Synthesis, Spectroscopy, and Reactivity of a Metallapyrylium[1]

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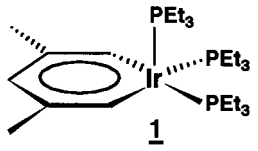
The first example of a stable metallapyrylium complex, [CH=C(Me)CH=C(Me)O=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (**2**), has been prepared, and its reaction chemistry has been explored. Compound **2** is obtained in ∼50% yield upon treatment of *mer*-CH=C(Me)CH=C(Me)OIr(H)(PEt$_3$)$_3$ (**3**) with silver tetrafluoroborate in tetrahydrofuran. The other major product of this reaction, [*mer*-CH=C(Me)CH$_2$C(Me)=OIr(H)(PEt$_3$)$_3$]$^+$BF$_4^-$ (**4**), is readily converted back to **3** (by treating with base) and can be reused. Compound **2** exhibits downfield ^{1}H NMR chemical shifts for its ring protons, consistent with its characterization as an aromatic metallacycle. The iridium center in **2** is reactive toward a variety of 2e$^-$ donor reagents, including hydride reagents, methyllithium, chloride reagents, and trimethylphosphine. The products of these reactions are octahedral Ir(III) compounds containing the iridaoxacyclohexa-1,3-diene ring skeleton. The chloride reaction product, *mer*-CH=C(Me)CH=C(Me)OIr(Cl)(PEt$_3$)$_3$ (**6**), has been characterized by X-ray diffraction. Compound **2** also undergoes [4 + 2] cycloaddition reactions with various unsaturated substrates, including acetone, alkynes, alkenes, and sulfur dioxide. In each of these reactions, the substrate adds across iridium and the central carbon atom of the ring (C3) to produce octahedral Ir(III) compounds containing the iridaoxacyclohexa-1,4-diene ring skeleton. The X-ray crystal structure of the sulfur dioxide cycloadduct, {*fac*-[CH=C(Me)CHC(Me)=OIrS(O)$_2$](PEt$_3$)$_3$}$^+$BF$_4^-$ (**13**), has been obtained. Finally, treatment of **2** with nitrosobenzene generates a novel adduct containing two fused five-membered rings, {*fac*-[C(Me)CH=C(Me)OIrON(Ph)=CH](PEt$_3$)$_3$}$^+$BF$_4^-$ (**14**). This reaction probably involves initial [2 + 2] cycloaddition, followed by rearrangement. The structure of **14** has been confirmed by X-ray diffraction.

Introduction

During the past decade, we have been exploring the chemistry of "iridabenzene" (**1**),[2] a rare example of a stable metallabenzene complex.[3,4] We have found that the physical and chemical properties of this species are consistent with the presence of a genuine—albeit fragile—aromatic ring system. We now report the synthesis and spectroscopic characterization of the oxygen-containing analogue of **1**, "iridapyrylium" (**2**),[5] which, to our knowledge, is the first example of a stable metalloxabenzene.[6] In addition, we describe the reaction chemistry of **2** and compare its chemical behavior to that of iridabenzene.



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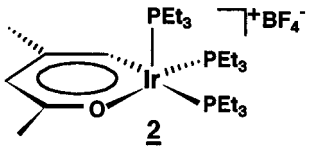

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Results and Discussion

A. Synthesis and Spectroscopy of Iridapyrylium 2. The synthesis of iridapyrylium is accomplished by the series of steps outlined in Scheme 1. Treatment of (Cl)-

(1) Metallacyclohexadiene and Metallabenzene Chemistry. 16. Part 15: Bleeke, J. R.; Hinkle, P. V. *J. Am. Chem. Soc.* **1999**, *121*, 595.

(2) (a) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118. (b) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271. (c) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606. (d) Bleeke, J. R.; Behm, R. *J. Am. Chem. Soc.* **1997**, *119*, 8503.

(3) For examples of other stable metallabenzenes, see: (a) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. (b) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 750. (c) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 2597. (d) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *Chem. Eur. J.* **2000**, *6*, 437.

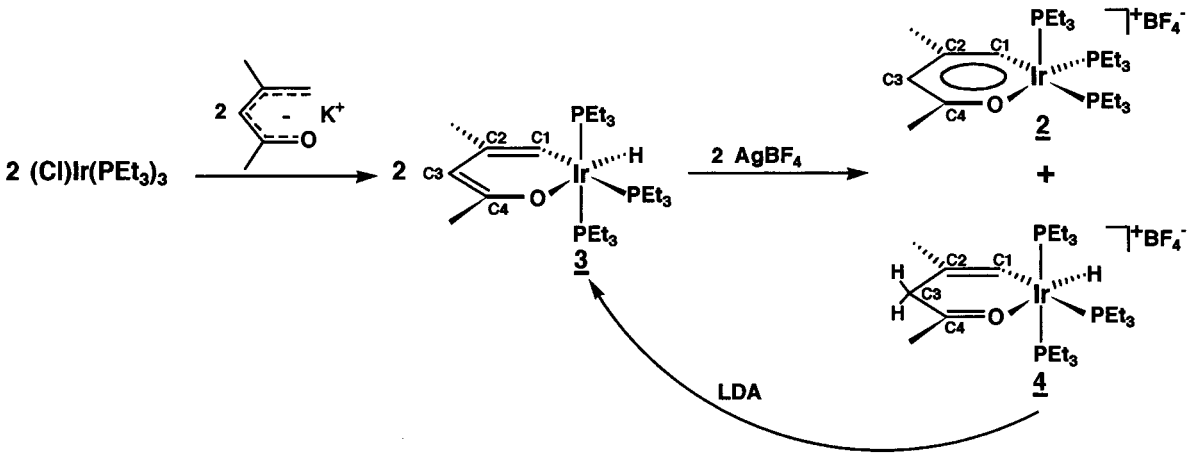
(4) Detection of a thermally unstable metallabenzene at low temperature has also been reported: Yang, J.; Jones, W. M.; Dixon, J. K.; Allison, N. *J. Am. Chem. Soc.* **1995**, *117*, 9976.

(5) A portion of this work has been communicated: Bleeke, J. R.; Blanchard, J. M. B. *J. Am. Chem. Soc.* **1997**, *119*, 5443.

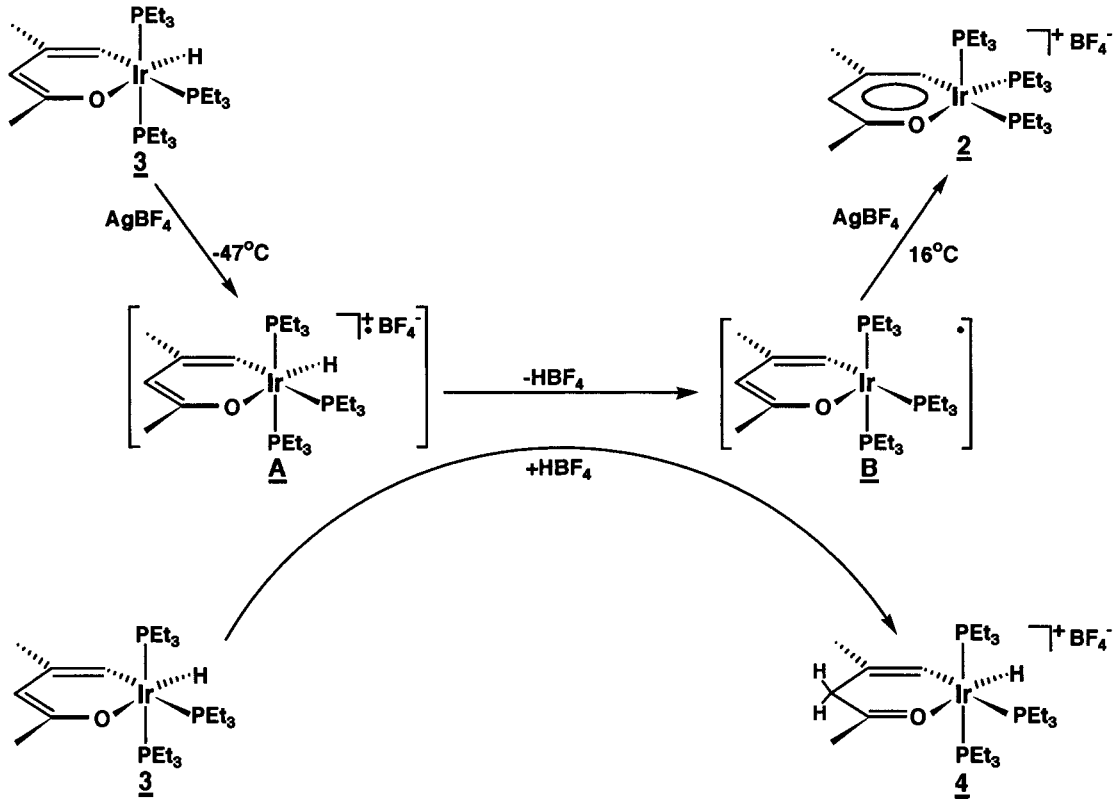
(6) Several examples of metalla*thia*benzenes have been reported: (a) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (b) Chin, R. M.; Jones, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 357. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731. (d) Bleeke, J. R.; Hinkle, P. V. *J. Am. Chem. Soc.* **1999**, *121*, 595.

10.1021/om0008068 CCC: $20.00
Publication on Web 12/15/2000

Scheme 1



Scheme 2



$Ir(PEt_3)_3$ with potassium 2,4-dimethyloxapentadienide generates the iridaoxacyclohexa-1,3-diene hydride complex (**3**; Scheme 1) via C−H bond activation.[7] When 2 equiv of this species is then reacted with 2 equiv of silver tetrafluoroborate ($AgBF_4$) in tetrahydrofuran, a clean 1:1 mixture of "iridapyrylium" (**2**; Scheme 1) and the protonated ring compound **4** (Scheme 1) is generated.[8,9] Treatment of this mixture with 1 equiv of lithium diisopropylamide in tetrahydrofuran results in selective deprotonation of **4** back to **3**, which can then be extracted with pentane, leaving pure **2** as a deep purple solid. The recovered starting material, **3**, can be treated again with $AgBF_4$ to produce additional iridapyrylium, raising the overall yield of the process.[10]

Although the detailed mechanism of the conversion of **3** to **2** and **4** is not known, the pathway outlined in Scheme 2 is consistent with our observations. Treatment of **3** with $AgBF_4$ at −47 °C probably leads to $1e^-$ oxidation, generating the $17e^-$ radical cation **A**. This species then transfers a proton to a second equivalent of **3**, generating **4** and the $17e^-$ neutral radical **B**. When it is warmed, species **B** is oxidized by the second equivalent of $AgBF_4$, producing iridapyrylium **2**. The characteristic deep purple color of **2** appears at about 16 °C, indicating that this is the temperature at which the final oxidation occurs.

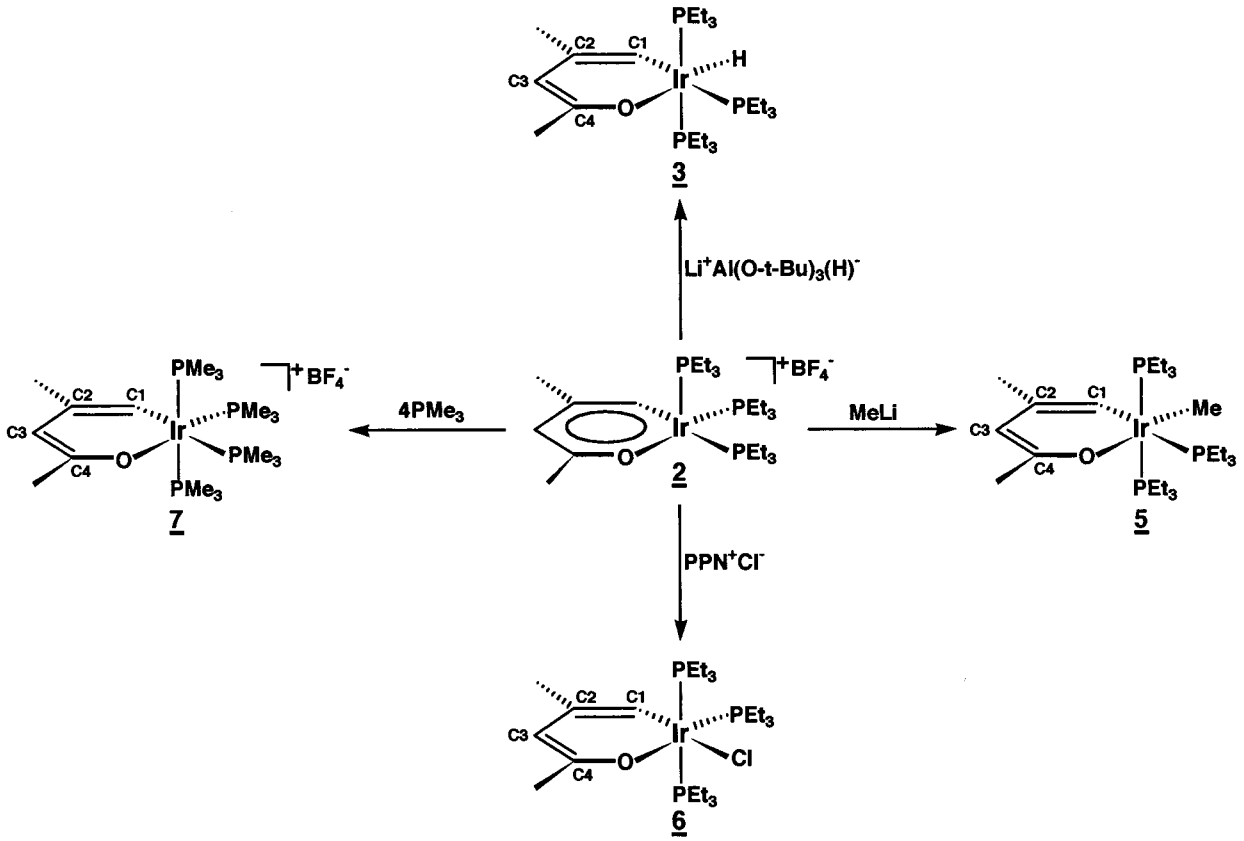
(7) The detailed synthesis and spectroscopy of **3** have been previously reported: Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517.

(8) Compound **4** can be synthesized independently by treating compound **3** with $HBF_4{\cdot}OEt_2$ (see Experimental Section).

(9) The triflate salt of **4** was first characterized by Haile: Haile, T. Ph.D. Dissertation, Washington University, St. Louis, MO, 1992.

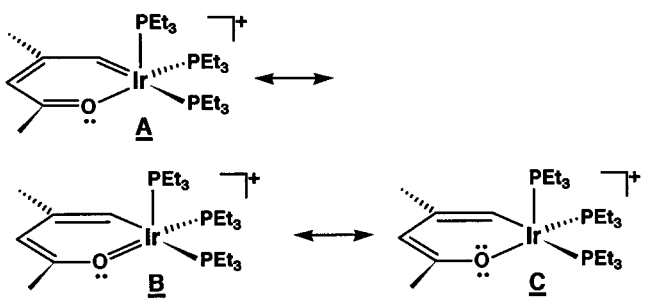
(10) Attempts to increase the ratio of **2** to **4** in the original reaction (Scheme 1) by adding external bases such as NEt_3 were unsuccessful.

Scheme 3



The $^{31}P\{^1H\}$ NMR spectrum of **2**, like that of iridabenzene **1**, consists of a sharp singlet, which does not broaden significantly, even upon cooling to −90 °C. This behavior is indicative of a low-energy fluxional process that exchanges the phosphine ligands. If compound **2** is isostructural with **1** (square pyamidal),[2a] the phosphine exchange probably occurs via a Berry-type process involving trigonal-bipyramidal intermediates. In the ^1H NMR spectrum of **2**, ring protons H1 and H3 are shifted downfield to δ 9.35 and 6.45, from their positions of δ 5.76 and 4.02, respectively, in precursor **3**.[11] This downfield shifting indicates metal orbital participation in ring π-bonding and the establishment of a ring current. The H1 signal is split into a quartet (J = 6.0 Hz) by the ^{31}P nuclei of the three exchanging phosphine ligands. In the $^{13}C\{^1H\}$ NMR spectrum, the ring carbons resonate at δ 170.7 (C4), 162.2 (C1), 147.3 (C2), and 112.2 (C3). The C1 signal is split into a phosphorus-coupled quartet (J = 22.7 Hz).

One can write three reasonable resonance structures for iridapyrylium **2** (**A**−**C**). In structures **A** and **B**, the



iridium center possesses 18 valence electrons, while in **C** it possesses 16e⁻. Structures **B** and **C** differ only in the position of one electron pair. In **B**, it resides between oxygen and iridium, forming the π bond, while in **C** it resides on the oxygen atom.[12]

B. Reactivity of Iridapyrylium 2: Addition to the Iridium Center. Because of the contribution from resonance structure **C**, the iridium atom in **2** is reactive toward a variety of 2e⁻ donor reagents, including hydride, methyllithium, chloride, and trimethylphosphine. The products of these reactions, all of which are yellow, six-coordinate iridaoxacyclohexa-1,3-diene compounds, are summarized in Scheme 3. Treatment of **2** with $Li^+Al(O\text{-}t\text{-}Bu)_3(H)^-$ regenerates the metal hydride precursor **3**. Similarly, treatment with methyllithium produces **5**, the methyl analogue of **3**.[13] The $^{31}P\{^1H\}$ NMR spectrum of **5**, like that of **3**, consists of a doublet (two axial phosphines) and a triplet (one equatorial phosphine), indicating a *mer* arrangement of the phosphine ligands. In the $^{13}C\{^1H\}$ NMR spectrum, the signal for ring carbon C1 is a doublet (J_{C-P} = 86.0 Hz) of triplets (J_{C-P} = 16.0 Hz). The strong doublet coupling indicates that C1 resides *trans* to a phosphine ligand. Hence, the methyl ligand must lie *trans* to oxygen. One interesting feature of the ^{13}C NMR spectrum is the extreme upfield shift of the iridium-bound methyl carbon, δ −39.6. The corresponding signal for the methyl hydrogens in the ^1H NMR spectrum is at δ 0.42.

(11) For comparison, the ^1H NMR data for both **2** and **3** were obtained in methylene chloride-d_2. In benzene-d_6, the chemical shift values for H1 and H3 in compound **3** were δ 6.04 and 4.70, respectively.[7]

(12) Note that in structures **A** and **B** the formal positive charge resides on oxygen, while in **C** it resides on the iridium center.

(13) This reaction is always accompanied by the production of a small quantity of hydride **3**. The origin of this byproduct is not known.

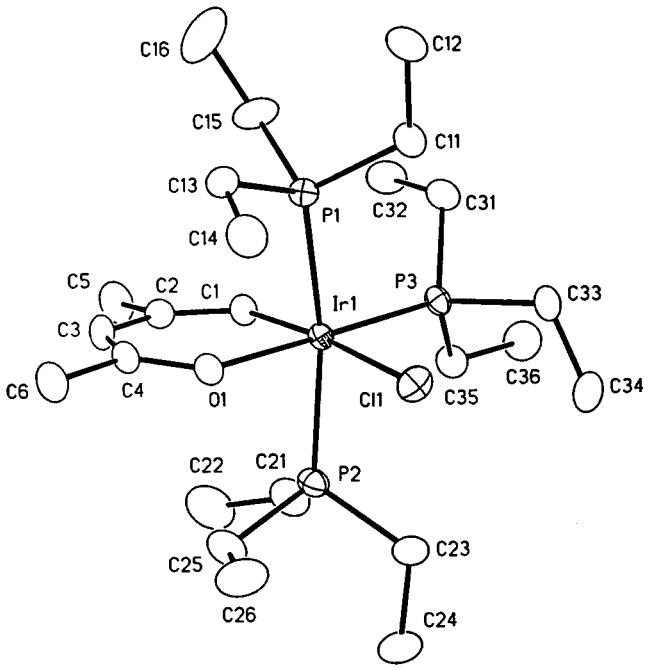


Figure 1. ORTEP drawing of *mer*-CH=C(Me)CH=C(Me)-OIr(Cl)(PEt_3)$_3$ (**6**).

Table 1. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for *mer*-CH=C(Me)CH=C(Me)OIr(Cl)(PEt_3)$_3$ (6)

Bond Distances			
Ir−Cl	2.508(2)	C1−C2	1.344(10)
Ir−P1	2.366(2)	C2−C3	1.467(10)
Ir−P2	2.379(2)	C2−C5	1.540(11)
Ir−P3	2.292(2)	C3−C4	1.334(10)
Ir−O1	2.089(4)	C4−C6	1.532(9)
Ir−C1	2.029(6)	O1−C4	1.314(8)
Bond Angles			
Cl−Ir−P1	88.60(6)	P2−Ir−O1	84.36(13)
Cl−Ir−P2	89.93(7)	P2−Ir−C1	86.9(2)
Cl−Ir−P3	93.87(7)	P3−Ir−O1	177.70(13)
Cl−Ir−O1	84.33(14)	P3−Ir−C1	91.4(2)
Cl−Ir−C1	174.2(2)	O1−Ir−C1	90.5(2)
P1−Ir−P2	168.11(6)	Ir−C1−C2	125.3(5)
P1−Ir−P3	94.78(6)	C1−C2−C3	125.1(7)
P1−Ir−O1	83.76(13)	C2−C3−C4	125.9(7)
P1−Ir−C1	88.60(6)	C3−C4−O1	127.3(6)
P2−Ir−P3	97.09(7)	Ir−O1−C4	125.2(4)

When **2** is treated with bis(triphenylphosphoranylidene)ammonium chloride (PPN^+Cl^-), chloride addition product **6** (Scheme 3) is generated. This compound bears a close resemblance to compounds **3** and **5**, except that the chloride ligand in **6** resides *trans* to ring carbon C1, while the equatorial phosphine lies *trans* to oxygen. This ligand arrangement is evident from the $^{13}C\{^1H\}$ NMR spectrum of **6**, where ring carbon C1 exhibits only weak coupling (J_{C-P} = 7.7 Hz) to the equatorial phosphine ligand. Ring proton H1, on the other hand, is rather strongly coupled to this *cis*-equatorial phosphine, giving rise to a doublet in the ^1H NMR spectrum (J_{H-P} = 10.5 Hz).

The structure of **6** has been confirmed by X-ray crystallography (see ORTEP drawing in Figure 1). Selected bond distances and angles are reported in Table 1. As expected, the molecule is octahedral with the phosphine ligands in a *mer* arrangement and the chloride ligand *trans* to ring carbon C1. The six-membered ring is essentially planar; the sum of the six internal angles is 719.3°, very close to the theoretical value of 720° for a planar hexagon. However, to compensate for the small O1−Ir−C1 angle (90.5°), the other five internal angles expand to values greater than 120° (range 125.1−127.3°; average 125.8°). The C−C and C−O distances within the ring show the bond length alternation expected for the iridaoxacyclohexa-1,3-diene skeleton. The reason that compound **6** adopts a ligand arrangement different from that of compounds **3** and **5** is not entirely clear but probably results from the fact that chloride exerts a much weaker *trans* influence than hydride or methyl.[14] Hence, it prefers to reside *trans* to ring carbon C1, a strong *trans*-influence ligand. The weak *trans* influence of chloride is reflected in the rather short bond distance between iridium and ring carbon C1, 2.029(6) Å.[15]

Treatment of **2** with excess trimethylphosphine leads to PMe_3 addition at the iridium center *and* complete replacement of the three bulky PEt_3 ligands with smaller PMe_3's, generating the tetrakis(trimethylphosphine) product **7** (Scheme 3). This reaction contrasts sharply with the room-temperature reaction of iridabenzene **1** with excess PMe_3, which results in replacement of one PEt_3 ligand with PMe_3 and retention of the aromatic ring system.[2c] The reason for this difference in behavior is that **1** reacts with PMe_3 by a dissociative mechanism, while the reaction of **2** with PMe_3 involves a series of *associative* steps, as shown in Scheme 4. The associative steps are made possible by the fact that the Ir−O π-electrons can be localized on the oxygen atom (cf. resonance structure **C**), rendering the iridium atom a reactive 16e$^-$ center.

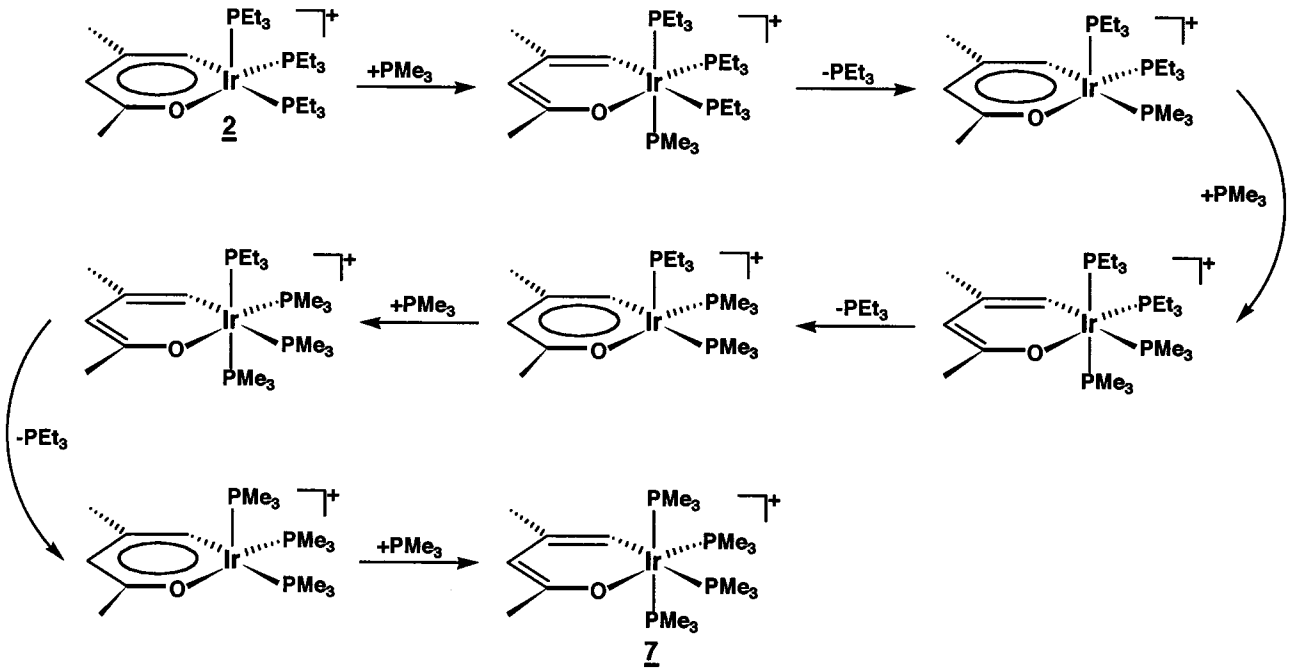
The $^{31}P\{^1H\}$ NMR spectrum of **7** consists of three signals—a doublet of doublets due to the two equivalent *trans*-diaxial phosphines and two triplets of doublets due to the inequivalent equatorial phosphines. In the $^{13}C\{^1H\}$ NMR spectrum, the signal for ring carbon C1 is a doublet of triplets of doublets pattern. The large doublet coupling (J = 74.0 Hz) is due to the *trans*-equatorial phosphine, while the smaller triplet (J = 11.3 Hz) and doublet (J = 5.0 Hz) couplings result from the axial and *cis*-equatorial phosphines, respectively. The ^1H NMR signal for ring proton H1 is likewise a complex multiplet, where the largest coupling (~10 Hz) is due to the *cis*-equatorial PMe_3 ligand.

All of the derivatives shown in Scheme 3 contain the iridaoxacyclohexa-1,3-diene ring skeleton and hence exhibit similar NMR chemical shifts for ring carbons and hydrogens. In each case, carbon C4 resonates farthest downfield (range δ 154.2−156.8; average δ 155.7) because it resides α to the oxygen atom, experiences a strong inductive effect, and is the most positive ring carbon. On the other hand, carbons C3 (range δ 97.4−100.4; average δ 98.9) and C1 (range δ 94.3−119.7; average δ 107.6) resonate farthest upfield due to resonance effects involving the oxygen lone pairs. As shown, minor resonance structures can be drawn (**B** and **C**) in

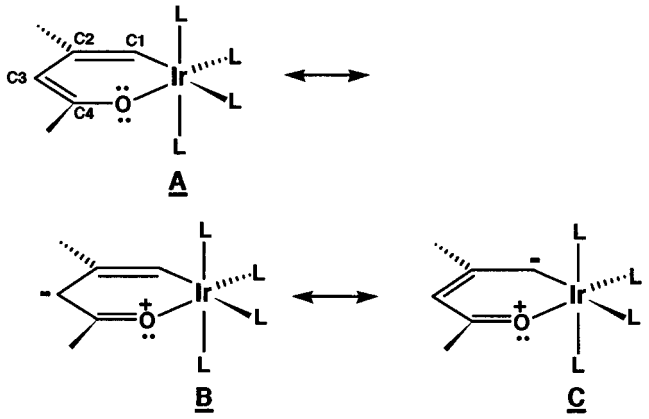
(14) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; pp 543−547.

(15) In *mer*-CH=CHCH=CHOIr(H)(PEt_3)$_3$, where C1 lies *trans* to a PEt_3 ligand, the Ir−C1 bond distance is 2.072(12) Å. See: Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19.

Scheme 4



which negative charge is localized on these ring carbon atoms.[16] Carbon C2 resonates in a chemical shift region



between C4 and C1/C3 (range δ 124.6−128.0; average δ 126.6). In the ^{1}H NMR, ring hydrogen H1 always resonates farther downfield than H3 due to the magnetic anisotropic influences of the large metal atom. The average H1 shift for compounds **3** and **5**−**7** is δ 6.04 (range δ 5.72−6.32), while the average H3 shift is δ 4.64 (range δ 4.38−4.76).

C. Reactivity of Iridapyrylium 2: [4 + 2] Cycloadditions.[17] When iridapyrylium **2** is dissolved in acetone-d_6 at room temperature, its ^{31}P NMR signal broadens dramatically and three new broad humps appear upfield in the ^{31}P NMR spectrum. As the sample is cooled to −40 °C, the iridapyrylium signal disappears and the upfield humps sharpen into three clean doublet-of-doublet signals, indicating the formation of a low-temperature adduct with a static, *facial* arrangement of PEt_3 ligands. This cooling process is accompanied by a color change from deep purple (**2**) to light yellow (adduct) and is reversible. The NMR spectra of the adduct, recorded at −40 °C in acetone-d_6, clearly demonstrate that it is the [4 + 2] cycloaddition product **8**, as shown in Scheme 5. In particular, the signals for H3 and C3 shift upfield to δ 3.95 and 74.9, respectively, indicating that these atoms are no longer aromatic or olefinic. Furthermore, the C4 signal shifts far downfield to δ 224.5, as expected for a carbonyl carbon, while the central carbon of the acetone moiety, C7, resonates at δ 64.9, consistent with alkoxide character. The connectivity of the molecule is further demonstrated by the observation of coupling between C3 and C7 (J = 30.3 Hz) when ^{13}C-labeled acetone is used in the experiment.[18]

While the acetone adduct (**8**) is stable only at low temperature, other unsaturated substrates, including alkynes and alkenes, react irreversibly with **2** to form [4 + 2] cycloadducts that are stable at room temperature. For example, treatment of **2** with methyl propiolate, phenylacetylene, or (trimethylsilyl)acetylene generates cycloadducts **9**−**11**, respectively (see Scheme 5), which possess iridaoxabarrelene frameworks.[18] Each of these reactions is accompanied by a dramatic color change from purple to yellow. The methyl propiolate reaction occurs upon warming to room temperature, while the (trimethylsilyl)acetylene reaction requires 1 h of stirring at room temperature, suggesting that electron-poor alkynes are the preferred substrates.

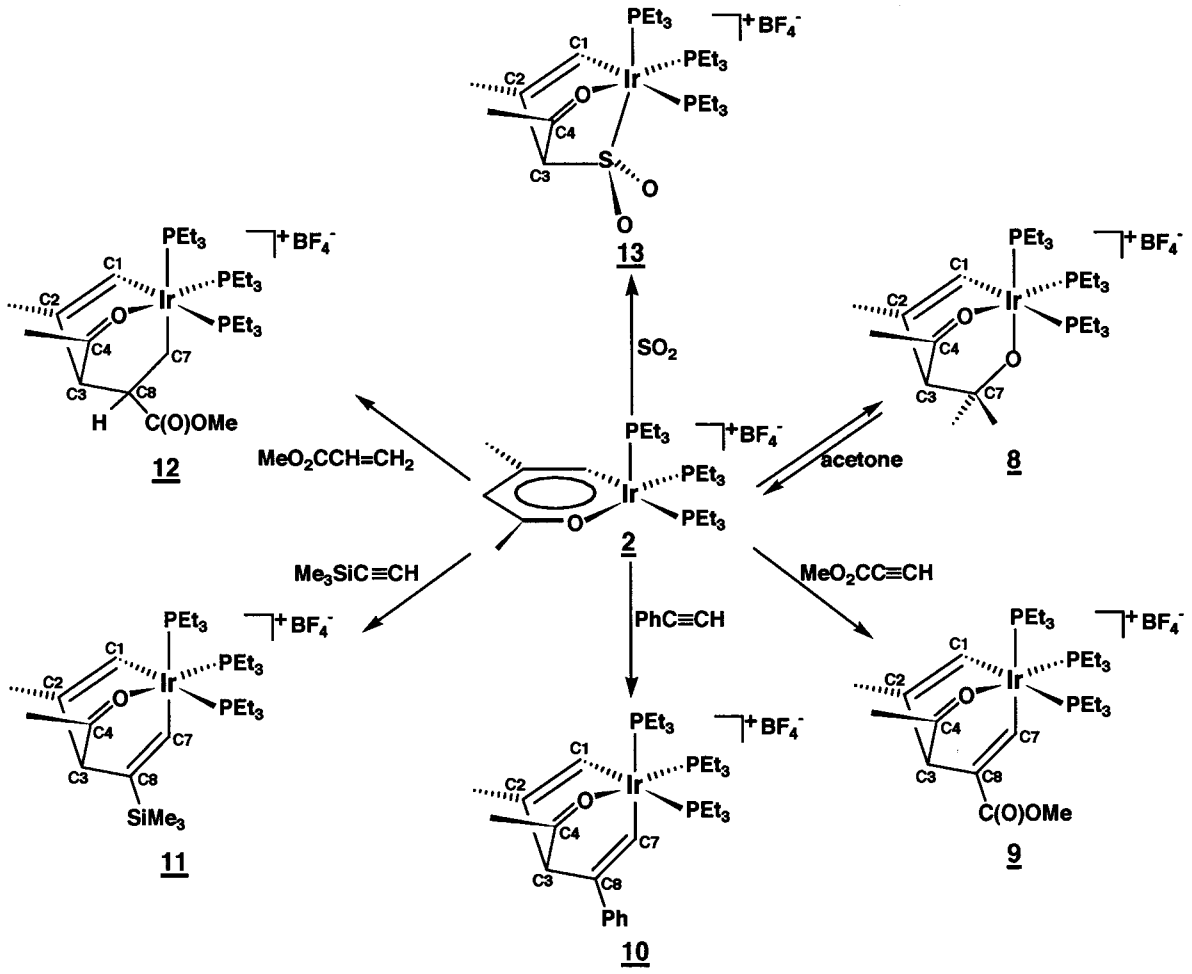
The ^{31}P{^{1}H} NMR spectra of **9**−**11** each consist of three separate doublet-of-doublet patterns, consistent with a *fac* phosphine geometry. As in the case of the acetone adduct **8**, the signal for C3 is shifted upfield in the ^{13}C NMR (range δ 67.5−72.0; average δ 70.4), indicating an sp^3 center. Carbon C4 is likewise shifted

(16) For a discussion of inductive effects vs resonance effects, see: Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon: Boston, 1987; pp 202−203.

(17) For a good summary of cycloaddition reactions involving organic components, see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 903−931.

(18) While [4 + 2] cycloadditions are common reactions of iridabenzene **1**, it shows no reactivity toward acetone or alkynes.

Scheme 5



far downfield (range δ 217.6−219.7; average δ 218.5), as expected for a carbonyl carbon. In each $^{13}C\{^1H\}$ NMR spectrum, there are two carbons that are strongly coupled to phosphorus (range 73.1−78.9 Hz; average 75.9 Hz), indicating that these are the α-ring carbons, C1 and C7. The signal for C7 (a former alkyne carbon) is always farther downfield (range δ 144.6−169.4; average δ 159.0) than that for C1 (range δ 137.4−137.9; average δ 137.6). β-Ring carbons C2 and C8 appear within a rather narrow chemical shift range, δ 124.3−131.0, and show little or no phosphorus coupling.

In the ^1H NMR spectra of **9**−**11**, there are always two signals far downfield, one for H1 (range δ 7.10−7.19; average δ 7.14) and the other for H7, the former alkyne hydrogen (range δ 7.89−9.66; average δ 8.68). The extreme downfield shift for H7 strongly supports the regiochemistry of cycloaddition shown in Scheme 5 (i.e., the CH end of the alkyne is bonded to the iridium center). This regiochemistry has been confirmed by two-dimensional HMQC experiments, which show that the downfield proton H7 is directly bonded to the phosphorus-coupled carbon C7. The ring proton H3, which is doubly allylic and is α to a C=O group, resonates in the range δ 5.12−5.50 (average δ 5.25), farther downfield than H3 in the acetone adduct **8** (δ 3.95).

Only terminal alkynes react cleanly with **2**; disubstituted alkynes such as 2-butyne and diphenylacetylene are unreactive or lead to slow decomposition of **2** upon stirring at room temperature. Similarly, many alkene substrates are unreactive toward **2** or lead to slow decomposition. These include terminal olefins such as styrene and *neo*-hexene as well as constrained olefins such as cyclopentene and maleic anhydride. The one exception is methyl acrylate, which reacts slowly (5 h) with **2** at room temperature to produce the [4 + 2] cycloadduct **12** (Scheme 5). As a cycloaddition substrate, methyl acrylate apparently benefits from the fact that it is both terminal and electron-poor.

The $^{31}P\{^1H\}$ NMR spectrum of **12** is similar to those of **9**−**11**, except that there are *two* sets of peaks in an approximate 55:45 ratio, indicating the presence of two isomers with *fac* phosphine geometries. Similarly, the ^{13}C NMR spectrum of **12** shows the presence of two isomers; each carbon peak has a partner with a similar chemical shift. The chemical shifts for ring carbons C1, C2, C3, and C4 are close to those observed in **9**−**11**, while C7 and C8 are shifted far upfield, consistent with their sp^3 character in **12**. In both isomers, the terminal (CH_2) carbon of the methyl acrylate moiety shows strong phosphorus coupling, indicating that it is bonded directly to iridium. This, in turn, implies that the isomers are not regioisomers but rather stereoisomers with opposite stereochemistries at C8. In the ^1H NMR spectrum of **12**, ring proton H1 resonates at δ 7.67 and 7.48 in the two isomers, while H3 resonates at δ 4.29 and 4.24. As expected, the protons on the ring's saturated moiety (H7's and H8) are shifted upfield and appear in the region δ 1.3−2.5.

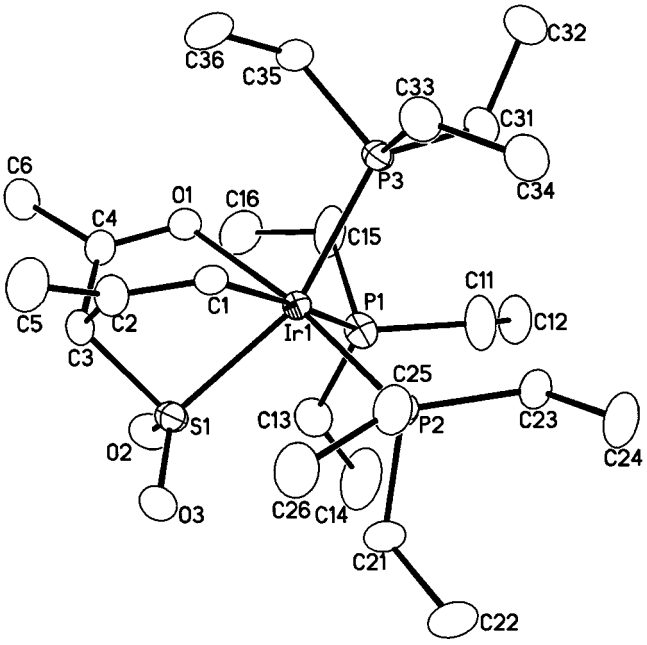


Figure 2. ORTEP drawing of {*fac*-[CH=C(Me)CHC(Me)=OIrS(O)$_2$](PEt$_3$)$_3$}$^+$BF$_4^-$ (**13**).

Although the detailed mechanisms of reactions leading to cycloadducts **8**−**12** are not known, it seems likely that they proceed in a concerted (Diels−Alder) fashion with the key orbital interaction involving a filled π-orbital on the iridapyrylium ring and an empty π^* orbital on the unsaturated substrate. Undoubtedly, these reactions are driven by the formation of a strong C−O double bond in the ring and a stable octahedral coordination geometry around the Ir(III) center. Note, however, that in the formation of the acetone adduct, a C−O double bond is also lost, which may explain why this reaction is reversible.

Finally, treatment of **2** with sulfur dioxide results in a cheleotropic [4 + 2] cycloaddition and production of adduct **13** (Scheme 5). The ^{31}P{^{1}H} NMR spectrum of **13** consists of three doublet-of-doublet patterns, indicative of a *fac* phosphine geometry. The ^{13}C{^{1}H} NMR spectrum is similar to those of cycloadducts **8**−**12** with carbonyl carbon C4 shifting downfield to δ 221.0 and olefinic carbons C1 and C2 resonating at δ 147.4 and 133.9, respectively. The chemical shift of saturated carbon C3 is, however, unusually high (δ 105.4), perhaps reflecting the strongly electron-withdrawing nature of the SO$_2$ group. Ring protons H1 and H3 resonate at δ 7.67 and 5.55, respectively.

The structure of **13** has been confirmed by X-ray crystallography. An ORTEP drawing is presented in Figure 2, while selected bond distances and angles are listed in Table 2. The sulfur atom of the SO$_2$ unit is bonded to Ir and ring carbon C3, causing the iridaoxacyclohexa-1,4-diene ring to adopt a boat conformation. Ir and C3 lie 1.063 and 0.727 Å, respectively, from the C1/C2/C4/O1 plane, while the dihedral angles made by planes C1/Ir/O1 and C2/C3/C4 with the C1/C2/C4/O1 plane are 41.8 and 55.0°, respectively. This rather severe bending of the ends of the boat is undoubtedly due to the demands of the five-membered rings in **13**.

Table 2. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for {*fac*-[CH=C(Me)CHC(Me)=OIrS(O)$_2$](PEt$_3$)$_3$}$^+$BF$_4^-$ (13)

Bond Distances			
Ir−P1	2.4202(18)	C2−C5	1.503(11)
Ir−P2	2.3058(18)	C3−C4	1.483(10)
Ir−P3	2.3788(17)	S1−C3	1.848(7)
Ir−S1	2.3685(17)	C4−C6	1.483(10)
Ir−O1	2.184(4)	O1−C4	1.263(8)
Ir−C1	2.078(6)	S1−O2	1.462(5)
C1−C2	1.326(10)	S1−O3	1.454(5)
C2−C3	1.516(11)		
Bond Angles			
P1−Ir−P2	97.33(7)	O1−Ir−C1	83.1(2)
P1−Ir−P3	97.24(6)	Ir−C1−C2	117.2(5)
P1−Ir−S1	94.35(6)	C1−C2−C3	116.5(6)
P1−Ir−O1	88.64(14)	C2−C3−C4	107.4(6)
P1−Ir−C1	170.49(19)	C2−C3−S1	104.2(5)
P2−Ir−P3	98.28(6)	C4−C3−S1	103.3(5)
P2−Ir−S1	96.30(6)	C3−C4−O1	118.7(6)
P2−Ir−O1	170.90(13)	Ir−O1−C4	115.6(4)
P2−Ir−C1	90.33(18)	Ir−S1−O2	116.0(2)
P3−Ir−S1	160.02(6)	Ir−S1−O3	120.6(2)
P3−Ir−O1	87.73(13)	Ir−S1−C3	89.6(2)
P3−Ir−C1	87.17(18)	O2−S1−O3	114.2(3)
S1−Ir−O1	76.31(13)	C3−S1−O2	105.2(3)
S1−Ir−C1	79.14(19)	C3−S1−O3	105.9(3)

Also notable is the constrained internal angle at sulfur (C3−S1−Ir = 89.6(2)°). Bonding within the iridaoxacyclohexa-1,4-diene ring is localized, as expected.

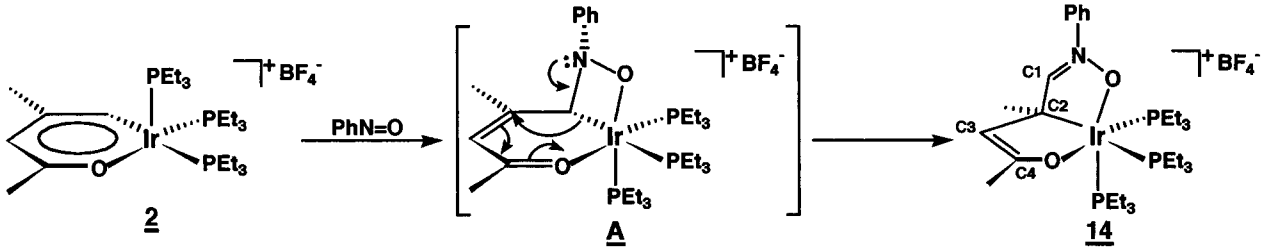
Cycloadducts **9**−**12** give lovely FAB mass spectra. In each case, the parent ion envelope [M]$^+$ is easily detected and the [M − PEt$_3$]$^+$ envelope contains the largest peaks in the spectrum. In contrast, the FAB mass spectrum of **13** does not feature prominent peaks for [M$^+$] and [M − PEt$_3$]$^+$. Instead, the largest peaks in the spectrum are those attributable to the parent iridapyrylium **2**, indicating that under the mass spectral analysis conditions, SO$_2$ is cleanly released.[19]

D. Reactivity of Iridapyrylium 2: [2 + 2] Cycloaddition and Rearrangement. When iridapyrylium **2** is treated with nitrosobenzene (PhN=O), a surprising product (**14**) is obtained. The ^{31}P{^{1}H} NMR spectrum of **14** indicates a *fac* arrangement of the three PEt$_3$ ligands, consistent with a cycloadduct. However, the ^{13}C{^{1}H} NMR spectrum of **14** shows clearly that ring carbon C1 is no longer bonded to the iridium center (no C−P coupling), while the neighboring carbon C2 is bonded to Ir (J_{C-P} = 78.7 Hz). Furthermore, the chemical shift of C2 (δ 42.7) indicates that it is no longer aromatic or olefinic. In contrast, the signals for ring carbons C1, C3, and C4 remain in the olefinic region of the spectrum (δ 156.8, 102.0, and 172.3, respectively). In the ^{1}H NMR, H1 and H3 resonate at δ 7.25 and 3.56, respectively.

The novel structure of **14** has been established by X-ray crystallography (see Figure 3 for an ORTEP drawing and Table 3 for selected bond distances and angles). The molecule contains two metallacycles, which are fused along the Ir−C2 bond. The sum of the five internal angles in the metallacycle Ir/C2/C3/C4/O1 is 538.8°, while the corresponding sum in the metallacycle

(19) The mass spectra of **2** obtained in this way are of higher quality than those obtained directly from pure **2**, which is more air-sensitive than **13** and harder to handle.

Scheme 6



2 **A** **14**

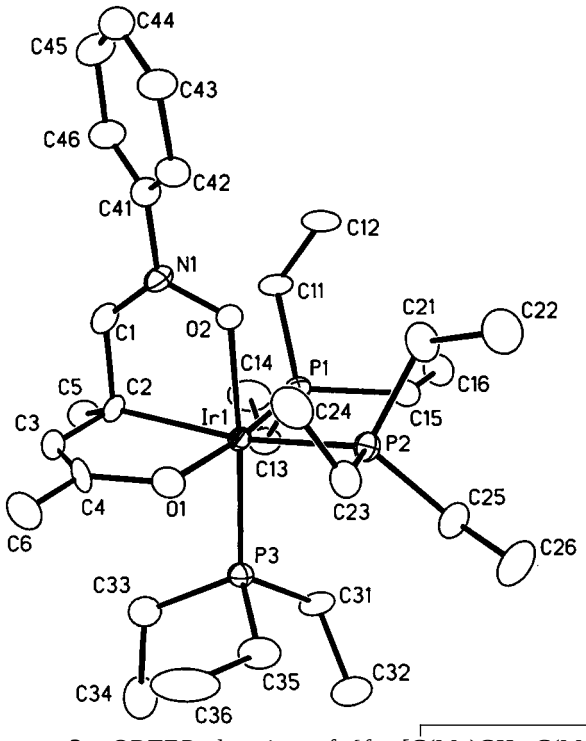


Figure 3. ORTEP drawing of {*fac*-[C(Me)CH=C(Me)-OIrON(Ph)=CH](PEt$_3$)$_3$}$^+$BF$_4^-$ (**14**).

Ir/O2/N1/C1/C2 is 539.1°. Both numbers are close to the theoretical value of 540° required for planar pentagons. The two rings are virtually perpendicular to one another, as dictated by the octahedral coordination geometry around the iridium atom. The dihedral angle made by the two ring planes is 89.1°. The phenyl ring on N1 is tilted at a 39.6° angle to the Ir/O2/N1/C1/C2 plane. Bond distances within the two metallacycles of **14** are consistent with the localized structure shown in Scheme 6.

Although the mechanism of this reaction is not known, the connectivity of the final product (i.e., nitrogen bonded to C1) suggests that the initial interaction may be a [2 + 2] cycloaddition involving the NO double bond of nitrosobenzene and the metal−carbene bond of **2**. Rearrangement of this strained cycloadduct, **A** (Scheme 6), could lead to the observed product **14**. It is interesting to note that iridabenzene **1** also reacts with nitrosobenzene, but the product in this case is a [4 + 2] cycloadduct which undergoes no further rearrangement.

Summary

The first example of a stable metallapyrylium, [CH=C(Me)CH=C(Me)O=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (**2**), has been synthesized. Compound **2**, like its metallabenzene analogue CH=C(Me)CH=C(Me)CH=Ir(PEt$_3$)$_3$ (**1**), exhibits downfield ^{1}H NMR chemical shifts for its ring protons, consistent with the presence of an aromatic ring current. Unlike **1**, compound **2** reacts with 2e$^-$ donors at iridium in an *associative* manner, generating six-coordinate Ir(III) products with the iridaoxacyclohexa-1,3-diene ring skeleton. This reactivity results primarily from the fact that the electrons in the Ir−O π bond of **2** can be localized on oxygen, rendering the iridium atom a reactive 16e$^-$ center. The positive charge on **2** also contributes to its enhanced reactivity toward anionic reagents such as hydride, methyllithium, and chloride. Like **1**, compound **2** undergoes [4 + 2] cycloaddition reactions with a variety of unsaturated substrates. For example, both **1** and **2** react in a cheleotropic fashion with sulfur dioxide and both undergo cycloaddition with electron-poor olefins in Diels−Alder type processes. However, **2** also forms cycloadducts with a series of alkyne substrates that are completely unreactive toward **1**. The enhanced reactivity of **2** in this case undoubtedly results from the fact that a strong, localized carbon−oxygen double bond is formed in the product. It is also interesting to note that **2** undergoes *reversible* cycloaddition with ketones such as acetone. In this case, the formation of a carbon−oxygen double bond in the product is offset by the loss of a carbon−oxygen double bond in the ketone substrate. One final contrast involves the reactivity of **1** with **2** with nitrosobenzene. **1** reacts

Table 3. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for {*fac*-[C(Me)CH=C(Me)OIrON(Ph)=CH](PEt$_3$)$_3$}$^+$BF$_4^-$ (14)

Bond Distances			
Ir−P1	2.315(3)	N1−C41	1.449(21)
Ir−P2	2.405(4)	C1−C2	1.517(22)
Ir−P3	2.300(4)	C2−C5	1.493(21)
Ir−O1	2.089(9)	C2−C3	1.496(25)
Ir−O2	2.112(9)	C3−C4	1.347(23)
Ir−C2	2.178(13)	C4−C6	1.524(24)
O2−N1	1.323(14)	O1−C4	1.337(20)
N1−C1	1.320(20)		
Bond Angles			
P1−Ir−P2	98.7(1)	O1−Ir−O2	85.7(4)
P1−Ir−P3	97.6(1)	O1−Ir−C2	80.9(5)
P1−Ir−O1	173.6(3)	O2−Ir−C2	81.5(4)
P1−Ir−O2	92.3(3)	Ir−O2−N1	112.6(8)
P1−Ir−C2	92.8(5)	O2−N1−C1	120.1(12)
P2−Ir−P3	94.9(1)	N1−C1−C2	122.2(12)
P2−Ir−O1	87.1(3)	Ir−C2−C1	102.4(9)
P2−Ir−C2	82.6(3)	C1−C2−C3	98.5(12)
P2−Ir−C2	160.6(4)	Ir−C2−C3	105.3(9)
P3−Ir−O1	84.5(3)	C2−C3−C4	118.9(4)
P3−Ir−O2	170.0(3)	C3−C4−O1	120.9(15)
P3−Ir−C2	98.9(4)	Ir−O1−C4	113.1(9)

with this substrate in a standard [4 + 2] fashion, while **2** appears to initially form a [2 + 2] cycloadduct, which then rearranges to a novel product containing two fused five-membered rings. The reasons for this divergent behavior are not understood.

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 and ^{13}C-labeled NMR solvents were obtained from Cambridge Isotope Laboratories or from Aldrich in sealed vials and used as received. The following reagents were used as obtained from the supplier indicated: silver tetrafluoroborate (Aldrich), lithium diisopropylamide (Aldrich), tetrafluoroboric acid (Aldrich), lithium tri-*tert*-butoxyaluminohydride (Aldrich), methyllithium (Aldrich), bis(triphenylphosphoranylidene)ammonium chloride (PPN^+Cl^-; Aldrich), trimethylphosphine (Strem), methyl propiolate (Aldrich), phenylacetylene (Aldrich), (trimethylsilyl)acetylene (Aldrich), sulfur dioxide (Aldrich), nitrosobenzene (Aldrich). Methyl acrylate (Aldrich) was dried over calcium hydride and distilled before use. A detailed synthesis and full NMR characterization of *mer*-CH=C(Me)CH=C(Me)OIr(H)(PEt_3)$_3$ (**3**) is given in ref 7. However, the J_{H-P} values for the metal hydride signal are incorrectly reported as 28.1 (t) and 17.2 Hz (d). The correct couplings are 15.6 (t) and 9.3 Hz (d).

NMR experiments were performed on a Varian Unity Plus-300 spectrometer (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz; ^{29}Si, 60 MHz), a Varian Unity Plus-500 spectrometer (^1H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz), or a Varian Unity-600 spectrometer (^1H, 600 MHz; ^{13}C, 150 MHz; ^{31}P, 242 MHz). ^1H, ^{13}C, and ^{29}Si spectra were referenced to tetramethylsilane, while ^{31}P spectra were referenced to external H_3PO_4. Some ^1H connectivities were determined from COSY ($^1H-^1H$ correlation spectroscopy) data. HMQC (^1H-detected multiple quantum coherence) and HMBC (heteronuclear multiple bond correlation) experiments aided in assigning some of the ^1H and ^{13}C peaks.

Low-resolution and high-resolution fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS50 three-sector tandem mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of [CH=C(Me)CH=C(Me)O=Ir(PEt_3)$_3$]$^+BF_4^-$ (2). Compound **3**, *mer*-CH=C(Me)CH=C(Me)OIr(H)(PEt_3)$_3$ (600 mg, 0.93 mmol), was dissolved in 75 mL of tetrahydrofuran (THF) to form a yellow solution and cooled to −47 °C. Silver tetrafluoroborate (180 mg, 0.93 mmol) was dissolved in 25 mL of THF and added to the stirred solution of **3** over 2 h. As the addition proceeded, the solution darkened to black-orange. When the addition was complete, the solution was warmed to room temperature, during which time it became opaque purple. After addition of 70 mL of pentane, the solution was filtered through a glass frit. The solvent was removed in vacuo to reveal a bright purple film containing a 1:1 product mixture of [CH=C(Me)CH=C(Me)O=Ir(PEt_3)$_3$]$^+BF_4^-$ (**2**) and [*mer*-CH=C(Me)CH_2C(Me)=OIr(H)(PEt_3)$_3$]$^+BF_4^-$ (**4**). Yield of mixture: 640 mg (94%).

The bright purple film was redissolved in 40 mL of THF and cooled to −30 °C. Lithium diisopropylamide (65 mg, 0.60 mmol) in 10 mL of THF was added dropwise to the stirred solution, and the solvent was then removed under vacuum. Addition and vacuum removal of a small amount of methylene chloride was repeated twice to facilitate residual THF removal.

The resultant film was dissolved in 4 mL of methylene chloride to which ~220 mL of pentane was added until a purple precipitate of compound **2** formed. The solution was passed through a glass frit to give a yellow filtrate of **3**, which was recovered and reused. Methylene chloride was added to redissolve the purple precipitate of **2**, and the solution was filtered. The methylene chloride was then removed under vacuum. Yield of **2**: 280 mg (42%).

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{24}H_{53}{}^{191}IrOP_3^+$), 641.2918; found, 641.2926.

^1H NMR (methylene chloride-d_2, 23 °C): δ 9.35 (qd, J_{H-P} = 6.0 Hz, J_{H-H3} = 1.6 Hz, 1, H1), 6.45 (d, J_{H-H1} = 1.6 Hz, 1, H3), 2.38 (s, 3, ring CH_3) 2.33 (s, 3, ring CH_3), 1.95 (dq, J_{H-P} = 7.5 Hz, J_{H-H} = 7.5 Hz, 18, PEt_3 CH_2's), 1.00 (dt, J_{H-P} = 15.5 Hz, J_{H-H} = 7.5 Hz, 27, PEt_3 CH_3's).

$^{13}C\{^1H\}$ NMR (methylene chloride-d_2, 23 °C): δ 170.7 (s, C4), 162.2 (q, J_{C-P} = 22.7 Hz, C1), 147.3 (s, C2), 112.2 (s, C3), 28.5 (d, J_{C-P} = 2.8 Hz, ring CH_3), 26.3 (br s, ring CH_3), 19.8 (d, J_{C-P} = 32.8 Hz, PEt_3 CH_2's), 9.0 (br s, PEt_3 CH_3's).

$^{31}P\{^1H\}$ NMR (methylene chloride-d_2, 23 °C): δ 1.9 (br s, 3, PEt_3's).

Independent Synthesis of [*mer*-CH=C(Me)CH_2C(Me)=OIr(H)(PEt_3)$_3$]$^+BF_4^-$ (4). Compound **3**, *mer*-CH=C(Me)CH=C(Me)OIr(H)(PEt_3)$_3$ (50 mg, 0.077 mmol), was dissolved in 10 mL of diethyl ether to form a yellow solution and cooled to −30 °C. To this solution was added HBF_4·OEt_2 (12 mg, 0.077 mmol) in 5 mL of cold (−30 °C) diethyl ether. As the addition proceeded, a white microfine precipitate of **4** formed and remained suspended in the ether. Upon standing at −30 °C, the precipitate dropped to the bottom of the flask, leaving a clear solution, which was decanted. The residual ether was removed in vacuo, and the product was washed with pentane and dried under vacuum. Yield of **4**: 54 mg (96%).

Anal. Calcd for $C_{24}H_{55}BF_4IrOP_3$: C, 39.39; H, 7.59. Found: C, 39.19; H, 7.49.

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{24}H_{55}{}^{193}IrOP_3^+$), 645.3096; found, 645.3097.

^1H NMR (methylene chloride-d_2, 22 °C): δ 6.67 (d, J_{H-P} = 3.0 Hz, 1, H1), 3.86 (t, J_{H-P} = 6.0 Hz, 2, H3's), 2.22 (s, 3, ring CH_3), 1.86 (dq, J_{H-P} = 7.5 Hz, J_{H-H} = 7.5 Hz, 6, PEt_3 CH_2's), 1.79−1.72 (m, 6, PEt_3 CH_2's), 1.71 (s, 3, ring CH_3), 1.66−1.58 (m, 6, PEt_3 CH_2's), 1.07 (dt, J_{H-P} = 14.5 Hz, J_{H-H} = 7.5 Hz, 9, PEt_3 CH_3's), 0.95 (m, 18, PEt_3 CH_3's), −27.51 (td, J_{H-P} = 16.5 Hz, 12.0 Hz, 1, Ir−H).

$^{13}C\{^1H\}$ NMR (methylene chloride-d_2, 22 °C): δ 215.7 (s, C4), 125.7 (dt, J_{C-P} = 75.0 Hz, 14.0 Hz, C1), 120.8 (t, J_{C-P} = 4.5 Hz, C2), 50.3 (s, C3), 31.0 (s, ring CH_3), 28.7 (d, J_{C-P} = 9.8 Hz, ring CH_3), 20.1 (d, J_{C-P} = 25.6 Hz, PEt_3 CH_2's), 16.8 (virtual t, J_{C-P} = 34.3 Hz, PEt_3 CH_2's), 8.4 (d, J_{C-P} = 2.2 Hz, PEt_3 CH_3's), 7.9 (s, PEt_3 CH_3's).

$^{31}P\{^1H\}$ NMR (methylene chloride-d_2, 22 °C): δ −6.0 (d, J_{P-P} = 17.0 Hz, 2, PEt_3's), −17.8 (t, J_{P-P} = 17.0 Hz, 1, PEt_3).

Synthesis of *mer*-CH=C(Me)CH=C(Me)OIr(H)(PEt_3)$_3$ (3) from 2. Compound **2**, [CH=C(Me)CH=C(Me)O=Ir(PEt_3)$_3$]$^+BF_4^-$ (40 mg, 0.055 mmol), was dissolved in 15 mL of tetrahydrofuran and cooled to −30 °C. Similarly, lithium tri-*tert*-butoxyaluminohydride (27 mg, 0.11 mmol) was dissolved in 5 mL of tetrahydrofuran and cooled to −30 °C. The hydride reagent solution was then added dropwise to the stirred solution of compound **2**, causing an immediate color change from purple to yellow. After the solution was warmed to room temperature, the solvent was removed under vacuum. Multiple extractions with pentane followed by filtration gave a translucent yellow solution. The pentane was removed in vacuo to give a yellow solid. Yield of **3**: 8 mg (23%).[7]

Synthesis of *mer*-CH=C(Me)CH=C(Me)OIr(CH_3)(PEt_3)$_3$ (5). A 100 μL amount of 1.4 M methyllithium in diethyl ether (0.14 mmol) was added to a stirred solution of compound **2**, [CH=C(Me)CH=C(Me)O=Ir(PEt_3)$_3$]$^+BF_4^-$ (50 mg, 0.068 mmol),

in 25 mL of tetrahydrofuran at −72 °C. After a few seconds the solution color changed from purple to a greenish yellow. The reaction mixture was warmed to room temperature, and the solvent was removed under vacuum. The resulting solid was extracted with ether and filtered, and the solvent was again removed under vacuum to give a yellow-green film. Yield of **5**: 13 mg (29%).

High-resolution FAB-MS: calcd for $[M - PEt_3 + H]^+$ ($C_{19}H_{42}{}^{191}IrOP_2{}^+$), 539.2317; found, 539.2318.

^{1}H NMR (benzene-d_6, 25 °C): δ 6.09 (br s, 1, H1), 4.73 (s, 1, H3), 2.20 (br s, 3, ring CH_3), 1.99 (s, 3, ring CH_3), 2.0−1.8 (m, 18, PEt_3 CH_2's), 1.1−0.9 (m, 27, PEt_3 CH_3's), 0.42 (pseudo q, J_{H-P} = 6.0 Hz, 3, Ir−CH_3).

^{13}C{^{1}H} NMR (benzene-d_6, 25 °C): δ 155.8 (s, C4), 126.4 (m, C2), 119.7 (dt, J_{C-P} = 86.0 Hz, 16.0 Hz, C1), 98.3 (s, C3), 29.5 (d, J_{C-P} = 10.7 Hz, ring CH_3), 26.4 (s, ring CH_3), 18.7 (d, J_{C-P} = 19.0 Hz, PEt_3 CH_2's), 14.5 (virtual t, J_{C-P} = 29.7 Hz, PEt_3 CH_2's), 8.6 (s, PEt_3 CH_3's), 8.3 (s, PEt_3 CH_3's), −39.6 (td, J_{C-P} = 7.4 Hz, 3.2 Hz, Ir−CH_3).

^{31}P{^{1}H} NMR (benzene-d_6, 25 °C): δ −24.3 (d, J_{P-P} = 16.0 Hz, 2, PEt_3's), −37.3 (t, J_{P-P} = 16.0 Hz, 1, PEt_3).

Synthesis of *mer*-[CH=C(Me)CH=C(Me)O]Ir(Cl)(PEt_3)$_3$ (6). Compound **2**, $[CH{=}C(Me)CH{=}C(Me)O{=}Ir(PEt_3)_3]^+BF_4^-$ (120 mg, 0.17 mmol), was dissolved in 20 mL of tetrahydrofuran to form a purple solution and cooled to −30 °C. This solution was added dropwise to a −30 °C solution of bis(triphenylphosphoranylidene)ammonium chloride (PPN^+Cl^-; 120 mg, 0.21 mmol) in 20 mL of tetrahydrofuran and 5 mL of methylene chloride. The purple solution instantly turned lemon yellow on contact with the PPN^+Cl^- solution. The solvent was removed in vacuo. The resulting yellow-brown solid was extracted with pentane and passed through a glass frit to give a translucent lemon yellow solution, which produced yellow crystals after concentration and cooling at −30 °C. Yield of **6**: 32 mg (28%). Anal. Calcd for $C_{24}H_{53}ClIrOP_3$: C, 42.49; H, 7.89. Found: C, 42.64; H, 8.22.

High-resolution FAB-MS: calcd for $[M + H]^+$ ($C_{24}H_{54}{}^{35}Cl{}^{191}IrOP_3{}^+$), 677.2685; found, 677.2697.

^{1}H NMR (benzene-d_6, 22 °C): δ 6.32 (d, J_{H-P} = 10.5 Hz, 1, H1), 4.76 (br s, 1, H3), 2.12 (s, 3, ring CH_3), 2.06 (s, 3, ring CH_3), 1.86−1.78 (m, 6, PEt_3 CH_2's), 1.76 (dq, J_{H-P} = 7.5 Hz, J_{H-H} = 7.5 Hz, 6, PEt_3 CH_2's), 2.08−2.01 (m, 6, PEt_3 CH_2's), 1.14 (virtual t of t, J_{H-P} = 14.0 Hz, J_{H-H} = 7.5 Hz, 18, PEt_3 CH_3's), 0.91 (dt, J_{H-P} = 13.5 Hz, J_{H-H} = 7.5 Hz, 9, PEt_3 CH_3's).

^{13}C{^{1}H} NMR (benzene-d_6, 22 °C): δ 156.2 (s, C4), 124.6 (s, C2), 99.1 (s, C3), 94.3 (pseudo q, J_{C-P} = 7.7 Hz, C1), 28.3 (s, ring CH_3), 25.6 (d, J_{C-P} = 7.6 Hz, ring CH_3), 19.0 (d, J_{C-P} = 32.3 Hz, PEt_3 CH_2's), 14.8 (virtual t, J_{C-P} = 30.0 Hz, PEt_3 CH_2's), 8.8 (br s, PEt_3 CH_3's).

^{31}P{^{1}H} NMR (benzene-d_6, 22 °C): δ −18.3 (d, J_{P-P} = 17.6 Hz, 2, PEt_3's), −34.4 (t, J_{P-P} = 17.6 Hz, 1, PEt_3).

Synthesis of $[CH{=}C(Me)CH{=}C(Me)OIr(PMe_3)_4]^+BF_4^-$ (7). Compound **2**, $[CH{=}C(Me)CH{=}C(Me)O{=}Ir(PEt_3)_3]^+BF_4^-$ (300 mg, 0.41 mmol), was dissolved in 50 mL of tetrahydrofuran to form a purple solution and cooled to −77 °C. Trimethylphosphine (1.04 g, 13.7 mmol) was dissolved in 10 mL of tetrahydrofuran and added to the stirred solution of **2** over 30 min. The solution lost the deep purple color and turned yellow during the addition. When it was warmed to 25 °C, the solution became translucent orange. After 3 h the tetrahydrofuran was removed in vacuo, and the resultant brown-yellow film was taken up in a minimum amount of methylene chloride. The product was precipitated with diethyl ether and recovered in methylene chloride. The methylene chloride solution was passed through a glass frit, and the solvent was removed in vacuo to give a yellow, slightly crystalline film. Yield of **7**: 200 mg (70%).

To obtain crystals, the above product was dissolved in tetrahydrofuran and vacuum-deposited onto silanized silica. Three times this volume of silica was placed into a column, followed by the product-containing fraction. The column was wetted with diethyl ether and eluted with a 20% mixture of tetrahydrofuran in ether. When this fraction ran clear, tetrahydrofuran was used to flush the column. A translucent yellow solution resulted. After in vacuo concentration, diffusion of ether into the tetrahydrofuran solution at −30 °C gave orange plates. Anal. Calcd for $C_{18}H_{44}BF_4IrOP_4$: C, 31.81; H, 6.54. Found: C, 31.72, H, 6.73.

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{18}H_{44}{}^{193}IrOP_4{}^+$), 593.1972; found, 593.1964.

^{1}H NMR (methylene chloride-d_2, 23 °C): δ 5.72 (br m, 1, H1), 4.38 (s, 1, H3), 1.74 (br s, 3, ring CH_3), 1.63 (d, J_{H-P} = 9.5 Hz, 9, PMe_3 CH_3's), 1.59 (s, 3, ring CH_3), 1.55 (d, J_{H-P} = 8.0 Hz, 9, PMe_3 CH_3's), 1.44 (virtual t, J_{H-P} = 7.0 Hz, 18, PMe_3 CH_3's).

^{13}C{^{1}H} NMR (methylene chloride-d_2, 23 °C): δ 154.2 (s, C4), 128.0 (m, C2), 107.6 (dtd, J_{C-P} = 74.0 Hz, 11.3 Hz, 5.0 Hz, C1), 100.4 (s, C3), 28.0 (d, J_{C-P} = 11.1 Hz, ring CH_3), 23.7 (d, J_{C-P} = 7.2 Hz, ring CH_3), 19.2 (d, J_{C-P} = 38.0 Hz, PMe_3 CH_3's), 17.4 (d, J_{C-P} = 28.2 Hz, PMe_3 CH_3's), 15.8 (virtual t, J_{C-P} = 38.0 Hz, PMe_3 CH_3's).

^{31}P{^{1}H} NMR (methylene chloride-d_2, 23 °C): δ −37.1 (dd, J_{P-P} = 20.0 Hz, 17.0 Hz, 2, PMe_3's), −52.4 (td, J_{P-P} = 17.0 Hz, 8.3 Hz, 1, PMe_3), −55.7 (td, J_{P-P} = 20.0 Hz, 8.3 Hz, 1, PMe_3).

Formation of {*fac*-[CH=C(Me)CHC(Me)=OIrOC(Me)$_2$]-(PEt_3)$_3$}$^+BF_4^-$ (8). Compound **2**, $[CH{=}C(Me)CH{=}C(Me)O{=}Ir(PEt_3)_3]^+BF_4^-$ (50 mg, 0.068 mmol), was dissolved in 0.5 mL of acetone-d_6 to form a purple solution. When the solution was cooled, the color changed, ultimately becoming clear yellow around −40 °C. When it was warmed, the solution reverted to its original purple color. Repeated cooling and warming cycles resulted in no significant product decomposition by NMR.

^{1}H NMR (acetone-d_6, −40 °C): δ 7.15 (ddd, J_{H-P} = 6.6 Hz, 6.6 Hz, 5.4 Hz, 1, H1), 3.95 (m, 1, H3), 2.61 (s, 3, ring CH_3), 1.86 (s, 3, ring CH_3), 2.1−1.7 (m's, 18, PEt_3 CH_2's), 1.0−0.7 (br m's, 27, PEt_3 CH_3's).

^{13}C{^{1}H} NMR (acetone-d_6, −40 °C): δ 224.5 (d, J_{C-P} = 2.2 Hz, C4), 137.6 (ddd, J_{C-P} = 85.0 Hz, 7.7 Hz, 6.4 Hz, C1), 127.6 (s, C2), 74.9 (s, C3), 64.9 (dd, J_{C-P} = 3.5 Hz, 2.3 Hz, central acetone C), 32.9 (d, J_{C-P} = 4.6 Hz, ring CH_3), 27.2 (d, J_{C-P} = 9.3 Hz, ring CH_3), 17.0 (d, J_{C-P} = 38.1 Hz, PEt_3 CH_2's), 16.9 (d, J_{C-P} = 33.6 Hz, PEt_3 CH_2's), 14.7 (d, J_{C-P} = 22.3 Hz, PEt_3 CH_2's), 8.9 (d, J_{C-P} = 7.0 Hz, PEt_3 CH_3's), 8.6 (d, J_{C-P} = 5.5 Hz, PEt_3 CH_3's), 7.9 (d, J_{C-P} = 5.5 Hz, PEt_3 CH_3's).

^{31}P{^{1}H} NMR (acetone-d_6, −40 °C): δ −20.6 (pseudo t, J_{P-P} = 10.5 Hz, 1, PEt_3), −22.2 (dd, J_{P-P} = 19.0 Hz, 10.5 Hz, 1, PEt_3), −26.1 (dd, J_{P-P} = 19.0 Hz, 10.5 Hz, 1, PEt_3).

Synthesis of {*fac*-[CH=C(Me)CHC(Me)=OIrCH=C-(CO_2Me)](PEt_3)$_3$}$^+BF_4^-$ (9). A 1 mL solution of methyl propiolate (58 mg, 0.69 mmol) in tetrahydrofuran was slowly added to a stirred solution of compound **2**, $[CH{=}C(Me)CH{=}C(Me)O{=}Ir(PEt_3)_3]^+BF_4^-$ (250 mg, 0.34 mmol), in 25 mL of tetrahydrofuran at −72 °C. When the cold bath was removed and the solution warmed to room temperature, the color changed from purple to a dark yellow. The solvent was removed under vacuum, and the resulting solid was washed three times with pentane (5 mL each) and three times with diethyl ether (10 mL each). Finally the solid was dissolved in acetone and filtered. The acetone was removed in vacuo to give a dark yellow foam. Yield of **9**: 170 mg (62%).

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{28}H_{57}{}^{193}IrO_3P_3{}^+$), 727.3150; found, 727.3138.

^{1}H NMR (acetone-d_6, 25 °C): δ 9.66 (dtd, J_{H-P} = 7.5 Hz, J_{H-P} = 4.5 Hz, J_{H-H3} = 2.0 Hz, 1, H7), 7.19 (m, 1, H1), 5.50 (d,

J_{H-H7} = 2.0 Hz, 1, H3), 3.70 (s, 3, OCH_3), 2.79 (br s, 3, ring CH_3), 2.11 (s, 3, ring CH_3), 2.3−1.7 (m, 18, PEt_3 CH_2's), 1.3−0.9 (m, 27, PEt_3 CH_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 25 °C): δ 219.7 (pseudo q, J_{C-P} = 3.5 Hz, C4), 169.4 (dm, J_{C-P} = 75.5 Hz, C7), 164.2 (d, J_{C-P} = 6.0 Hz, CO_2), 137.9 (dt, J_{C-P} = 73.1 Hz, 7.8 Hz, C1), 125.8 (pseudo t, J_{C-P} = 3.6 Hz, C2), 124.3 (pseudo t, J_{C-P} = 3.6 Hz, C8), 67.5 (s, C3), 51.9 (s, OCH_3), 31.5 (d, J_{C-P} = 3.5 Hz, ring CH_3), 25.4 (d, J_{C-P} = 7.1 Hz, ring CH_3), 20.0 (d, J_{C-P} = 39.4 Hz, PEt_3 CH_2's), 17.7 (d, J_{C-P} = 25.2 Hz, PEt_3 CH_2's), 17.3 (d, J_{C-P} = 25.1 Hz, PEt_3 CH_2's), 9.0−8.6 (m, PEt_3 CH_3's).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 25 °C): δ −18.8 (dd, J_{P-P} = 13.4 Hz, 12.5 Hz, 1, PEt_3), −25.2 (dd, J_{P-P} = 18.9 Hz, 12.5 Hz, 1, PEt_3), −26.1 (dd, J_{P-P} = 18.9 Hz, 13.4 Hz, 1, PEt_3).

Synthesis of {*fac*-[CH=C(Me)CHC(Me)=OIrCH=C(Ph)](PEt$_3$)$_3$}$^+$BF$_4^-$ (10). A 2.5 mL solution of phenylacetylene (51 mg, 0.50 mmol) in tetrahydrofuran was added dropwise to a stirred solution of compound **2**, [CH=C(Me)CH=C(Me)O=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (250 mg, 0.34 mmol), in 25 mL of tetrahydrofuran at −23 °C. This caused the color of the solution to change from purple to red. After the solution was warmed to room temperature, the solvent was removed under vacuum. Extraction with benzene was followed by filtration over a glass frit. The volume of solvent was reduced to 3 mL, and diethyl ether (100 mL) was added to form a yellow solution and a precipitate or film. The precipitate was isolated via filtration and dried under vacuum to give a brownish white solid. Yield of **10**: 110 mg (39%).

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{32}H_{59}{}^{191}IrOP_3^+$), 743.3385; found, 743.3395.

^1H NMR (methylene chloride-d_2, 25 °C): δ 7.89 (m, 1, H7), 7.34−7.16 (m, 5, phenyl H's), 7.10 (m, 1, H1), 5.12 (br s, 1, H3), 2.63 (br s, 3, ring CH_3), 2.12 (s, 3, ring CH_3), 2.1−1.8 (m, 18, PEt_3 CH_2's), 1.3−0.9 (m, 27, PEt_3 CH_3's).

$^{13}C\{^1H\}$ NMR (methylene chloride-d_2, 25 °C): δ 218.3 (s, C4), 144.6 (dm, J_{C-P} = 76.3 Hz, C7), 142.9 (s, phenyl ipso), 137.6 (dm, J_{C-P} = 77.6 Hz, C1), 131.0 (s, C8), 128.8 (s, phenyl meta), 126.4 (s, phenyl para), 125.8 (s, phenyl ortho), 125.5 (s, C2), 72.0 (s, C3), 31.8 (d, J_{C-P} = 4.2 Hz, ring CH_3), 25.6 (d, J_{C-P} = 6.1 Hz, ring CH_3), 19.9 (d, J_{C-P} = 39.3 Hz, PEt_3 CH_2), 17.6 (d, J_{C-P} = 24.9 Hz, PEt_3 CH_2), 17.4 (d, J_{C-P} = 24.8 Hz, PEt_3 CH_2), 9.0−7.0 (m, PEt_3 CH_3's).

$^{31}P\{^1H\}$ NMR (methylene chloride-d_2, 25 °C): δ −20.6 (pseudo t, J_{P-P} = 12.3 Hz, 1, PEt_3), −26.3 (dd, J_{P-P} = 18.0 Hz, 12.3 Hz, 1, PEt_3), −26.7 (dd, J_{P-P} = 18.0 Hz, 12.3 Hz, 1, PEt_3).

Synthesis of {*fac*-[CH=C(Me)CHC(Me)=OIrCH=C(SiMe$_3$)](PEt$_3$)$_3$}$^+$BF$_4^-$ (11). A 1 mL solution of (trimethylsilyl)acetylene (70 mg, 0.71 mmol) in tetrahydrofuran was added to a stirred solution of compound **2**, [CH=C(Me)CH=C(Me)O=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (50 mg, 0.068 mmol), in 25 mL of tetrahydrofuran at −72 °C. When the solution was warmed to room temperature and stirred for 1 h, the color changed from purple to yellow. The solvent was removed under vacuum, and the solid was washed with three successive 5 mL portions of pentane followed by three 5 mL portions of diethyl ether. The solid was further extracted with benzene, and the extracts were filtered over a glass frit and dried under vacuum. Yield of **11**: 23 mg (41%).

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{29}H_{63}{}^{191}IrOP_3Si^+$), 739.3467; found, 739.3468.

^1H NMR (acetone-d_6, 25 °C): δ 8.50 (pseudo q, J_{H-P} = 6.6 Hz, 1, H7), 7.13 (br s, 1, H1), 5.12 (s, 1, H3), 2.70 (br s, 3, ring CH_3), 2.06 (br s, 3, ring CH_3), 2.3−1.7 (m, 18, PEt_3 CH_2's), 1.3−0.9 (m, 27, PEt_3 CH_3's), 0.11 (s, 9, Si−CH_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 25 °C): δ 217.6 (s, C4), 163.1 (d, J_{C-P} = 74.2 Hz, C7), 137.4 (d, J_{C-P} = 78.9 Hz, C1), 131.0 (s, C8), 124.8 (s, C2), 71.7 (s, C3), 31.2 (s, ring CH_3), 25.6 (s, ring CH_3), 19.8 (d, J_{C-P} = 37.1 Hz, PEt_3 CH_2's), 17.6 (d, PEt_3 CH_2's), 17.2 (d, PEt_3 CH_2's), 10.0−7.0 (m, PEt_3 CH_3's), −1.2 (s, Si−CH_3's).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 25 °C): δ −19.8 (dd, J_{P-P} = 12.4 Hz, 11.9 Hz, 1, PEt_3), −25.3 (dd, J_{P-P} = 18.3 Hz, 12.4 Hz, 1, PEt_3), −26.1 (dd, J_{P-P} = 18.3 Hz, 11.9 Hz, 1, PEt_3).

$^{29}Si\{^1H\}$ NMR (acetone-d_6, 25 °C): δ −5.9 (d, J_{Si-P} = 9.0 Hz, 1, Si).

Synthesis of {*fac*-[CH=C(Me)CHC(Me)=OIrCH$_2$CH(CO$_2$Me)](PEt$_3$)$_3$}$^+$BF$_4^-$ (12). Methyl acrylate (32 mg, 0.37 mmol) was added dropwise to a stirred solution of compound **2**, [CH=C(Me)CH=C(Me)O=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (53 mg, 0.073 mmol), in 15 mL of tetrahydrofuran at −30 °C. The reaction mixture was warmed to room temperature and stirred for 5 h, during which time the color changed from purple to red and finally to dark yellow. The solvent was removed under vacuum, and the resulting solid was washed three times with pentane (5 mL each) and three times with diethyl ether (10 mL each). Finally the solid was dissolved in acetone and filtered. The acetone was removed in vacuo to give a dark yellow film of a mixture of two isomers. Yield of **12**: 21 mg (35%).

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{28}H_{59}{}^{193}IrO_3P_3^+$), 729.3307; found, 729.3315.

Major Isomer. ^1H NMR (acetone-d_6, 25 °C): δ 7.67 (br pseudo q, J_{H-P} = 7.2 Hz, 1, H1), 4.29 (br s, 1, H3), 3.63 (s, 3, OCH_3), 2.73 (s, 3, ring CH_3), 2.22 (buried, 1, H8), 2.05 (buried, 3, ring CH_3), 1.55 (m, 1, H7a), 1.33 (buried, 1, H7b), 2.3−1.7 (m, 18, PEt_3 CH_2's), 1.4−0.9 (m, 27, PEt_3 CH_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 25 °C): δ 223.8 (s, C4), 175.2 (s, CO_2), 142.3 (dm, J_{C-P} = 82.5 Hz, C1), 125.2 (s, C2), 64.1 (s, C3), 51.7 (s, OCH_3), 35.1 (s, C8), 30.7 (d, J_{C-P} = 3.8 Hz, ring CH_3), 27.3 (d, J_{C-P} = 8.8 Hz, ring CH_3), 24.0−17.0 (m, PEt_3 CH_2's), 11.0−7.0 (m, PEt_3 CH_3's), −0.5 (dm, J_{C-P} = 68.8 Hz, C7).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 25 °C): δ −24.9 (dd, J_{P-P} = 15.8 Hz, 11.5 Hz, 1, PEt_3), −25.4 (pseudo t, J_{P-P} = 11.5 Hz, PEt_3), −26.4 (dd, J_{P-P} = 15.8 Hz, 11.5 Hz, 1, PEt_3).

Minor Isomer. ^1H NMR (acetone-d_6, 25 °C): δ 7.48 (br pseudo q, J_{H-P} = 7.2 Hz, 1, H1), 4.24 (br s, 1, H3), 3.66 (s, 3, OCH_3), 2.73 (s, 3, ring CH_3), 2.47 (m, 1, H8), 1.97 (buried, 3, ring CH_3), 1.71 (buried, 1, H7a), 1.35 (buried, 1, H7b), 2.3−1.7 (m, 18, PEt_3 CH_2's), 1.4−0.9 (m, 27, PEt_3 CH_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 25 °C): δ 224.0 (s, C4), 178.4 (s, CO_2), 138.7 (dm, J_{C-P} = 82.5 Hz, C1), 127.4 (s, C2), 64.9 (s, C3), 52.0 (s, OCH_3), 41.9 (s, C8), 33.0 (d, J_{C-P} = 4.0 Hz, ring CH_3), 25.4 (d, J_{C-P} = 8.8 Hz, ring CH_3), 24.0−17.0 (m, PEt_3 CH_2's), 11.0−7.0 (m, PEt_3 CH_3's), 1.1 (dm, J_{C-P} = 70.0 Hz, C7).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 25 °C): δ −22.8 (dd, J_{P-P} = 12.0 Hz, 10.0 Hz, 1, PEt_3), −25.7 (dd, J_{P-P} = 15.2 Hz, 12.0 Hz, 1, PEt_3), −27.4 (dd, J_{P-P} = 15.2 Hz, 10.0 Hz, 1, PEt_3).

Synthesis of {*fac*-[CH=C(Me)CHC(Me)=OIrS(O)$_2$](PEt$_3$)$_3$}$^+$BF$_4^-$ (13). Compound **2**, [CH=C(Me)CH=C(Me)O=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (190 mg, 0.26 mmol), was dissolved in 25 mL of tetrahydrofuran and cooled to −72 °C. Sulfur dioxide gas was condensed into the solution, causing an immediate color change from purple to a light brownish red. The reaction mixture was warmed to room temperature and left under a nitrogen flow for 1 h. After removal of the solvent under vacuum, the residue was extracted with methylene chloride and filtered, and the solvent was again removed. A small amount of acetone (1.5 mL) was used to redissolve the residue, and 5−6 mL of diethyl ether was added. The mixture was then cooled to −30 °C to obtain an oily yellow solid. The solution was removed via pipet and the solid washed twice with −30 °C diethyl ether, withdrawing the ether each time. The solid was dried under vacuum and then redissolved in a minimum amount of acetone. Diethyl ether was added (∼5 mL) to give an orange solution and a solid residue. After filtration the solid

Table 4. X-ray Diffraction Structure Summary

	6	13	14
formula	$C_{24}H_{53}ClIrOP_3$	$C_{24}H_{53}BF_4IrO_3P_3S$	$C_{33.5}H_{62}BF_4IrNO_2P_3$
fw	678.2	793.64	882.8
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	11.244(5)	11.2386(3)	11.987(4)
b, Å	15.914(10)	16.7463(4)	11.712(2)
c, Å	16.591(7)	17.4531(4)	28.215(5)
α, deg	90.0	90.0	90.0
β, deg	90.75(4)	98.124(2)	91.05(2)
γ, deg	90.0	90.0	90.0
V, Å^3	2969(3)	3251.80(14)	3960.4(15)
Z	4	4	4
cryst dimens, mm	0.51 × 0.46 × 0.39	0.20 × 0.12 × 0.05	0.25 × 0.45 × 0.50
cryst color and habit	orange irregular	orange plate	yellow prism
calcd density, g/cm^3	1.518	1.621	1.480
radiation, Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
temp, K	295	200	298
2*θ* range, deg	3.0−50.0	3.38−52.84	3.0−50.0
data collected			
h	0 to 13	−14 to +13	0 to 14
k	0 to 18	−20 to +20	0 to 13
l	−14 to +14	−21 to +21	−33 to +33
total decay	none detected	none detected	none detected
no. of data collected	4971	41 077	7301
no. of unique data	4735	6656	6944
no. of obsd data[a]	3728	5296	3452
Mo Kα linear abs coeff, cm^{-1}	47.63	43.65	35.40
abs cor applied	semiempirical	empirical, sadabs	semi-empiral
data to param ratio	17.5:1	19.2:1	9.3:1
final *R* indices (obsd data)[a]	R1 = 0.0340, wR2 = 0.0783	R1 = 0.0448, wR2 = 0.0845	R1 = 0.0340, wR2 = 0.0783
R indices (all data)	R1 = 0.0508, wR2 = 0.0872	R1 = 0.0665, wR2 = 0.0932	R1 = 0.0508, wR2 = 0.0872
goodness of fit	1.053	1.093	1.13

[a] For **6** and **13**, $I > 2\sigma(I)$; for **14**, $I > 3\sigma(I)$.

was discarded, and the filtrate was dried under vacuum. The resulting residue was redissolved in a minimum amount of acetone. Addition of diethyl ether and a few drops of toluene, followed by cooling to −30 °C, gave X-ray-quality crystals. Yield of **13**: 93 mg (45%).

High-resolution FAB-MS: calcd for $[M - SO_2]^+$ ($C_{24}H_{53}{}^{193}IrOP_3{}^+$), 643.2939; found, 643.2941.

^{1}H NMR (acetone-d_6, 25 °C): δ 7.67 (m, 1, H1), 5.55 (s, 1, H3), 2.89 (s, 3, ring CH_3), 2.17 (s, 3, ring CH_3), 2.50−2.10 (m, 18, PEt_3 CH_2's), 1.30−1.00 (m, 27, PEt_3 CH_3's).

^{13}C{^{1}H} NMR (acetone-d_6, 25 °C): δ 221.0 (s, C4), 147.4 (dt, J_{C-P} = 71.2 Hz, 7.5 Hz, C1), 133.9 (s, C2), 105.4 (s, C3), 29.2 (d, J_{C-P} = 3.4 Hz, ring CH_3), 22.3 (d, J_{C-P} = 6.6 Hz, ring CH_3), 20.3 (d, J_{C-P} = 38.8 Hz, PEt_3 CH_2's), 18.8 (d, J_{C-P} = 25.6 Hz, PEt_3 CH_2's), 18.1 (d, J_{C-P} = 30.0 Hz, PEt_3 CH_2's), 9.5 (d, J_{C-P} = 6.6 Hz, PEt_3 CH_3's), 8.6 (d, J_{C-P} = 5.6 Hz, PEt_3 CH_3's).

^{31}P{^{1}H} NMR (acetone-d_6, 25 °C): δ −21.3 (dd, J_{P-P} = 14.0 Hz, 10.0 Hz, 1, PEt_3), −21.7 (dd, J_{P-P} = 15.0 Hz, 10.0 Hz, 1, PEt_3), −24.9 (pseudo t, J_{P-P} = 14.5 Hz, 1, PEt_3).

Synthesis of {*fac*-[C(Me)CH=C(Me)OIrON(Ph)=CH](PEt$_3$)$_3$}$^+$BF$_4^-$ (14). Compound **2**, [CH=C(Me)CH=C(Me)O=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (110 mg, 0.15 mmol), was dissolved in 20 mL of tetrahydrofuran to form a purple solution and cooled to −30 °C. Nitrosobenzene (18 mg, 0.17 mmol) was dissolved in 10 mL of tetrahydrofuran, cooled to −30 °C, and added to the stirred purple solution, causing it to turn orange-yellow. The solution was stirred at 25 °C for 30 min before the tetrahydrofuran was removed in vacuo. The resultant film was repeatedly extracted with toluene, and each successive extraction was passed through a glass frit. The toluene volume was reduced by ∼75% and stored at −30 °C.

Multiple crops of microfine yellow crystals were recovered on a glass frit with subsequent in vacuo solvent reductions. The recovered microfine crystals were washed with cold toluene and pentane and dissolved in a minimum of acetone. Diethyl ether diffusion at −30 °C gave a bright yellow crystalline product. Yield of **14**: 85 mg (66%).

Anal. Calcd for $C_{30}H_{58}BF_4IrNO_2P_3$: C, 43.06; H, 7.00. Found: C, 43.45; H, 6.95.

High-resolution FAB-MS: calcd for $[M]^+$ ($C_{30}H_{58}{}^{193}IrNO_2P_3{}^+$), 750.3310; found, 750.3313.

^{1}H NMR (methylene chloride-d_2, −40 °C): δ 7.53 (d, J_{H-H} = 7.8 Hz, 2, phenyl ortho), 7.45 (m, 3, phenyl meta & para), 7.25 (d, J_{H-P} = 4.2 Hz, 1, H1), 3.56 (d, J_{H-P} = 5.4 Hz, 1, H3), 2.21−2.16 (br m, 6, PEt_3 CH_2's), 1.99−1.94 (br m, 6, PEt_3 CH_2's), 1.91−1.86 (br m, 6, PEt_3 CH_2's), 1.70 (s, 3, ring CH_3), 1.44 (d, J_{H-P} = 6.6 Hz, 3, ring CH_3), 1.16−1.10 (br m, 18, PEt_3 CH_3's), 0.99 (m, 9, PEt_3 CH_3's).

^{13}C{^{1}H} NMR (methylene chloride-d_2, −40 °C): δ 172.3 (d, J_{C-P} = 10.5 Hz, C4), 156.8 (s, C1), 139.8 (s, phenyl ipso), 129.7 (s, phenyl para), 129.5 (s, phenyl meta), 120.4 (s, phenyl ortho), 102.0 (pseudo t, J_{C-P} = 4.1 Hz, C3), 42.7 (ddd, J_{C-P} = 78.7 Hz, 6.3 Hz, 4.0 Hz, C2), 27.9 (s, ring CH_3), 19.0 (s, ring CH_3), 18.6 (d, J_{C-P} = 23.7 Hz, PEt_3 CH_2's), 17.8 (d, J_{C-P} = 24.0 Hz, PEt_3 CH_2's), 15.3 (d, J_{C-P} = 24.8 Hz, PEt_3 CH_2's), 10.1 (d, J_{C-P} = 5.9 Hz, PEt_3 CH_3's), 9.5 (d, J_{C-P} = 5.4 Hz, PEt_3 CH_3's), 8.2 (d, J_{C-P} = 6.4 Hz, PEt_3 CH_3's).

^{31}P{^{1}H} NMR (methylene chloride-d_2, −40 °C): δ −22.9 (pseudo t, J_{P-P} = 10.5 Hz, 1, PEt_3), −34.3 (dd, J_{P-P} = 15.0 Hz, 10.5 Hz, 1, PEt_3), −34.4 (dd, J_{P-P} = 15.0 Hz, 10.5 Hz, 1, PEt_3).

X-ray Diffraction Studies of *mer*-CH=C(Me)CH=C(Me)OIr(Cl)(PEt$_3$)$_3$ (6), {*fac*-[CH=C(Me)CHC(Me)=OIrS(O)$_2$](PEt$_3$)$_3$}$^+$BF$_4^-$ (13), and {*fac*-[C(Me)CH=C(Me)OIrON(Ph)=CH](PEt$_3$)$_3$}$^+$BF$_4^-$ (14). Single crystals of compounds **6**, **13**, and **14** were either sealed in a glass capillary or mounted on a glass fiber under a nitrogen atomosphere. X-ray data for **6** and **14** were collected on a Siemens R3m/V diffractometer at room temperature, while data for **13** was obtained using a

Bruker SMART charge coupled device (CCD) detector system at 200 K. In each case, graphite-monochromated Mo Kα radiation was supplied by a sealed-tube X-ray source.

Structure solution and refinement were carried out using the SHELXTL-PLUS software package (PC version).[20] The iridium atom positions were determined by direct methods. The 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, while hydrogen atoms were placed at idealized positions and assumed the riding model.

In compound **14**, the tetrafluoroborate anion was disordered and was, therefore, refined using DFIX constraints. Its F−B−F angles were fixed at 109.5°, and a common B−F distance was refined. The toluene molecule of crystallization ($^1/_2$ equiv) was refined isotropically. Its disordered methyl group was assigned an occupancy factor of 0.5.

Crystal data and details of both collection and structure analysis are listed in Table 4.

(20) Sheldrick, G. M. Bruker Analytical X-ray Division, Madison, WI, 1997.

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Supporting Information Available: Text giving structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **6**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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