Synthesis, Structure, and Reactivity of Iridacyclohexadienone and Iridaphenol Complexes[1]

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Received May 27, 1997[⊗]

Abstract: Iridacyclohexadienone complexes, a new class of unsaturated six-membered metallacycles, have been synthesized, and their reactions with acids have been investigated. Treatment of $\overline{CH=C(Me)-CH=C(Me)-CH=Ir}$-(PMe$_3$)$_3$ ("iridabenzene" **1**) with nitrous oxide produces the iridacyclohexadienone complex $\overline{CH=C(Me)-CH=C}$-$\overline{(Me)-C(O)-Ir(PMe_3)_3(H)}$ (**2**), which upon stirring in diethyl ether solution slowly isomerizes to (1,2,5-η-2,4-dimethylpenta-1,3-dien-5-oyl)Ir(PMe$_3$)$_3$ (**3**). Treatment of **2** with methyl trifluoromethanesulfonate leads to removal of the metal hydride and production of $\overline{CH=C(Me)-CH=C(Me)-C(O)-Ir(PMe_3)_3(O_3SCF_3)}$ (**4**). In acetone solution, **4** forms an equilibrium mixture with a ring-contracted iridacyclopentadiene isomer, [$\overline{CH=C(Me)-CH=C}$-$\overline{(Me)-Ir(PMe_3)_3(CO)}$]$^+O_3SCF_3^-$ (**5**). Treatment of **4** with trimethylphosphine generates the tetrakis(trimethylphosphine)iridacyclohexadienone complex [$\overline{CH=C(Me)-CH=C(Me)-C(O)-Ir(PMe_3)_4}$]$^+O_3SCF_3^-$ (**6**). Iridacyclohexadienone **2** reacts with trifluoromethanesulfonic acid to produce the iridacyclopentene complex [$\overline{CH_2-C(Me)=}$ $\overline{CH-CH(Me)-Ir(PMe_3)_3(CO)}$]$^+O_3SCF_3^-$ (**7**). In contrast, treatment of iridacyclohexadienones **4** and **6** with trifluoromethanesulfonic acid leads to protonation of oxygen and production of the corresponding "iridaphenols" **8** and **10**. When **4** is treated with trifluoroacetic acid, an iridaphenol product is again generated (compound **9**), but in this case the phenol proton forms an intramolecular hydrogen bond with the carbonyl oxygen of the trifluoroacetate ligand. The ring protons in compounds **8**, **9**, and **10** exhibit downfield ^{1}H NMR chemical shifts consistent with aromatic character. Compounds **3**, **4**, **6**, **7**, **8**, and **9** have been structurally characterized by single-crystal X-ray diffraction.

Introduction

Six-membered metallacycles, particularly those containing *unsaturated* rings, have been studied to a much lesser extent than their five-membered ring counterparts.[2] This situation is due in large part to the fact that few general synthetic pathways to unsaturated six-membered metallacycles have been developed. We have, therefore, embarked on a program to investigate the use of pentadienide and heteropentadienide reagents as possible synthons for the production of unsaturated six-membered metallacycles. Using this approach, we have succeeded in synthesizing iridacyclohexadiene complexes which can, in turn, be dehydrogenated to "iridabenzenes".[1] These novel metallacycles exhibit delocalized π-bonding and aromatic character.

We now report that treatment of iridabenzenes with nitrous oxide, an oxygen atom source, leads to the production of another new class of unsaturated six-membered metallacycles, iridacyclohexadienones. These molecules exhibit a variety of interesting reactions, including reversible ring contraction and conversion to "iridaphenols".

Results and Discussion

A. Treatment of Iridabenzene 1 with Nitrous Oxide. As shown in Scheme 1, treatment of $\overline{CH=C(Me)-CH=C(Me)-}$ $\overline{CH=Ir(PMe_3)_3}$ (iridabenzene **1**) with nitrous oxide (N$_2$O) results in the synthesis of an iridacyclohexadienone complex, $\overline{CH=C}$-$\overline{(Me)-CH=C(Me)-C(O)-Ir(PMe_3)_3(H)}$ (**2**). Although the detailed mechanism of this reaction is not known, metallaepoxide **A** (Scheme 1) appears to be a likely intermediate. Activation of the C5−H bond in **A** by the iridium center would lead to the observed product.[3]

The ^{1}H NMR spectrum of **2** shows downfield signals for H1 (δ 8.16) and H3 (δ 6.76) and an upfield signal for the iridium hydride (δ −10.80). The H1 signal is a broad doublet ($J =$

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1997.

(1) Metallacyclohexadiene and Metallabenzene Chemistry. 14. For previous papers in this series, see: (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118. (c) Bleeke, J. R.; Peng, W.-J.; Xie, Y.-F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113. (d) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19. (e) Bleeke, J. R.; Xie, Y.-F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4703. (f) Bleeke, J. R.; Bass, L. A.; Xie, Y.-F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213. (g) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740. (h) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517. (i) Bleeke, J. R.; Rohde, A. M.; Boorsma, D. W. *Organometallics* **1993**, *12*, 970. (j) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Clayton, Jr., T. W.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093. (k) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606. (l) Bleeke, J. R.; Behm, R.; Beatty, A. M. *Organometallics* **1997**, *16*, 1103. (m) Bleeke, J. R.; Blanchard, J. M. B. *J. Am. Chem. Soc.* **1997**, *119*, 5443. See also: Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271.

(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; pp 512−513.
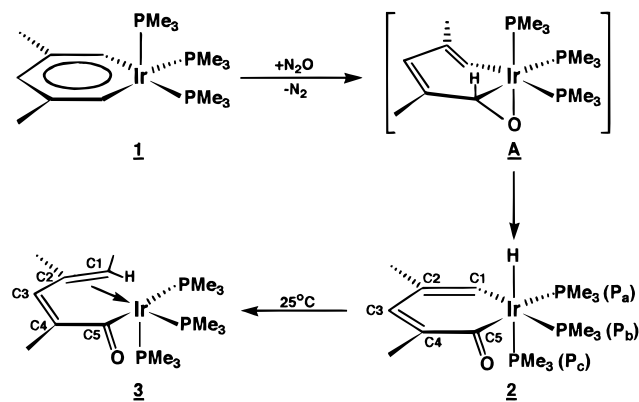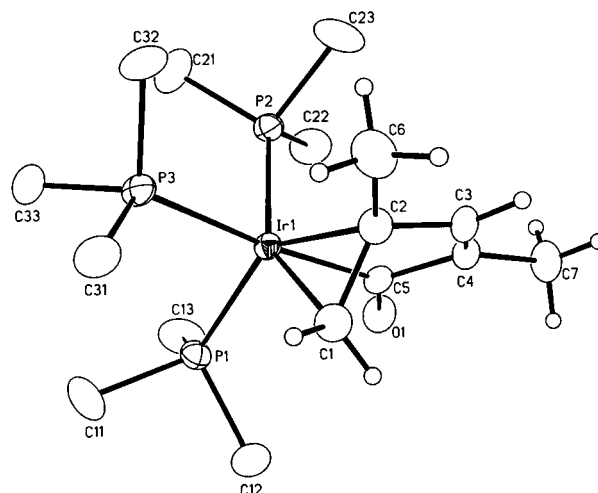
(3) Intermediate **A** can also be viewed as an (η^2-aldehyde)metal complex, and dissociation of the aldehyde CO bond from the iridium center may precede C5−H bond activation.

Scheme 1

Figure 1. ORTEP drawing of (1,2,5-η-2,4-dimethylpenta-1,3-dien-5-oyl)Ir(PMe$_3$)$_3$ (**3**). Selected bond distances (Å): Ir1–P1, 2.310(3); Ir1–P2, 2.297(2); Ir1–P3, 2.360(2); Ir1–C1, 2.135(7); Ir1–C2, 2.143(6); Ir1–C5, 2.063(6); O1–C5, 1.235(8); C1–C2, 1.464(9); C2–C3, 1.481-(9); C2–C6, 1.533(10); C3–C4, 1.300(10); C4–C5, 1.508(9); C4–C7, 1.531(10). Selected bond angles (deg): P1–Ir1–P2, 106.4(1); P1–Ir1–P3, 98.1(1); P2–Ir1–P3, 93.7(1); P1–Ir1–C1, 103.0(2); P2–Ir1–C1, 148.2(2); P3–Ir1–C1, 93.9(2); P1–Ir1–C2, 141.4(2); P2–Ir1–C2, 108.4(2); P3–Ir1–C2, 95.8(2); P1–Ir1–C5, 87.8(2); P2–Ir1–C5, 83.8(2); P3–Ir1–C5, 174.0(2); C1–Ir1–C2, 40.0(2); C1–Ir1–C5, 85.5(3); C2–Ir1–C5, 79.9(3); Ir1–C1–C2, 70.3(4); Ir1–C2–C1, 69.7 (4); Ir1–C2–C3, 107.8(4); C1–C2–C3, 114.6(6); C2–C3–C4, 121.7(6); C3–C4–C5, 114.2(6); Ir1–C5–O1, 128.7(5); Ir1–C5–C4, 113.3(4); O1–C5–C4, 118.0(6).

20.3 Hz) due to coupling to the ^{31}P nucleus of the adjacent PMe$_3$ ligand in the ring plane, P$_a$ (see Scheme 1),[4] while the hydride signal is split into a doublet (J = 114.9 Hz) of triplets (J = 20.5 Hz), as a result of coupling to the *trans* ^{31}P nucleus (P$_c$) and the *cis* ^{31}P nuclei (P$_a$ and P$_b$), respectively. In the ^{13}C{^{1}H} NMR spectrum, the carbonyl carbon (C5) resonates far downfield at δ 230.4 and is split into a doublet (J = 98.1 Hz) by *trans* ^{31}P nucleus P$_a$. The other four ring carbon signals appear in the normal olefinic region of the spectrum (between δ 127.5 and δ 140.6). The C1 signal is a doublet (J = 80.7 Hz) as a result of strong coupling to *trans* ^{31}P nucleus P$_b$. The ^{31}P{^{1}H} spectrum consists of three separate but coupled signals, due to the three inequivalent PMe$_3$ ligands.
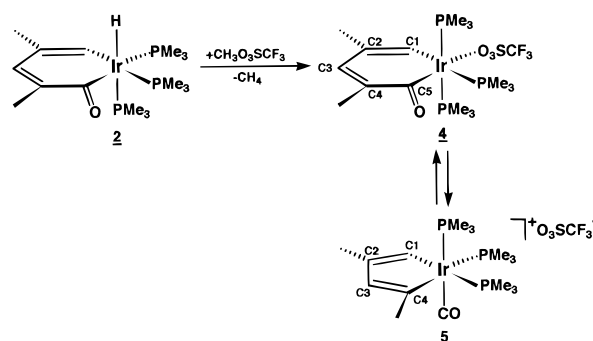
Although compound **2** can be crystallized and is indefinitely stable in the solid state under nitrogen, it slowly isomerizes in diethyl ether solution to (1,2,5-η-2,4-dimethylpenta-1,3-dien-5-oyl)Ir(PMe$_3$)$_3$, **3** (Scheme 1). It is interesting to note that the overall conversion of compound **1** to compound **3** involves metal-mediated migration of a hydrogen from C5 to C1. In the ^{1}H NMR spectrum of **3**, only the H3 signal appears downfield (δ 7.21); the two H1 resonances are found at δ 2.16 and 1.87. In the ^{13}C{^{1}H} NMR spectrum, the carbonyl carbon signal (C5) remains far downfield at δ 237.3 and is split into a wide doublet (J_{C-P} = 101.3 Hz). The signals for ring carbons C3 and C4 likewise remain in the olefinic region at δ 166.7 and 144.7, respectively, but the signals for C2 and C1 are shifted upfield to δ 46.9 and 37.8, respectively, as a result of their π-coordination to the iridium center. As expected, they exhibit moderate coupling (J_{C-P} = 36.0 and 33.5 Hz, respectively) to ^{31}P nuclei in the PMe$_3$ ligands. The ^{31}P{^{1}H} NMR spectrum consists of three separate but coupled signals, due to the three inequivalent PMe$_3$ ligands.

The structure of **3** has been confirmed by a single-crystal X-ray diffraction study.[5,6] The ORTEP drawing is reproduced in Figure 1, while key bond distances and angles are reported in the figure caption. Compound **3** can perhaps best be viewed as a distorted octahedron in which the six coordination sites

(4) Similar large H–P couplings between ring α-protons and adjacent phosphines in the ring plane have been observed in (η^6-iridabenzene)Mo-(CO)$_3$ complexes (see ref 1f).

(5) Several other (1,2,5-η-penta-1,3-dien-5-oyl)metal complexes have been previously characterized by X-ray diffraction: (a) Brammer, L.; Crocker, M.; Dunne, B. J.; Green, M.; Morton, C. E.; Nagle, K. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1226. (b) Crocker, M.; Dunne, B. J.; Green, M.; Orpen, A. G. *J. Chem. Soc. Dalton Trans.* **1991**, 1589. (c) Garlaschelli, L.; Malatesta, M. C.; Panzeri, S. *Organometallics* **1987**, *6*, 63.

(6) (η^5-Penta-1,3-dien-5-oyl)metal complexes have been postulated as intermediates in the photolytic synthesis of hydroxyferrocenes from (η^5-cyclopentadienyl)(CO)$_2$Fe(η^1-buta-1,3-dienyl) complexes: Yongskulrote, W.; Bramlett, J. M.; Mike, C. A.; Durham, B.; Allison, N. T. *Organometallics* **1989**, *8*, 556.
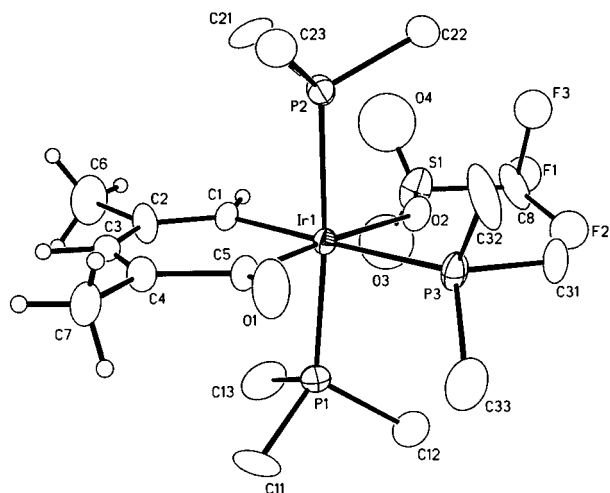
are occupied by C1, C2, and C5 of the penta-1,3-dien-5-oyl ligand and the three PMe$_3$ phosphorus atoms. The σ-bonded carbon atom, C5, lies approximately *trans* to P3 and *cis* to P1 and P2. The π-bonded carbons, C1 and C2, reside nearly in the Ir–P1–P2 plane and experience substantial back-bonding as evidenced by the relatively long C1–C2 distance of 1.464-(9) Å. In fact, the Ir–C1–C2 interaction approximates a metallacyclopropane in which the iridium center is formally Ir-(III). The carbon–carbon bond distances in the remainder of the penta-1,3-dien-5-oyl ligand show the expected long–short–long pattern, and the C5–O1 distance of 1.235(8) Å is normal for a carbon–oxygen double bond.

B. Treatment of Iridacyclohexadienone 2 with Methyl Triflate. When iridacyclohexadienone **2** is treated with methyl trifluoromethanesulfonate (methyl triflate) in diethyl ether at -10 °C, the hydride ligand is cleanly removed (as CH$_4$) and triflate coordinates to the iridium center (see Scheme 2). The ^{31}P{^{1}H} NMR spectrum of product **4** consists of a doublet (intensity 2) and a triplet (intensity 1), indicating a meridional arrangement of phosphine ligands and mirror plane symmetry. The position of the triflate group (*trans* to C5) is clear from the

Scheme 2

Figure 2. ORTEP drawing of $\overline{CH=C(Me)-CH=C(Me)-C(O)-Ir}$-$(PMe_3)_3(O_3SCF_3)$ (**4**). Two independent molecules crystallized in the asymmetric unit; selected bond distances and angles for molecule 1 are reported. Selected bond distances (Å): Ir1−P1, 2.347(6); Ir1−P2, 2.349(5); Ir1−P3, 2.405(5); Ir1−O2, 2.360(12); Ir1−C1, 2.052(17); Ir1−C5, 1.987(19); O1−C5, 1.197(25); C1−C2, 1.332(26); C2−C3, 1.438(31); C2−C6, 1.492(32); C3−C4, 1.340(31); C4−C5, 1.523(27); C4−C7, 1.492(32). Selected bond angles (deg): P1−Ir1−P2, 170.3-(2); C1−Ir1−C5, 92.9(7); Ir1−C1−C2, 129.1(15); C1−C2−C3, 119.9-(18); C2−C3−C4, 132.6(20); C3−C4−C5, 122.5(19); Ir1−C5−O1, 122.6(15); Ir1−C5−C4, 122.7(13); O1−C5−C4, 114.4(18).

$^{13}C\{^1H\}$ NMR spectrum, where the C5 signal is a singlet. In contrast, the C1 signal is a strongly-coupled doublet (J_{C-P} = 78.2 Hz), due to C1's *trans* relationship to a PMe$_3$ ligand. The ^1H and ^{13}C NMR chemical shifts in **4** are similar to those in precursor **2**, although H1 and C1 are shifted somewhat downfield to δ 9.25 and 156.7, respectively, while carbonyl carbon C5 is shifted upfield to δ 188.7.

The solid state structure of **4** has been confirmed by X-ray diffraction and is shown in Figure 2; key bond distances and angles are reported in the figure caption. As expected, the bonding around the metallacycle in **4** is localized with double bonds between C1 and C2 and between C3 and C4 and single bonds between C2 and C3 and between C4 and C5. The carbonyl C5−O1 bond distance of 1.197(25) Å is typical for a carbon−oxygen double bond. The internal angles within the six-membered metallacycle sum to 719.7°, very close to the value of 720° required for a planar hexagon, and range from 92.9(7)° for C1−Ir1−C5 to 132.6(20)° for C2−C3−C4.

When compound **4** is dissolved in acetone, it establishes an equilibrium with the iridacyclopentadiene−carbonyl compound **5** (see Scheme 2). This process involves dissociation of the labile triflate ligand and reversible "deinsertion" of the carbonyl group. At room temperature, the equilibrium slightly favors **4** (the ratio of compound **4** to compound **5** is approximately 60:40), but at 60 °C, equal quantities of **4** and **5** are observed by NMR. Upon cooling, the equilibrium shifts back toward **4**, and at −30 °C, pure **4** crystallizes from the mixture as yellow blocks.

The ^1H NMR spectrum of **5** includes two downfield signals at δ 6.44 and 6.31, due to H3 and H1, respectively. In the $^{13}C\{^1H\}$ NMR spectrum of **5**, there are five downfield signals (δ 124.2−171.8), and carbons C1, C4, and C5 (the carbonyl carbon) all exhibit strong C−P coupling due to their *trans* relationships to PMe$_3$ ligands. C5's very large J_{C-P} value of 110.7 Hz is typical for a metal-bound carbonyl ligand.[7] The $^{31}P\{^1H\}$ NMR spectrum consists of three doublet-of-doublet
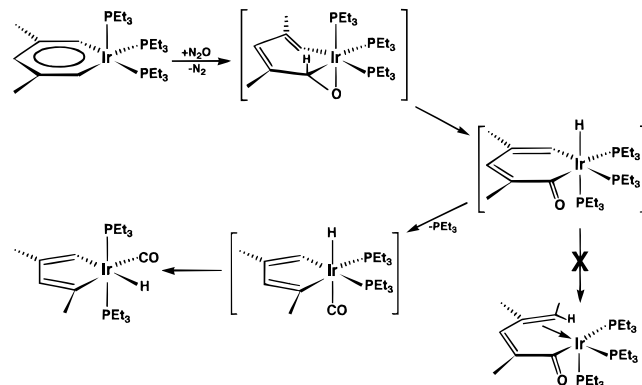
Scheme 3

Scheme 4
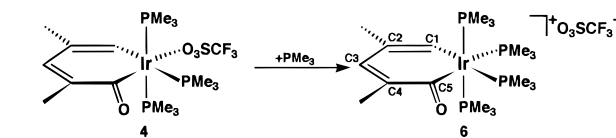
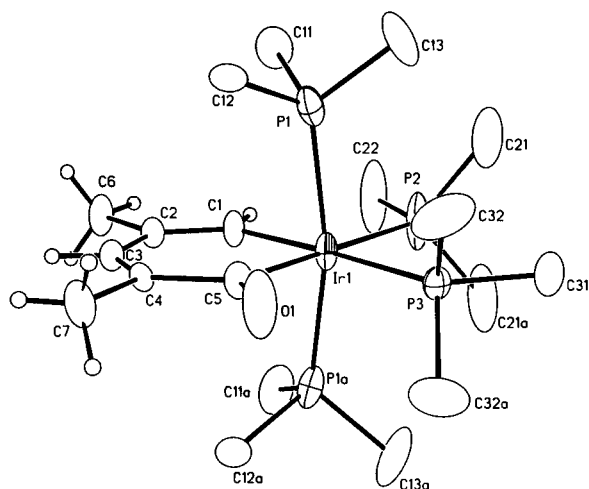

signals, consistent with a facial arrangement of PMe$_3$ ligands. In the infrared spectrum of **5**, the carbonyl C≡O stretching band is observed at 2054 cm^{-1}.

It is interesting to note that treatment of the tris(PEt$_3$) analogue of compound **1**, $\overline{CH=C(Me)-CH=C(Me)-CH=Ir(PEt_3)_3}$, with N$_2$O leads to the formation of a stable iridacyclopentadiene-carbonyl product (see Scheme 3).[1j,k] In this reaction, no intermediates have been isolated, but the key step is apparently a ring contraction similar to that shown in Scheme 2, except accompanied by PEt$_3$ loss rather than triflate dissociation. The PEt$_3$ extrusion probably results from the unfavorable steric interactions of three mutually-*cis*-PEt$_3$ ligands in the iridacyclohexadienone intermediate.

C. Treatment of Iridacyclohexadienone 4 with Trimethylphosphine. When iridacyclohexadienone **4** is treated with trimethylphosphine, the tetrakis(PMe$_3$) product **6** (see Scheme 4) is obtained.[8] This reaction, like the ring contraction reaction outlined in Scheme 2, involves dissociation of the labile triflate ligand. Compound **6** is stable and shows no tendency to lose PMe$_3$ or contract to a five-membered ring in solution. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** are very similar to those of iridacyclohexadienone **2** (*vide supra*). In particular, the signal for H1 is found at δ 7.97 and is a doublet (J = 19.1 Hz) due to coupling to the *cis*-PMe$_3$ ligand in the ring plane. H3 gives rise to a singlet at δ 6.67. Ring carbons C1−C4 resonate in the normal olefinic region of the ^{13}C NMR spectrum (δ 129.3−142.1), and C1 is a strongly coupled doublet (J_{C-P} = 73.0 Hz) due to its *trans* relationship to a PMe$_3$ ligand. Carbonyl carbon C5 resonates at δ 220.1 and is likewise a doublet (J_{C-P} = 86.1 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **6** consists of three signals—a doublet of doublets, due to the two equivalent *trans*-diaxial phosphines (related by mirror-plane symmetry), and two triplets of doublets, due to the two inequivalent equatorial phosphines.

The solid state structure of **6** has been determined by X-ray crystallography and is shown in Figure 3; key distances and angles are reported in the caption. The molecule resides on a crystallographically-imposed mirror plane, which includes the ring carbons, the iridium center, and the phosphorus atoms of the equatorial PMe$_3$ ligands. The metallacyclic ring in **6**, like

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(7) In general, the J_{C-P} value increases with increasing s character in the carbon hybridization.

(8) The same product is obtained when equilibrium mixtures of **4** and **5** react with PMe$_3$.

Figure 3. ORTEP drawing of the cation in [CH=C(Me)—CH=C(Me)—C(O)—Ir(PMe₃)₄]⁺O₃SCF₃⁻ (**6**). Two independent molecules crystallized in the asymmetric unit; selected bond distances and angles for molecule 1 are reported. Selected bond distances (Å): Ir1—P1, 2.368(5); Ir1—P2, 2.437(6); Ir1—P3, 2.405(4); Ir1—C1, 2.064(18); Ir1—C5, 2.082(21); O1—C5, 1.214(24); C1—C2, 1.383(28); C2—C3, 1.456-(31); C2—C6, 1.504(26); C3—C4, 1.319(26); C4—C5, 1.516(26); C4—C7, 1.535(35). Selected bond angles (deg): P1—Ir1—P1a, 166.9(2); C1—Ir1—C5, 90.8(8); Ir1—C1—C2, 128.3(17); C1—C2—C3, 122.1(17); C2—C3—C4, 131.7(18); C3—C4—C5, 122.7(19); Ir1—C5—O1, 122.3-(15); Ir1—C5—C4, 124.4(13); O1—C5—C4, 113.3(19).

that in compound **4** (*vide supra*), exhibits localized bonding and the expected short—long—short—long alternation in carbon—carbon bond lengths. The C5—O1 bond distance of 1.214(24) Å is a normal carbon—oxygen double bond length. The internal angles within the metallacycle range from 90.8(8)° (C1—Ir1—C5) to 131.7(18)° (C2—C3—C4) and sum to 720°, as required for a planar hexagon.

It is interesting to compare the iridium—ring carbon distances in compounds **4** and **6**. While the Ir1—C1 distances are very similar (2.052(17) Å in **4** vs 2.064(18) Å in **6**), the Ir1—C5 distances are quite different. In compound **4**, this distance is 1.987(19) Å, but in **6**, it lengthens significantly to 2.082(21) Å. This lengthening is probably due to the *trans*-PMe₃ ligand, which exerts a stronger *trans* influence on C5 than the weakly coordinating triflate ligand.[9]

D. Treatment of Iridacyclohexadienone 2 with Triflic Acid. Metallacyclohexadienone complexes can potentially serve as synthetic precursors to metallaphenols.[10] However, when iridacyclohexadienone **2** is treated with trifluoromethanesulfonic (triflic) acid, an iridacyclopentene—carbonyl complex, **7**, is generated instead (see Scheme 5). Although intermediates have not been isolated in this reaction, the pathway outlined in Scheme 5 seems reasonable. Direct protonation at C4 (or protonation at oxygen, followed by enol—keto tautomerization) would generate proposed intermediate **C**, and subsequent migration of the metal hydride to C1 would lead to **D**. Triflate dissociation and ring contraction, analogous to the conversion of **4** to **5** (cf. Scheme 2), would generate the observed product, **7**.[11] Unlike compound **5**, **7** does not equilibrate with a six-membered ring-containing isomer.

(9) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper and Row: New York, 1972; pp 423—440.

(10) To our knowledge, there have been no prior reports of metallaphenols. Perhaps the closest reported relative is an metalla*thia*phenol, synthesized by Roper: Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

(11) Consistent with the proposed pathway is the observation that deuterium is incorporated exclusively at C4 when DO₃SCF₃ is used in place of HO₃SCF₃.
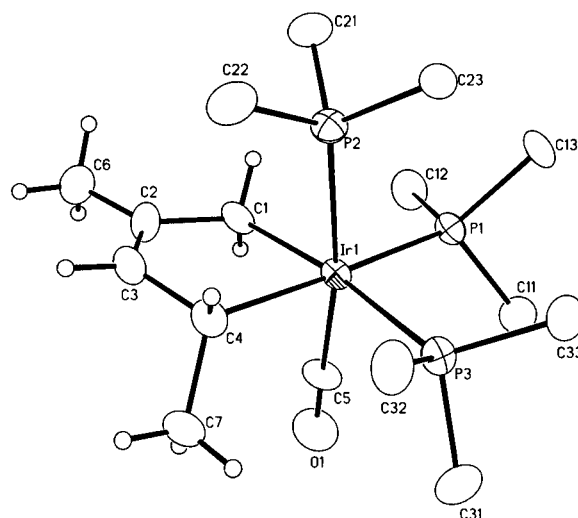
Figure 4. ORTEP drawing of the cation in [CH₂—C(Me)=CH—CH-(Me)—Ir(PMe₃)₃(CO)]⁺O₃SCF₃⁻·¹/₂Me₂C(O) (**7**). Selected bond distances (Å): Ir1—P1, 2.390(5); Ir1—P2, 2.378(5); Ir1—P3, 2.390(5); Ir1—C1, 2.159(18); Ir1—C4, 2.159(21); Ir1—C5, 1.855(18); C1—C2, 1.514(30); C2—C3, 1.279(33); C2—C6, 1.444(29); C3—C4, 1.544(27); C4—C7, 1.563(28); C5—O1, 1.143(25). Selected bond angles (deg): P2—Ir1—C5, 169.7(6); C1—Ir1—C4, 80.8(7); Ir1—C1—C2, 110.7(14); C1—C2—C3, 117.7(18); C1—C2—C6, 119.2(21); C3—C2—C6, 123.1-(22); C2—C3—C4, 121.8(20); Ir1—C4—C3, 107.7(14); Ir1—C4—C7, 118.3(15); C3—C4—C7, 107.4(14); Ir1—C5—O1, 175.8(21).
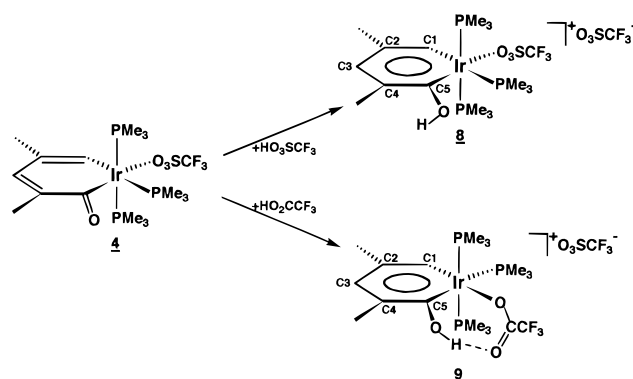
Scheme 5
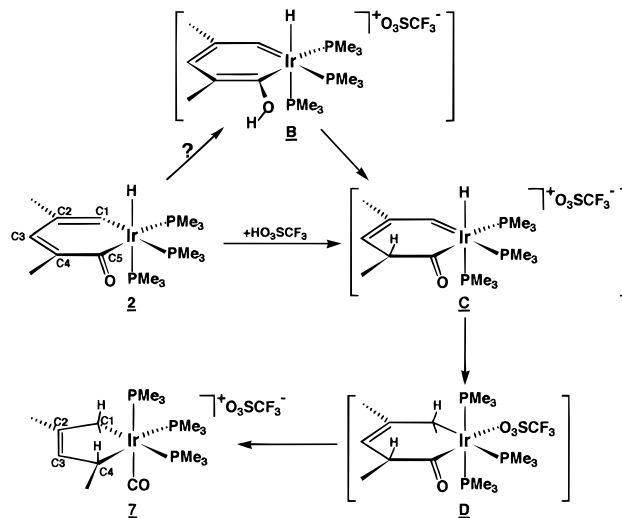
The ¹H NMR spectrum of compound **7** includes just one downfield signal, a doublet (J_{H-P} = 7.0 Hz) at δ 5.25 due to H3; the sp³ protons (H1's and H4) resonate in the δ 1.83—2.55 range. In the ¹³C{¹H} NMR spectrum, sp² carbons C2 and C3 appear downfield at δ 145.5 and 142.2, respectively, while sp³ carbons C1 and C4 shift upfield to δ 13.4 and 20.6, respectively, and exhibit strong coupling to the *trans*-PMe₃ ligands. The carbonyl carbon, C5, resonates at δ 174.9 and shows the very strong phosphorus coupling (J = 122.6 Hz) that is characteristic of metal-bound carbonyl ligands.[7] The ³¹P{¹H} NMR spectrum consists of three doublet-of-doublet signals, consistent with a *facial* arrangement of the three PMe₃ ligands. In the infrared spectrum of **7**, the C≡O stretch is seen at 2036 cm⁻¹.

The structure of **7** has been confirmed by X-ray diffraction and is reproduced in Figure 4; key bond distances and angles are reported in the caption. The iridacyclopentene ring shows the expected long—short—long alternation in carbon—carbon
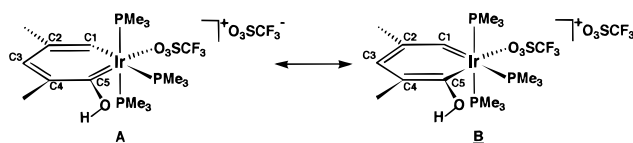
Scheme 6

Figure 5. ORTEP drawing of the cation in $[\overline{CH=C(Me)-CH=}$ $C(Me)-C(OH)=Ir(PMe_3)_3(O_3SCF_3)]^+O_3SCF_3^-\cdot CCl_2H_2$ (**8**). Selected bond distances (Å): Ir1−P1, 2.374(4); Ir1−P2, 2.372(4); Ir1−P3, 2.436(5); Ir1−O2, 2.214(12); Ir1−C1, 2.031(16); Ir1−C5, 1.916(16); O1−C5, 1.331(20); C1−C2, 1.352(25); C2−C3, 1.406(26); C2−C6, 1.523(28); C3−C4, 1.355(26); C4−C5, 1.464(25); C4−C7, 1.532(28). Selected bond angles (deg): P1−Ir1−P2, 172.2(2); C1−Ir1−C5, 90.2-(7); Ir1−C1−C2, 129.1(12); C1−C2−C3, 121.0(16); C2−C3−C4, 129.7(16); C3−C4−C5, 121.3(16); Ir1−C5−O1, 116.1(12); Ir1−C5−C4, 128.4(12); O1−C5−C4, 115.2(14).

bond lengths. The iridium−ring carbon bond lengths (Ir1−C1 and Ir1−C4) are each 2.159 Å, substantially longer than the iridium−carbon bonds in iridacyclohexadienones **4** and **6**. This is consistent with the fact that C1 and C4 in compound **7** are sp^3 hybridized, while the iridium-bound ring carbon atoms in **4** and **6** are sp^2 hybridized.[12]

E. Treatment of Iridacyclohexadienone 4 with Acids. Treatment of iridacyclohexadienone complex **4** with acids leads to protonation at the carbonyl oxygen and the production of stable iridaphenols. For example, when compound **4** is reacted with triflic acid in tetrahydrofuran, the solution immediately turns from yellow to dark red-orange, signaling the formation of iridaphenol **8** (see Scheme 6).[13] The aromatization of the ring in **8** is indicated by the downfield shifting of ring protons H1 and H3. H1 moves downfield from δ 9.25 in precursor **4** to δ 10.54 in **8**, while H3 shifts from δ 6.66 in **4** to δ 7.49 in **8**. Significant downfield shifts are also observed in the ^{13}C NMR for ring carbons C1, C3, and C5. These carbons appear at δ 179.0, 165.1, and 219.3, respectively, while C2 and C4 resonate at δ 126.6 and 132.0. The C5 signal remains a singlet (as in precursor **4**), indicating that the triflate ligand remains *trans* to C5. The ^{31}P{^{1}H} NMR spectrum consists of a doublet (intensity 2) and a triplet (intensity 1), consistent with a *mer* arrangement of PMe$_3$ ligands.

The structure of compound **8** has been determined by X-ray diffraction and is shown in Figure 5; key distances and angles are reported in the figure caption. As expected for a metal-laphenol, the carbon−carbon bond distances within the ring have moved toward equalization. Bonds C1−C2, C2−C3, C3−C4, and C4−C5 exhibit distances of 1.352(25), 1.406(26), 1.355-(26), and 1.464(25) Å, respectively. The phenol carbon−oxygen bond, C5−O1, has lengthened from 1.197(25) Å in precursor **4** to 1.331(20) Å in **8**. Furthermore, the iridium−carbon bonds Ir1−C1 and Ir1−C5 have shortened to 2.031(16) and 1.916-(16) Å, respectively, from their values of 2.052(17) and 1.987-(19) Å in **4**, indicating significant metal participation in ring π-bonding. While the trend toward delocalization is clear, the small differences observed in bond distances within the ring appear to be real. This suggests that, of the two resonance structures shown below, structure **A** contributes more strongly than **B** to the bonding in compound **8**. This may result, in part,

from the fact that the triflate ligand (*trans* to C5) exerts a weaker *trans* influence than the phosphine ligand (*trans* to C1).[9] In addition, resonance structure **A** may benefit from heteroatom (oxygen) stabilization of the metal carbene. The iridaphenol ring in **8** is nearly planar; the iridium atom resides less than 0.1 Å out of the best plane made by ring carbons C1, C2, C3, C4, and C5, and the dihedral angle between planes C1−C2−C3−C4−C5 and C1−Ir1−C5 is a mere 3.8°. The sum of the internal angles within the ring is 719.7°, close to the value of 720° required for a planar hexagon. The phenol hydrogen in **8** is hydrogen-bonded to an oxygen atom in the triflate counteranion. The distance between the phenol oxygen (O1) and the triflate oxygen is 2.654 Å, typical for oxygen atoms that are hydrogen-bonded.[14]

Treatment of iridacyclohexadienone **4** with trifluoroacetic acid also leads to the production of an iridaphenol, compound **9**. As shown in Scheme 6, this reaction is accompanied by exchange of the triflate ligand for a trifluoroacetate ligand, which coordinates *cis* to C5 (*trans* to C1), allowing intramolecular hydrogen bonding to occur between the phenol hydrogen and the carbonyl oxygen of the trifluoroacetate group. The position of the trifluoroacetate ligand in **9** is evident from the ^{13}C NMR spectrum, where the C5 signal is now phosphorus-coupled (*J* = 93.8 Hz) due to its *trans* relationship to PMe$_3$ and the C1 signal is a singlet. Similarly, in the ^{1}H NMR spectrum of **9**, the H1 signal (δ 8.95) splits into a doublet (*J* = 19.2 Hz), because it resides adjacent to an equatorial phosphine. The H3 and phenol protons appear as singlets at δ 7.50 and 17.50, respectively.

The structure of compound **9** has been confirmed by X-ray diffraction and is shown in Figure 6; key bond distances and angles are reported in the figure caption. The bonding within the metallacycle in compound **9** is even more highly delocalized than in compound **8**. The Ir1−C1 and Ir1−C5 distances are nearly identical at 2.002(12) and 2.023(13) Å, respectively, while

(12) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(13) Compound **1** and related aromatic metallacycles are typically orange or red in color (see ref 1).
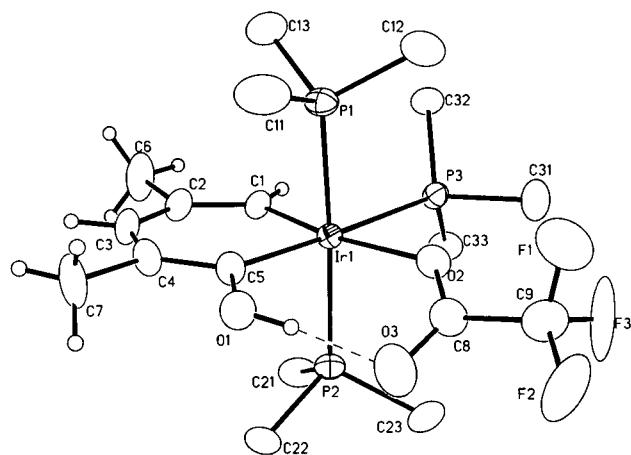
(14) Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination*; Macmillan Publishing Co., Inc.: New York, 1968; pp 302−303.

Figure 6. ORTEP drawing of the cation in [CH=C(Me)—CH=
C(Me)—C(OH)=Ir(PMe₃)₃(O₂CCF₃)]⁺O₃SCF₃⁻·CCl₂H₂ (**9**). Selected
bond distances (Å): Ir1—P1, 2.371(3); Ir1—P2, 2.355(3); Ir1—P3,
2.424(4); Ir1—O2, 2.236(10); Ir1—C1, 2.002(12); Ir1—C5, 2.023(13);
C1—C2, 1.371(19); C2—C3, 1.427(21); C2—C6, 1.513(24); C3—C4,
1.398(22); C4—C5, 1.371(20); C4—C7, 1.530(25); C5—O1, 1.345(15);
O2—C8, 1.253(19); C8—O3, 1.199(22). Selected bond angles (deg):
P1—Ir1—P2, 173.4; C1—Ir1—C5, 89.7(5); Ir1—C1—C2, 127.6(10); C1—
C2—C3, 123.4(13); C2—C3—C4, 128.4(14); C3—C4—C5, 120.5(14);
Ir1—C5—O1, 121.0(9); Ir1—C5—C4, 130.0(10); O1—C5—C4, 109.0-
(12); Ir1—O2—C8, 135.4(10); O2—C8—O3, 125.8(17).

ring C—C bonds C1—C2, C2—C3, C3—C4, and C4—C5 exhibit
distances of 1.371(19), 1.427(21), 1.398(22), and 1.371(20) Å,
respectively. Hence, it appears that resonance structures **C** and
D below contribute almost equally to the bonding in compound
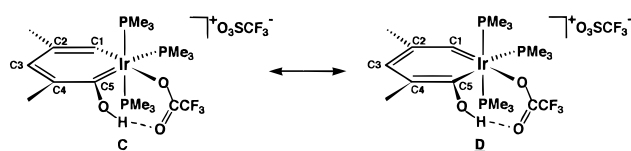
9. Structure **C** may be stabilized by the presence of a
heteroatom (oxygen) on the carbene carbon, while resonance
structure **D** probably benefits from the weaker *trans* influence
of the trifluoroacetate group. The metallacycle in **9** is nearly
planar; the iridium atom lies only 0.100 Å out of the C1—C2—
C3—C4—C5 plane, and the dihedral angle between this plane
and the C1—Ir1—C5 plane is 4.0°. The sum of the six internal
angles within the metallaphenol ring is 719.6°.

As mentioned above, the placement of the trifluoroacetate
ligand *cis* to C5 allows the phenol hydrogen to form an
intramolecular hydrogen bond, and the observed distance of
2.576 Å between the phenol oxygen (O1) and the trifluoroacetate
carbonyl oxygen (O3) is fully consistent with this type of
interaction. The molecule achieves the desired O1—O3 distance
by twisting the trifluoroacetate group out of the equatorial plane,
placing carbonyl oxygen O3 0.929 Å below the C1—C5—Ir1—
P3—O2 plane.

**F. Treatment of Iridacyclohexadienone 6 with Triflic
Acid.** As shown in Scheme 7, treatment of iridacyclohexadi-
enone **6** with triflic acid leads to production of iridaphenol **10**.
Again, comparison of the ¹H NMR spectrum of **10** vs that of
precursor **6** shows significant downfield shifting of ring protons
H1 and H3, consistent with aromatization of the ring. The H1
signal moves from δ 7.97 in **6** to δ 9.18 in **10**, while H3 shifts
from δ 6.67 to δ 7.55. In the ¹³C NMR, downfield shifts of
20—30 ppm are observed for ring carbons C1, C3, and C5.
Unlike iridacyclohexadienone **4**, compound **6** does not react with

Scheme 7
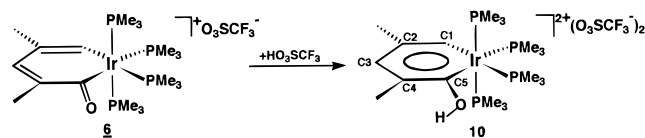
trifluoroacetic acid. Apparently, the cationic charge on **6** and/
or the inertness of the tetrakis(PMe₃) ligand set renders this
compound less reactive than **4** toward CF₃CO₂H.

Summary

Iridacyclohexadienones, a new class of unsaturated six-
membered metallacycles, have been synthesized by treating
iridabenzenes with nitrous oxide, an oxygen atom source. These
molecules undergo a number of interesting reactions, including
isomerization to (1,2,5-η-penta-1,3-dien-5-oyl)iridium com-
plexes via metal-mediated hydrogen transfer and reversible ring
contraction to iridacyclopentadiene complexes, an equilibrium
process that involves carbonyl insertion and deinsertion. When
treated with acids, iridacyclohexadienones generally protonate
at oxygen, producing iridaphenol complexes with aromatic
character. However, ring contraction can also occur upon
protonation, leading to iridacyclopentene products.

Experimental Section

General Comments. All manipulations were carried out under a
nitrogen atmosphere, using either glovebox or double-manifold Schlenk
techniques. Solvents were stored under nitrogen after being distilled
from the appropriate drying agents. Deuterated NMR solvents were
obtained from Cambridge Isotope Laboratories in 1 g sealed vials and
used as received. The following reagents were used as obtained from
the supplier indicated: nitrous oxide (Aldrich), methyl trifluoromethane-
sulfonate (Aldrich), trimethylphosphine (Strem), trifluoromethane-
sulfonic acid (Aldrich), and trifluoroacetic acid (Aldrich). A detailed
synthesis and full NMR characterization of CH=C(Me)—CH=C-
(Me)—CH=Ir(PMe₃)₃ (**1**) is given in ref 1k.

NMR experiments were performed on a Varian Unity-300 spec-
trometer (¹H, 300 MHz; ¹³C, 75 MHz; ³¹P, 121 MHz), a Varian Unity-
500 spectrometer (¹H, 500 MHz; ¹³C, 125 MHz; ³¹P, 202 MHz), or a
Varian VXR-600 spectrometer (¹H, 600 MHz; ¹³C, 150 MHz; ³¹P, 242
MHz). ¹H and ¹³C spectra were referenced to tetramethylsilane, while
³¹P spectra were referenced to external H₃PO₄. Some ¹H connectivities
were determined from COSY (¹H–¹H correlation spectroscopy) data.
HMQC (¹H-detected multiple quantum coherence) and HMBC (het-
eronuclear multiple bond correlation) experiments aided in assigning
some of the ¹H and ¹³C peaks.

The infrared spectra were recorded on a Mattson Polaris FT IR
spectrometer.

Microanalyses were performed by Galbraith Laboratories, Inc.,
Knoxville, TN.

Synthesis of CH=C(Me)—CH=C(Me)—C(O)—Ir(PMe₃)₃(H) (2).
N₂O gas was bubbled through a stirring solution of orange CH=C-
(Me)—CH=C(Me)CH=Ir(PMe₃)₃ (**1**) (0.31 g, 6.0 × 10⁻⁴ mol) in
diethyl ether at 25 °C until it turned a clear yellow color (~30 s).
Crystallization from acetone at −30 °C resulted in dark yellow crystals
of **2**. Yield: 0.25 g, 79%. Anal. Calcd for C₁₆H₃₆IrOP₃: C, 36.29;
H, 6.85. Found: C, 36.06; H, 6.93. ¹H NMR (benzene-*d₆*, 25 °C): δ
8.16 (br d, *J*ₕ₋ₚ = 20.3 Hz, 1, H1), 6.76 (s, 1, H3), 2.31 (d, *J*ₕ₋ₚ = 2.9
Hz, 3, ring CH₃'s), 2.15 (s, 3, ring CH₃'s), 1.41 (d, *J*ₕ₋ₚ = 8.0 Hz, 9,
PMe₃ CH₃'s), 1.06 (d, *J*ₕ₋ₚ = 8.0 Hz, 9, PMe₃ CH₃'s), 1.04 (d, *J*ₕ₋ₚ =
8.0 Hz, 9, PMe₃ CH₃'s), −10.80 (dt, *J*ₕ₋ₚ = 114.9, 20.5 Hz, 1, Ir—H).
¹³C{¹H} (benzene-*d₆*, 25 °C): δ 230.4 (br d, *J*ᴄ₋ₚ = 98.1 Hz, C5),
140.6 (s, C3), 136.9 (d, *J*ᴄ₋ₚ = 29.6 Hz, C4), 136.3 (br d, *J*ᴄ₋ₚ = 80.7
Hz, C1), 127.5 (s, C2), 29.5 (d, *J*ᴄ₋ₚ = 9.2 Hz, ring CH₃), 22.6 (d,
*J*ᴄ₋ₚ = 28.8 Hz, PMe₃ CH₃'s), 20.3 (d, *J*ᴄ₋ₚ = 23.2 Hz, PMe₃ CH₃'s),
19.2 (s, ring CH₃), 18.5 (d, *J*ᴄ₋ₚ = 27.8 Hz, PMe₃ CH₃'s). ³¹P{¹H}

NMR (benzene-d_6, 25 °C): δ −51.1 (dd, J_{P-P} = 20.9, 20.3 Hz, 1, PMe₃), −56.5 (d, J_{P-P} = 20.9 Hz, 1, PMe₃), −63.3 (d, J_{P-P} = 20.3 Hz, 1, PMe₃).

Synthesis of (1,2,5-η-2,4-Dimethylpenta-1,3-dien-5-oyl)Ir(PMe₃)₃ (3). A solution of compound **2** (0.33 g, 6.6 × 10⁻⁴ mol) in diethyl ether was stirred at 25 °C for 24 h. Crystallization from acetone at −30 °C resulted in pale yellow crystals of **3**. Yield: 0.27 g, 81%. Anal. Calcd for C₁₆H₃₆IrOP₃: C, 36.29; H, 6.85. Found: C, 36.13; H, 7.05. ¹H NMR (benzene-d_6, 25 °C): δ 7.21 (d, J_{H-P} = 9.4 Hz, 1, H3), 2.16 (br d, J_{H-P} = 13.6 Hz, 1, H1), 1.98 (d, J_{H-P} = 8.5 Hz, 3, ring CH₃'s), 1.87 (m, 1, H1), 1.83 (s, 3, ring CH₃'s), 1.42 (d, J_{H-P} = 7.2 Hz, 9, PMe₃ CH₃'s), 1.22 (d, J_{H-P} = 7.2 Hz, 9, PMe₃ CH₃'s), 0.97 (d, J_{H-P} = 6.0 Hz, 9, PMe₃ CH₃'s). ¹³C{¹H} NMR (benzene-d_6, 25 °C): δ 237.3 (dt, J_{C-P} = 101.3, 9.0 Hz, C5), 166.7 (s, C3), 144.7 (d, J_{C-P} = 24.1 Hz, C4), 46.9 (dd, J_{C-P} = 36.0, 6.6 Hz, C2), 37.8 (ddd, J_{C-P} = 33.5, 8.0 Hz, 3.0 Hz, C1), 28.1 (s, ring CH₃), 22.4−22.1 (complex m, PMe₃ CH₃'s), 20.9 (dt, J_{C-P} = 21.4, 3.5 Hz, PMe₃ CH₃'s), 11.8 (s, ring CH₃). ³¹P{¹H} NMR (benzene-d_6, 25 °C): −50.9 (dd, J_{P-P} = 35.5, 5.5 Hz, 1, PMe₃), −52.3 (dd, J_{P-P} = 35.5, 21.3 Hz, 1, PMe₃), −63.4 (dd, J_{P-P} = 21.3, 5.5 Hz, 1, PMe₃).

Synthesis of ⌐CH=C(Me)−CH=C(Me)−C(O)−Ir(PMe₃)₃(O₃SCF₃) (4). Excess CH₃O₃SCF₃ (0.16 g, 9.8 × 10⁻⁴ mol) in diethyl ether was added dropwise via syringe to a solution of compound **2** (0.36 g, 7.1 × 10⁻⁴ mol) in diethyl ether at −10 °C, causing the clear yellow solution to become cloudy. The ether was removed under vacuum, and the yellow residue was washed with pentane to remove any excess CH₃O₃SCF₃. Crystallization from acetone at −30 °C produced orange/yellow crystals of **4**. Yield: 0.32 g, 66%. Anal. Calcd for C₁₇H₃₅F₃IrO₄P₃S: C, 30.13; H, 5.21. Found: C, 29.92; H, 5.18. ¹H NMR (acetone-d_6, 25 °C): δ 9.25 (s, 1, H1), 6.66 (s, 1, H3), 2.02 (s, 3, ring CH₃'s), 1.61 (s, 3, ring CH₃'s), 1.60 (d, J_{H-P} = 9.8 Hz, 9, PMe₃ CH₃'s), 1.41 (virtual t, J_{H-P} = 8.6 Hz, 18, PMe₃ CH₃'s). ¹³C{¹H} NMR (benzene-d_6, 25 °C): δ 188.7 (s, C5), 156.7 (dt, J_{C-P} = 78.2, 13.1 Hz, C1), 145.7 (s, C3), 127.9 (s, C2), 127.1 (s, C4), 26.8 (d, J_{C-P} = 8.8 Hz, ring CH₃), 20.0 (s, ring CH₃), 15.7 (d, J_{C-P} = 40.1 Hz, PMe₃ CH₃'s), 15.1 (virtual t, J_{C-P} = 38.2 Hz, PMe₃ CH₃'s). ³¹P{¹H} NMR (acetone-d_6, 25 °C): δ −32.3 (d, J_{P-P} = 25.0 Hz, 2, PMe₃'s), −39.9 (t, J_{P-P} = 25.0 Hz, 1, PMe₃).

Synthesis of [⌐CH=C(Me)−CH=C(Me)−Ir(PMe₃)₃(CO)]⁺O₃SCF₃⁻ (5). Crystals of compound **4** were dissolved in acetone at room temperature. After 1 h, the NMR spectrum revealed an equilibrium mixture of compounds **4** and **5** in a ratio of 60:40. ¹H NMR (acetone-d_6, 25 °C): δ 6.44 (d, J_{H-P} = 8.7 Hz, 1, H3), 6.31 (t, J_{H-P} = 10.3 Hz, 1, H1), 2.44 (d, J_{H-P} = 6.0 Hz, 3, ring CH₃'s), 1.95 (d, J_{H-P} = 8.6 Hz, 9, PMe₃ CH₃'s), 1.92 (d, J_{H-P} = 9.8 Hz, 9, PMe₃ CH₃'s), 1.92 (s, 3, ring CH₃'s), 1.62 (d, J_{H-P} = 7.3 Hz, 9, PMe₃ CH₃'s). ¹³C{¹H} NMR (benzene-d_6, 25 °C): δ 171.8 (dt, J_{C-P} = 110.7, 6.2 Hz, CO), 153.7 (s, C2), 148.1 (s, C3), 143.7 (d, J_{C-P} = 65.8 Hz, C4), 124.2 (ddd, J_{C-P} = 67.1, 13.0, 5.9 Hz, C1), 32.6 (m, ring CH₃), 20.8 (d, J_{C-P} = 7.0 Hz, ring CH₃), 20.5 (d, J_{C-P} = 31.7 Hz, PMe₃ CH₃'s), 18.5 (d, J_{C-P} = 32.4 Hz, PMe₃ CH₃'s), 17.6 (d, J_{C-P} = 28.0 Hz, PMe₃ CH₃'s). ³¹P{¹H} NMR (acetone-d_6, 25 °C): δ −48.0 (dd, J_{P-P} = 26.7, 26.0 Hz, 1, PMe₃), −61.2 (dd, J_{P-P} = 26.0, 13.4 Hz, 1, PMe₃), −66.1 (dd, J_{P-P} = 26.7, 13.4 Hz, 1, PMe₃). IR (Nujol mull): 2054 cm⁻¹ (C≡O stretch).

Synthesis of [⌐CH=C(Me)−CH=C(Me)−C(O)−Ir(PMe₃)₄]⁺O₃SCF₃⁻ (6). Excess PMe₃ (0.16 g, 2.1 × 10⁻³ mol) was added dropwise to compound **4** (0.10 g, 1.5 × 10⁻⁴ mol) in tetrahydrofuran at 25 °C, and the resulting solution was stirred for 30 min. Crystallization from acetone at −30 °C resulted in yellow crystals of **6**. Yield: 0.09 g, 80%. Anal. Calcd for C₂₀H₄₄F₃IrO₄P₄S: C, 31.87; H, 5.90. Found C, 31.85; H, 6.23. ¹H NMR (acetone-d_6, 25 °C): δ 7.97 (d, J_{H-P} = 19.1 Hz, 1, H1), 6.67 (s, 1, H3), 2.06 (s, 3, ring CH₃'s), 1.71 (d, J_{H-P} = 7.9 Hz, 9, PMe₃ CH₃'s), 1.66 (d, J_{H-P} = 7.3 Hz, 9, PMe₃ CH₃'s), 1.59 (s, 3, ring CH₃'s), 1.52 (virtual t, J_{H-P} = 7.33 Hz, 18, *trans*-diaxial PMe₃ CH₃'s). ¹³C{¹H} NMR (acetone-d_6, 25 °C): δ 220.1 (d, J_{C-P} = 86.1 Hz, C5), 142.1 (s, C3), 136.7 (dtd, J_{C-P} = 73.0, 13.8, 4.2 Hz, C1), 133.1 (d, J_{C-P} = 27.9 Hz, C4), 129.3 (s, C2), 27.7 (d, J_{C-P} = 7.8 Hz, ring CH₃), 20.3 (d, J_{C-P} = 30.9 Hz, PMe₃ CH₃'s), 17.8 (s, ring CH₃), 17.7 (virtual t, J_{C-P} = 39.4 Hz, *trans*-diaxial PMe₃ CH₃'s), 17.2 (d, J_{C-P} = 25.3 Hz, PMe₃ CH₃'s). ³¹P{¹H} NMR (acetone-d_6, 25 °C):

δ −44.9 (dd, J_{P-P} = 23.1, 22.0 Hz, 2, *trans*-diaxial PMe₃'s), −62.7 (td, J_{P-P} = 22.0, 2.5 Hz, 1, PMe₃), −68.5 (td, J_{P-P} = 23.1, 2.5 Hz, 1, PMe₃).

Synthesis of [⌐CH₂−C(Me)=CH−CH(Me)−Ir(PMe₃)₃(CO)]⁺O₃SCF₃⁻ (7). Excess HO₃SCF₃ (0.063 g, 4.2 × 10⁻⁴ mol) in diethyl ether was added dropwise via syringe to compound **2** (0.20 g, 3.8 × 10⁻⁴ mol) in diethyl ether at −78 °C, causing the clear yellow solution to become orange and cloudy. Upon warming to 25 °C, the solution turned colorless with a fine white precipitate. After removal of the ether under vacuum, the white residue was washed with pentane to remove excess HO₃SCF₃. Crystallization from acetone at −30 °C resulted in colorless crystals of **7**. Yield: 0.12 g, 46%. Anal. Calcd for C₁₇H₃₇F₃IrO₄P₃S·C₁.₅H₃O₀.₅: C, 31.35; H, 5.69. Found: C, 31.31; H, 5.79. ¹H NMR (acetone-d_6, 25 °C): δ 5.25 (d, J_{H-P} = 7.0 Hz, 1, H3), 2.55 (m, 1, H1), 2.51 (m, 1, H4), 1.86 (d, J_{H-P} = 8.6 Hz, 9, PMe₃ CH₃'s), 1.83 (partially obscured, H1), 1.79 (partially obscured, ring CH₃'s), 1.79 (d, J_{H-P} = 9.3 Hz, 9, PMe₃ CH₃'s), 1.62 (partially obscured, ring CH₃'s), 1.61 (d, J_{H-P} = 9.3 Hz, 9, PMe₃ CH₃'s). ¹³C{¹H} NMR (acetone-d_6, 25 °C): δ 174.9 (dt, J_{C-P} = 122.6, 6.4 Hz, CO), 145.5 (dt, J_{C-P} = 12.9, 2.3 Hz, C2), 142.2 (dt, J_{C-P} = 9.5, 3.3 Hz, C3), 28.8 (s, ring CH₃), 20.6 (ddd, J_{C-P} = 58.7, 5.7, 3.5 Hz, C4), 20.1 (s, ring CH₃), 18.4 (d, J_{C-P} = 31.3 Hz, PMe₃ CH₃'s), 18.3 (d, J_{C-P} = 31.9 Hz, PMe₃ CH₃'s), 14.4 (d, J_{C-P} = 37.6 Hz, PMe₃ CH₃'s), 13.4 (ddd, J_{C-P} = 55.5, 7.0, 3.0 Hz, C1). ³¹P{¹H} NMR (acetone-d_6, 25 °C): δ −49.6 (dd, J_{P-P} = 26.4, 25.7 Hz, 1, PMe₃), −62.0 (dd, J_{P-P} = 25.7, 12.2 Hz, 1, PMe₃), −63.3 (dd, J_{P-P} = 26.4, 12.2 Hz, 1, PMe₃). IR (Nujol mull): 2036 cm⁻¹ (C≡O stretch).

Synthesis of [⌐CH=C(Me)−CH=C(Me)−C(OH)=Ir(PMe₃)₃(O₃SCF₃)]⁺O₃SCF₃⁻ (8). Excess HO₃SCF₃ (0.10 g, 6.8 × 10⁻⁴ mol) was added dropwise to a stirring solution of compound **4** (0.31 g, 4.6 × 10⁻⁴ mol) in tetrahydrofuran at 25 °C, causing the yellow solution to turn a dark orange color. After removing the solvent under vacuum, the residue was washed with diethyl ether to remove any excess HO₃-SCF₃. Crystallization from methylene chloride at −30 °C resulted in red crystals of **8**. Yield: 0.24 g, 64%. Anal. Calcd for C₁₈H₃₆F₆IrO₇P₃S₂: C, 26.12; H, 4.39. Found: C, 25.87; H, 4.37. ¹H NMR (methylene chloride-d_2, 25 °C): δ 10.54 (s, 1, H1), 7.49 (s, 1, H3), 2.24 (s, 3, ring CH₃'s), 2.08 (s, 3, ring CH₃'s), 1.69 (d, J_{H-P} = 7.8 Hz, 9, PMe₃ CH₃'s), 1.44 (t, J_{H-P} = 8.8 Hz, 18, PMe₃ CH₃'s). NOTE: The phenol proton appears as a broad resonance in the δ 12−14 region. ¹³C{¹H} NMR (methylene chloride-d_2, 25 °C): δ 219.3 (s, C5), 179.0 (d, J_{C-P} = 76.9 Hz, C1), 165.1 (s, C3), 132.0, 126.6 (s's, C2 and C4), 25.6 (d, J_{C-P} = 8.0 Hz, ring CH₃), 19.0 (s, ring CH₃), 16.7 (d, J_{C-P} = 30.1 Hz, PMe₃ CH₃'s), 15.4 (virtual t, J_{C-P} = 38.9 Hz, PMe₃ CH₃'s). ³¹P{¹H} NMR (methylene chloride-d_2, 25 °C): δ −29.70 (d, J_{P-P} = 25.1 Hz, 2, PMe₃'s), −41.3 (t, J_{P-P} = 25.1 Hz, 1, PMe₃).

Synthesis of [⌐CH=C(Me)−CH=C(Me)−C(OH)=Ir(PMe₃)₃(O₂CCF₃)]⁺O₃SCF₃⁻ (9). A synthetic procedure similar to that described for compound **8** was employed, except that CF₃COOH (0.20 g, 1.7 × 10⁻³ mol) was substituted for HO₃SCF₃. Crystallization from methylene chloride/diethyl ether resulted in orange crystals of **9**. Yield: 0.29 g, 80%. Anal. Calcd for C₁₉H₃₆F₆IrO₆P₃S: C, 28.82; H, 4.59. Found: C, 28.39; H, 4.61. ¹H NMR (methylene chloride-d_2, 25 °C): δ 17.50 (s, 1, phenol H), 8.95 (d, J_{H-P} = 19.2 Hz, 1, H1), 7.50 (s, H3), 2.14 (s, 3, ring CH₃'s), 2.00 (s, 3, ring CH₃'s), 1.66 (d, J_{H-P} = 8.6 Hz, 9, PMe₃ CH₃'s), 1.33 (virtual t, J_{H-P} = 7.7 Hz, 18, PMe₃ CH₃'s). ¹³C{¹H} (methylene chloride-d_2, 25 °C): δ 250.8 (d, J_{C-P} = 93.8 Hz, C5), 162.1 (s, C3), 146.3 (s, C1), 132.7 (d, J_{C-P} = 9.6 Hz, C4), 131.2 (s, C2), 26.0 (s, ring CH₃), 18.4 (s, ring CH₃), 15.3 (virtual t, J_{C-P} = 39.2 Hz, PMe₃ CH₃'s), 13.9 (d, J_{C-P} = 30.8 Hz, PMe₃ CH₃'s). ³¹P{¹H} NMR (methylene chloride-d_2, 25 °C): δ −34.5 (d, J_{P-P} = 28.6 Hz, 2, PMe₃'s), −43.7 (t, J_{P-P} = 28.6 Hz, 1, PMe₃).

Synthesis of [⌐CH=C(Me)−CH=C(Me)−C(OH)=Ir(PMe₃)₄]²⁺(O₃SCF₃⁻)₂ (10). Excess HO₃SCF₃ (0.12 g, 8.0 × 10⁻⁴ mol) was added dropwise to a stirring solution of compound **6** (0.11 g, 1.5 × 10⁻⁴ mol) in tetrahydrofuran at 25 °C, causing the yellow solution to turn a clear orange color with some precipitation of the final product. After the solvent was removed under vacuum, the residue was washed with diethyl ether to remove any excess HO₃SCF₃. Crystallization from methylene chloride resulted in dark orange crystals of **10**. Yield: 0.09

Table 1.   X-ray Diffraction Structure Summary

	3	**4**	**6**	**7**	**8**	**9**
Crystal Parameters and Data Collection Summary						
formula	$C_{16}H_{36}IrOP_3$	$C_{17}H_{35}F_3IrO_4P_3S$	$C_{20}H_{44}F_3IrO_4P_4S$	$C_{18.5}H_{40}F_3IrO_{4.5}P_3S$	$C_{19}H_{38}Cl_2F_6IrO_7P_3S_2$	$C_{20}H_{38}Cl_2F_6IrO_6P_3S$
formula weight	529.6	677.6	753.7	708.7	912.6	876.6
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/m$	$C2/c$	$P2_1/c$	$P2_1/c$
a, Å	9.359(1)	9.100(2)	15.196(6)	30.485(8)	9.109(3)	8.930(3)
b, Å	15.743(3)	29.364(8)	11.117(2)	11.613(3)	22.210(11)	22.446(11)
c, Å	14.871(4)	20.080(6)	18.505(7)	16.948(4)	17.370(11)	17.436(8)
α, deg	90.0	90.0	90.0	90.0	90.0	90.0
β, deg	95.68(2)	93.05(2)	103.57(3)	108.48(2)	92.10(4)	91.37(4)
γ, deg	90.0	90.0	90.0	90.0	90.0	90.0
V, Å^3	2180.4(8)	5358(2)	3038(2)	5691(2)	3512(3)	3494(3)
Z	4	8	4	8	4	4
crystal dimensions, mm	0.65 × 0.45 × 0.35	0.48 × 0.46 × 0.34	0.12 × 0.20 × 0.30	0.50 × 0.45 × 0.35	0.54 × 0.34 × 0.30	0.32 × 0.34 × 0.32
crystal color and habit	yellow prism	yellow prism	yellow prism	colorless block	orange prism	orange prism
density$_{cald}$, g/cm^3	1.613	1.680	1.647	1.654	1.726	1.666
radiation, Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
scan type	$\theta{:}2\theta$	ω	$\theta{:}2\theta$	ω	$\theta{:}2\theta$	$\theta{:}2\theta$
scan rate, deg/min in ω	var; 4.00−29.30	var; 4.00−29.30	var; 4.19−29.30	var; 4.19−29.30	var; 4.19−29.30	var; 5.00−29.30
2θ range, deg	3.0−50.0	3.0−50.0	3.0−50.0	3.0−50.0	3.0−50.0	3.0−50.0
scan range (ω), deg	1.20	1.20	1.40	1.60	1.60	1.40
data collected	$h\ 0 \rightarrow 11$ $k\ 0 \rightarrow 18$ $l\ -17 \rightarrow 17$	$h\ 0 \rightarrow 10$ $k\ 0 \rightarrow 34$ $l\ -23 \rightarrow 23$	$h\ 0 \rightarrow 18$ $k\ 0 \rightarrow 13$ $l\ -22 \rightarrow 21$	$h\ 0 \rightarrow 36$ $k\ 0 \rightarrow 14$ $l\ -21 \rightarrow 21$	$h\ 0 \rightarrow 10$ $k\ 0 \rightarrow 26$ $l\ -20 \rightarrow 20$	$h\ 0 \rightarrow 10$ $k\ 0 \rightarrow 26$ $l\ -20 \rightarrow 20$
total decay	none detected	none detected	none detected	none detected	40%	none detected
temperature, K	298	298	298	298	298	298
Treatment of Intensity Data and Refinement Summary						
no. of data collected:	4098	10055	5916	5076	6534	6615
no. of unique data:	3851	9425	5688	4972	6126	6195
no. of observed data $I > 3\sigma(I)$	2976	4815	3389	2763	3492	3709
Mo Kα linear abs coeff, cm^{-1}	63.42	52.80	47.14	49.77	42.75	42.33
abs correction applied	semiempirical	semiempirical	semiempirical	semiempirical	semiempirical	semiempirical
data to parameter ratio	15.6:1	9.8:1	9.9:1	11.2:1	9.6:1	10.0:1
R^a	0.0270	0.0515	0.0447	0.0589	0.0559	0.0478
$R_w{}^a$	0.0373^b	0.0726^c	0.0711^d	0.0837^e	0.0692^f	0.0639^g
GOF^h	1.14	0.66	0.61	0.90	1.58	1.14

^{a} R = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. R_w = $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. ^{b} $w = [\sigma^2(F_o) + 0.0006(F_o)^2]^{-1}$. ^{c} $w = [\sigma^2(F_o) + 0.0098(F_o)^2]^{-1}$. ^{d} $w = [\sigma^2(F_o) + 0.0119(F_o)^2]^{-1}$. ^{e} $w = [\sigma^2(F_o) + 0.0065(F_o)^2]^{-1}$. ^{f} $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1}$. ^{g} $w = [\sigma^2(F_o) + 0.0019(F_o)^2]^{-1}$. ^{h} GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$.

g, 64%. Anal. Calcd for $C_{21}H_{45}F_6IrO_7P_4S_2$: C, 27.90, H, 5.03. Found: C, 27.25; H, 5.06. ^{1}H NMR (methylene chloride-d_2, 25 °C): δ 9.18 (dd, J_{H-P} = 18.7, 6.1 Hz, 1, H1), 7.55 (s, 1, H3), 2.27 (s, 3, ring CH$_3$'s), 2.11 (s, 3, ring CH$_3$'s), 1.81 (d, J_{H-P} = 8.5 Hz, 9, PMe$_3$ CH$_3$'s), 1.78 (d, J_{H-P} = 8.5 Hz, 9, PMe$_3$ CH$_3$'s), 1.51 (virtual t, J_{H-P} = 7.5 Hz, 18, *trans*-diaxial PMe$_3$ CH$_3$'s). NOTE: The phenol proton appears as a broad resonance in the δ 12−14 region. ^{13}C{^{1}H} NMR (methylene chloride-d_2, 25 °C): δ 246.0 (d, J_{C-P} = 98.3 Hz, C5), 165.6 (s, C3), 164.6 (d, J_{C-P} = 72.5 Hz, C1), 134.4 (s, C2), 131.1 (d, J_{C-P} = 10.8 Hz, C4), 27.4 (d, J_{C-P} = 7.6 Hz, ring CH$_3$), 25.6 (s, ring CH$_3$), 21.3 (d, J_{C-P} = 32.9 Hz, PMe$_3$ CH$_3$'s), 18.5 (virtual t, J_{C-P} = 41.7 Hz, *trans*-diaxial PMe$_3$ CH$_3$'s), 17.8 (d, J_{C-P} = 32.0 Hz, PMe$_3$ CH$_3$'s). ^{31}P{^{1}H} NMR (methylene chloride-d_2, 25 °C): δ −49.0 (dd, J_{P-P} = 27.7 Hz, 21.7 Hz, 2, *trans*-diaxial PMe$_3$'s), −63.5 (td, J_{P-P} = 21.7, 8.5 Hz, 1, PMe$_3$), −65.2 (td, J_{P-P} = 27.7, 8.5 Hz, 1, PMe$_3$).

X-ray Diffraction Studies of (1,2,5-η-2,4-Dimethylpenta-1,3-dien-5-oyl)Ir(PMe$_3$)$_3$ (3), $\overline{\text{CH=C(Me)−CH=C(Me)−C(O)−Ir(PMe_3)_3}}$-(O$_3SCF_3$) (4), [$\overline{\text{CH=C(Me)−CH=C(Me)−C(O)−Ir(PMe_3)_4}}$]$^+O_3SCF_3^-$

(6), [$\overline{\text{CH}_2\text{−C(Me)=CH−CH(Me)−Ir(PMe_3)_3(CO)}}$]$^+O_3SCF_3^-$·^{1}/$_2Me_2$C-(O) (7), [$\overline{\text{CH=C(Me)−CH=C(Me)−C(OH)=Ir(PMe_3)_3(O_3SCF_3)}}$]$^+O_3$-SCF$_3^-$·CCl$_2H_2$ (8), and [$\overline{\text{CH=C(Me)−CH=C(Me)−C(OH)=Ir(P-Me_3)_3(O_2CCF_3)}}$]$^+O_3SCF_3^-$·CCl$_2H_2$ (9). Single crystals of compounds **3**, **4**, **6**, **7**, **8**, and **9** were sealed in glass capillaries under an inert atmosphere. Data were collected on a Siemens R3m/V diffractometer at room temperature, using graphite-monochromated Mo Kα radiation. Three standard reflections were measured every one hundred events as check reflections for crystal deterioration and/or misalignment.

All data reduction and refinement were done using the Siemens SHELXTL PLUS package on a VAX 3100 workstation.[15] Crystal data and details of data collection and structure analysis are listed in Table 1.

The iridium atom positions in compounds **3**, **4**, **6**, and **8** were determined by direct methods; its positions in compounds **7** and **9** were

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

calculated from Patterson maps. In all cases, remaining non-hydrogen atoms were found by successive full-matrix least-squares refinement and difference Fourier map calculations. In general, non-hydrogen atoms were refined anisotropically except in cases of disorder, while hydrogen atoms were placed in idealized positions and assumed the riding model.

Supporting Information Available: Structure determination summaries, listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **3**, **4**, **6**, **7**, **8**, and **9**, and ORTEP drawings of the second independent molecules in compounds **4** and **6** (56 pages). See any current masthead page for ordering and Internet access instructions.

JA971721+