phosphines appear as a single resonance, while each of the remaining phosphines gives rise to a separate signal.

In summary, we have synthesized two new unsaturated six-membered iridacycles, an iridacyclohexene complex and its iridacyclohexadiene analogue, from (pentadienyl)-iridium precursors. This work furnishes further evidence that (pentadienyl)metal chemistry provides a convenient entry to the synthesis of novel six-membered metallacycles.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Solvents were stored under nitrogen after being distilled from appropriate drying agents. (1,2,5-η-2,4-Dimethylpentadienyl)Ir(PMe$_3$)$_3$ (**1**) and *fac*-CH=C(Me)CH=C(Me)CH$_2$Ir(PMe$_3$)$_3$(H) (**2**) were synthesized using the method published earlier.[11] Triflic acid (Aldrich), methyl triflate (Aldrich), trimethylphosphine (Strem), and deuterated trifluoroacetic acid (Aldrich) were used as received.

NMR experiments were performed on a Varian XL-300 or Varian VXR-500 spectrometer. ^{1}H and ^{13}C spectra were referenced to tetramethylsilane, while ^{31}P spectra were referenced to external H_3PO_4. In general, ^{13}C peak assignments were made with the aid of APT (attached proton test) results. ^{13}C–^{1}H correlations were ascertained using HETCOR (^{13}C–^{1}H heteronuclear correlation spectroscopy) or HMQC (^{1}H-detected multiple quantum coherence) data. In some cases, ^{1}H assignments were made on the basis of COSY (^{1}H–^{1}H correlation spectroscopy) experiments. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of [CH$_2$CH(Me)CH=C(Me)CH$_2$Ir(PMe$_3$)$_3$]$^+$O$_3$SCF$_3^-$ (3). (1,2,5-η-2,4-Dimethylpentadienyl)Ir(PMe$_3$)$_3$ (**1**) (0.20 g, 0.39 mmol) was added to ~15 mL of cold (−40 °C) diethyl ether and swirled to dissolve. Triflic acid (0.06 g, 0.39 mmol) was added with stirring, causing a white solid (compound **3**) to precipitate. The reaction mixture was placed in a −40 °C freezer for 1 h, after which the supernatant solution was decanted and the remaining white powder was dried in vacuo. After washing with diethyl ether, the powder was recrystallized from methylene chloride/diethyl ether at −40 °C. Yield: 0.19 g (75%). Anal. Calcd for $C_{17}H_{39}F_3IrO_3P_3S$: C, 30.68; H, 5.92. Found: C, 30.26; H, 5.77.

^{1}H NMR (acetone-d_6, 25 °C): δ 4.53 (d, $J_{\text{H–H}}$ = 6.4 Hz, 1, H3), 3.33 (m, 1, H5), 2.67 (m, 1, H2), 2.52 (m, 1, H5), 2.33 (s, 3, H7's), 1.86 (d, $J_{\text{H–P}}$ = 9.0 Hz, 9, PMe$_3$), 1.69 (d, $J_{\text{H–P}}$ = 10.0 Hz, 9, PMe$_3$), 1.52 (d, $J_{\text{H–P}}$ = 8.0 Hz, 9, PMe$_3$), 0.65 (d, $J_{\text{H–H}}$ = 7.0 Hz, 3, H6's), 0.65 (m, 1, H1), −0.83 (m, 1, H1). ^{13}C{^{1}H} NMR (acetone-d_6, 25 °C): δ 123.6 (s, C4), 60.5 (d, $J_{\text{C–P}}$ = 20.0 Hz, C3), 41.0 (d, $J_{\text{C–P}}$ = 36.0 Hz, C5), 38.4 (d, $J_{\text{C–P}}$ = 4.8 Hz, C2), 32.5 (d, $J_{\text{C–P}}$ = 9.2 Hz, C6), 24.8 (s, C7), 20.6 (d, $J_{\text{C–P}}$ = 30.0 Hz, PMe$_3$), 19.1 (m, PMe$_3$'s), −8.4 (d of t, $J_{\text{C–P}}$ = 64.0, 4.3 Hz, C1). ^{31}P{^{1}H} NMR (acetone-d_6, 25 °C): δ −43.7 (d, $J_{\text{P–P}}$ = 11.0 Hz, 1), −48.8 (d, $J_{\text{P–P}}$ = 17.0 Hz, 1), −54.8 (dd, $J_{\text{P–P}}$ = 17.0, 11.0 Hz, 1).

Synthesis of [CH$_2$CH(Me)CH=C(Me)CH$_2$Ir(PMe$_3$)$_4$]$^+$O$_3$SCF$_3^-$ (4). Compound **3** (0.20 g, 0.30 mmol) was dissolved in ~1 mL of acetone, and PMe$_3$ (0.10 g, 1.3 mmol) was added. The solution was stirred for 24 h and then filtered through Celite. Removal of the volatiles under vacuum produced **4** as a white solid, which was recrystallized from methylene chloride/diethyl ether at −40 °C. Yield: 0.21 g (94%). Anal. Calcd for $C_{20}H_{48}F_3IrO_3P_4S$: C, 32.38; H, 6.54. Found: C, 32.11; H, 6.55.

^{1}H NMR (acetone-d_6, 25 °C): δ 5.14 (m, 1, H3), 1.98 (br m, 1, H2), 1.74 (m, 2, H5's), 1.74 (s, 3, H7's), 1.69 (d, $J_{\text{H–P}}$ = 7.5 Hz, 9, PMe$_3$), 1.65 (d, $J_{\text{H–P}}$ = 7.5 Hz, 9, PMe$_3$), 1.63 (d, $J_{\text{H–P}}$ = 7.5 Hz, 9, PMe$_3$), 1.62 (d, $J_{\text{H–P}}$ = 7.5 Hz, 9, PMe$_3$), 1.32 (br m, 1, H1), 1.12 (br m, 1, H1), 1.02 (d, $J_{\text{H–H}}$ = 7.0 Hz, 3, H6's). ^{13}C{^{1}H} NMR (acetone-d_6, 25 °C): δ 138.4 (d, $J_{\text{C–P}}$ = 5.0 Hz, C4), 131.2 (d, $J_{\text{C–P}}$ = 15.0 Hz, C3), 31.2 (s, C2), 28.6 (d, $J_{\text{C–P}}$ = 8.0 Hz, C7), 28.4 (d, $J_{\text{C–P}}$ = 8.0 Hz, C6), 19.7 (d, $J_{\text{C–P}}$ = 27.0 Hz, PMe$_3$), 19.4 (d, $J_{\text{C–P}}$ = 27.0 Hz, PMe$_3$), 18.3 (virtual t, $J_{\text{C–P}}$ = 26.0 Hz, PMe$_3$), 16.9 (virtual t, $J_{\text{C–P}}$ = 26.0 Hz, PMe$_3$), 8.7 (d, $J_{\text{C–P}}$ = 66.0 Hz, C1), −0.1 (d, $J_{\text{C–P}}$ = 66.0 Hz, C5). ^{31}P{^{1}H} NMR (acetone-d_6, 25 °C): δ −43.5 (ddd, $J_{\text{P–P}}$ = 365.0, 21.0, 18.0 Hz, 1, axial PMe$_3$), −45.6 (ddd, $J_{\text{P–P}}$ = 365.0, 21.0, 18.0 Hz, 1, axial PMe$_3$), −57.1 (t of d, $J_{\text{P–P}}$ = 21.0, 10.6 Hz, 1, equatorial PMe$_3$), −58.8 (t of d, $J_{\text{P–P}}$ = 18.0, 10.6 Hz, 1, equatorial PMe$_3$). NOTE: ^{31}P chemical shifts and coupling constants for the axial PMe$_3$ ligands were determined by using a spin simulation program to model the experimental (second-order) spectra.

Synthesis of [CH=C(Me)CH=C(Me)CH$_2$Ir(PMe$_3$)$_3$]$^+$O$_3$SCF$_3^-$ (5). *fac*-CH=C(Me)CH=C(Me)CH$_2$Ir(PMe$_3$)$_3$(H) (**2**) (0.52 g, 1.0 mmol) was added to ~30 mL of cold (−40 °C) diethyl ether. Methyl triflate (0.16 g, 1.0 mmol) was then added dropwise with stirring, causing compound **5** to precipitate as a white powder. The reaction mixture was maintained at −40 °C for 6 h, after which the supernatant solution was decanted and the remaining white powder was dried in vacuo. Recrystallization from acetone at −40 °C yielded clear colorless prisms of **5**. Yield: 0.53 g (80%). Anal. Calcd for $C_{17}H_{37}F_3IrO_3P_3S$: C, 30.76; H, 5.63. Found: C, 30.35; H, 5.64.

^{1}H NMR (acetone-d_6, 25 °C): δ 5.65 (br t, $J_{\text{H–P}}$ = 11.6 Hz, 1, H1), 5.07 (s, 1, H3), 2.74 (br m, 1, H5), 2.36 (br m, 1, H5), 2.34 (s, 3, H7's), 1.81 (d, $J_{\text{H–P}}$ = 10.3 Hz, 9, PMe$_3$), 1.70 (d, $J_{\text{H–P}}$ = 9.1 Hz, 9, PMe$_3$), 1.54 (d, $J_{\text{H–P}}$ = 7.7 Hz, 9, PMe$_3$), 1.40 (s, 3, H6's). ^{13}C{^{1}H} NMR (acetone-d_6, 25 °C): δ 136.7 (s, C2), 123.1 (s, C4), 117.4 (d, $J_{\text{C–P}}$ = 82.2 Hz, C1), 73.7 (d, $J_{\text{C–P}}$ = 18.3 Hz, C3), 32.6 (d, $J_{\text{C–P}}$ = 38.9 Hz, C5), 28.7 (d, $J_{\text{C–P}}$ = 10.9 Hz, C6), 22.0 (s, C7), 20.1 (d, $J_{\text{C–P}}$ = 23.6 Hz, PMe$_3$), 19.7 (d, $J_{\text{C–P}}$ = 28.0 Hz, PMe$_3$), 18.6 (d, $J_{\text{C–P}}$ = 29.3 Hz, PMe$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, 25 °C): δ −38.0 (t, $J_{\text{P–P}}$ = 12.7 Hz, 1), −49.7 (dd, $J_{\text{P–P}}$ = 17.4, 12.7 Hz, 1), −53.8 (dd, $J_{\text{P–P}}$ = 17.4, 12.7 Hz, 1).

Synthesis of [CH=C(Me)CH=C(Me)CH$_2$Ir(PMe$_3$)$_4$]$^+$O$_3$SCF$_3^-$ (6). Compound **5** (0.10 g, 0.15 mmol) was dissolved in 10 mL of acetone, and PMe$_3$ (0.030 g, 0.40 mmol) was added. After stirring for 10 min, the volatiles were removed under vacuum. The resulting white powder (compound **6**) was recrystallized from acetone at −40 °C. Yield: 0.092 g (83%). Anal. Calcd for $C_{20}H_{46}F_3IrO_3P_4S$: C, 32.47; H, 6.28. Found: C, 32.00; H, 5.95.

^{1}H NMR (acetone-d_6, 25 °C): δ 6.52 (d, $J_{\text{H–P}}$ = 17.0 Hz, 1, H1), 5.53 (s, 1, H3), 2.42 (tt, $J_{\text{H–P}}$ = 17.0, 6.0 Hz, 2, H5's), 1.85 (s, 3, H7's), 1.76 (s, 3, H6's), 1.73 (d, $J_{\text{H–P}}$ = 8.0 Hz, 9, PMe$_3$), 1.64 (d, $J_{\text{H–P}}$ = 9.0 Hz, 9, PMe$_3$), 1.52 (virtual t, $J_{\text{H–P}}$ = 6.0 Hz, 18, PMe$_3$'s). ^{13}C{^{1}H} NMR (acetone-d_6, 25 °C): δ 135.9 (d, $J_{\text{C–P}}$ = 6.0 Hz, C2), 131.0 (d, $J_{\text{C–P}}$ = 7.0 Hz, C4), 128.8 (s, C3), 118.2 (d of t, $J_{\text{C–P}}$ = 72.0, 13.0 Hz, C1), 27.6 (s, C6), 27.1 (s, C7), 19.5 (d, $J_{\text{C–P}}$ = 29.0 Hz, PMe$_3$), 18.8 (d, $J_{\text{C–P}}$ = 29.0 Hz, PMe$_3$), 16.6 (virtual t, $J_{\text{C–P}}$ = 38.0 Hz, PMe$_3$'s), 3.4 (d of t, $J_{\text{C–P}}$ = 65.0, 8.0 Hz, C5). ^{31}P{^{1}H} NMR (acetone-d_6, 25 °C): δ −44.5 (dd, $J_{\text{P–P}}$ = 21.0, 16.0 Hz, 2, trans diaxial PMe$_3$'s), −57.1 (t of d, $J_{\text{P–P}}$ = 16.0, 12.0 Hz, 1, equatorial PMe$_3$), −58.0 (t of d, $J_{\text{P–P}}$ = 21.0, 12.0 Hz, 1, equatorial PMe$_3$).

X-ray Diffraction Study of [CH$_2$CH(Me)CH=C(Me)CH$_2$Ir(PMe$_3$)$_3$]$^+$O$_3$SCF$_3^-$ (3). A single crystal of **3** ($C_{17}H_{39}F_3IrO_3P_3S$, pale yellow needle, 0.46 mm × 0.16 mm × 0.16 mm) was sealed in a glass capillary under inert atmosphere. Data were collected at 295 K on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All data reduction and refinement were done using the Siemens

SHELXTL PLUS package on a Micro VAX II computer.[17] Crystal data and details of data collection and structure analysis are summarized below: triclinic $P\bar{1}$, $a = 8.858(2)$ Å, $b = 11.162(2)$ Å, $c = 13.857(5)$ Å, $\alpha = 87.37(2)°$, $\beta = 74.96(2)°$, $\gamma = 85.29(2)°$, $V = 1318.3(6)$ Å^3, $Z = 2$, $d_{calcd} = 1.677$ g/cm^3, $\mu = 53.61$ cm^{-1}, θ–2θ scanning technique, $\pm h,-k,\pm l$ collected, 4929 reflections with $3.5 < 2\theta < 50.0°$, 4668 independent reflections, 3467 reflections with $I > 3\sigma(I)$ used in refinement, semiempirical absorption correction (min/max transmission factors = 0.8136/0.9694), extinction correction, $R = 0.0571$, $R_w = 0.0803$, goodness-of-fit = 1.01.

The position of the iridium atom was determined using Patterson techniques. Remaining non-hydrogen atoms were found by successive full-matrix least-squares refinement and difference Fourier map calculations. The iridium atom, phosphorus atoms, and carbon atoms on the pentenediyl ligand were refined anisotropically, while the phosphine carbons and the triflate anion were refined isotropically. Hydrogens on the pentenediyl ligand were placed at idealized positions and assumed the riding model. A common isotropic U value was refined.

The methyl groups on both P1 and P2 exhibited 2-fold rotational disorder, which was successfully modeled. A more serious disorder was encountered in the triflate anion. The eight atoms in the anion were located in the electron difference maps, and their *relative* distances were fixed at idealized values, using DFIX in the SHELXTL PLUS package. The atoms were then allowed to refine within the distance constraints.

Acknowledgment. We thank the National Science Foundation (Grants CHE-8520680 and CHE-9003159) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A loan of $IrCl_3 \cdot 3H_2O$ from Johnson-Matthey Alfa/Aesar is gratefully acknowledged. Washington University's X-ray Crystallography Facility was funded by the National Science Foundation's Chemical Instrumentation Program (Grant CHE-8811456). The High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Supplementary Material Available: Structure determination summary, ORTEP drawing, and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compound 3 (7 pages). Ordering information is given on any current masthead page.

OM920583O

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[17] Atomic scattering factors were obtained from the following: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.