Silapentadienyl−Iridium−Phosphine Chemistry[1]

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A series of η^1-silapentadienyl−iridium complexes have been synthesized by reacting (η^2-cyclooctene)(X)Ir(PMe_3)$_3$ (X = Cl or Me) with butadienyldimethylsilanes, and the reactivity of these species has been investigated. Treatment of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ with *E*- or (*Z*-butadienyl)dimethylsilane produces, via Si−H bond activation, (η^1-*E*-dimethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$, **1E**. Similarly, treatment of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with *E*- or (*Z*-butadienyl)dimethylsilane produces η^1-*E*- or (η^1-*Z*-dimethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$, **2E** or **2Z**. Upon heating in benzene at 100 °C (under pressure), **2E** decomposes, but **2Z** loses methane and coordinates the terminal double bond of the silapentadienyl ligand, producing (η^1,η^2-dimethylsilapentadienyl)Ir(PMe_3)$_3$, **3**. Treatment of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ with (*E*-2,3-dimethylbutadienyl)dimethylsilane produces (η^1-*E*-2,3,5,5-tetramethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$, **4E**. In acetone, this species isomerizes via 2,3-dimethylbutadienyl migration from silicon to iridium, leading ultimately to production of (η^1-*E*-2,3-dimethylbutadienyl)(H)($SiMe_2Cl$)Ir(PMe_3)$_3$, **5**. Treatment of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ with the *Z* isomer of (2,3-dimethylbutadienyl)dimethylsilane produces transient (η^1-*Z*-2,3,5,5-tetramethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$, **4Z**, which also rearranges. In this case, hydride first migrates from iridium to C2 of the silapentadienyl ligand, and then the resulting butenyl group migrates from silicon to iridium, forming an iridacyclopentene product, **6**. The reactions of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with *E*- or (*Z*-2,3-dimethylbutadienyl)dimethylsilane generate η^1-*E*- or (η^1-*Z*-2,3,5,5-tetramethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$, **7E** or **7Z**. Heating these compounds in toluene or benzene (under pressure) leads to methane loss, followed by C−H bond activation. In the case of **7E**, a silapentadienyl methyl group is activated, producing an iridasilacyclopentene product, **8**. In the case of **7Z**, a C−H bond on the end of the silapentadienyl chain is activated, producing the first example of an iridasilacyclohexadiene, **9**. X-ray crystal structures of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$, **5**-acetone, **6**, and **7E** are reported here, while structures of **1E** and **3** were reported in a prior communication.[1]

Introduction

Pentadienyl−metal complexes have been extensively investigated,[2] and increasing attention is being paid to heteroatom-containing analogues.[3] These species often exhibit enhanced reactivity due to the accessibility of a range of η^5, η^3, and η^1 bonding modes, and facile interconversions between these modes could potentially lead to catalysis.[3b] Furthermore, when the central metal is iridium, these complexes can serve as precursors to a variety of novel metallacycles, including aromatic metallacycles such as iridabenzene, iridapyrylium, and iridathiabenzene.[4]

While recent studies have focused on oxapentadienyl−, azapentadienyl−, thiapentadienyl−, and even phosphapentadienyl−metal complexes,[3] no examples of the closely related silicon-containing systems have been reported. With this in mind, we set out to synthesize a series of silapentadienyl−iridium−phosphine complexes and to explore their reactivity. In this paper, we report a successful synthetic strategy for producing the desired complexes, based on Si−H bond activation, along with structural and spectroscopic data on key members of this compound class. In addition, we show that these complexes can be used as precursors to novel iridasilacycles. A portion of this work has been previously communicated.[1]

Results and Discussion

(A) Reactions of Butadienylsilanes with (η^2-Cyclooctene)(Cl)Ir(PMe_3)$_3$. *E*- and (*Z*-butadienyl)dimethylsilanes were synthesized as described earlier[1] by reacting the corresponding *E*- and *Z*-1-bromobutadienes with *tert*-butyllithium and chlorodimethylsilane. These silane reagents were then treated with (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$,[5] which exists in solution as 16e$^-$ (Cl)Ir(PMe_3)$_3$. As shown in Scheme 1 (upper path), the reaction involving (*E*-butadienyl)dimethylsilane produced *fac*-(η^1-*E*-dimethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$ (***fac*-1E**) via Si−H

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(1) Pentadienyl−Metal−Phosphine Chemistry. 35. For Part 34, see: Bleeke, J. R.; Thananatthanachon, T.; Rath, N. P. *Organometallics* **2007**, *26*, 3904–3907.

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(3) For recent reviews of heteropentadienyl−metal chemistry, see: (a) Bleeke, J. R. *Organometallics* **2005**, *24*, 5190–5207. (b) Paz-Sandoval, M. A.; Rangel-Salas, I. I. *Coord. Chem. Rev.* **2006**, *250*, 1071–1106.

(4) Bleeke, J. R. *Acc. Chem. Res.* **2007**, *40*, 1035–1047, and references therein.

(5) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615–1616.

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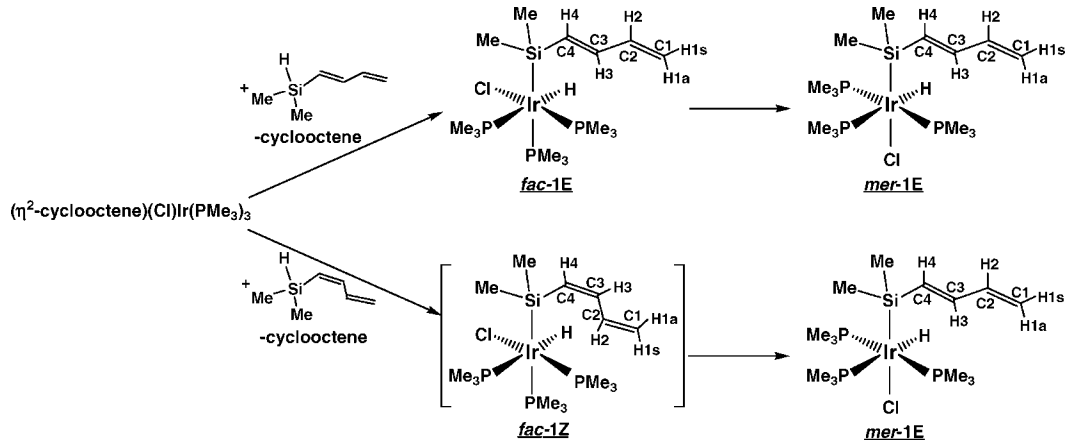
Scheme 1



bond activation.[6] The *fac* geometry of this product is evident from the ^{31}P NMR spectrum, which exhibits three phosphorus-coupled doublet-of-doublet (dd) patterns for the three inequivalent phosphines. Similarly, in the ^{1}H NMR spectrum, the hydride signal appears as a phosphorus-coupled doublet-of-doublets-of-doublets (ddd) signal with one very large coupling (145.5 Hz) due to the *trans* phosphine and two smaller couplings (27.5 and 17.1 Hz) due to the two *cis* phosphines. Upon stirring for an additional 4 h at room temperature, the *fac* isomer (which has not been isolated) cleanly converts to the thermodynamically preferred *mer* isomer (***mer*-1E**). The ^{31}P NMR of this isomer exhibits just two peaks, a doublet due to the equivalent mutually *trans* phosphines and a triplet due to the unique *cis* phosphine. In the ^{1}H NMR, the hydride signal now appears as a doublet of triplets. The large doublet coupling (133.8 Hz) indicates that the hydride resides *trans* to a phosphine, which then implies that the chloride sits *trans* to the silapentadienyl ligand. All of the silapentadienyl protons resonate downfield at δ 6.63 (H3), 6.47 (H2), 6.30 (H4), 5.20 ($H1_{anti}$), and 5.01 ($H1_{syn}$), indicating an η^1-bonding mode. Similarly, downfield shifts are observed for all of the silapentadienyl carbons (resonances range from δ 148.5 to 115.9). The large coupling between H3 and H4 (17.7 Hz) is diagnostic for the *E* stereochemistry at double bond C3−C4.

The structure of ***mer*-1E** has been confirmed by X-ray diffraction and was reported in our prior communication.[1]

Surprisingly, treatment of the *Z* isomer of butadienyldimethylsilane with (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ (Scheme 1, lower path) also leads to the *E* isomer of the silapentadienyl product, ***mer*-1E**. While the detailed mechanism of this isomerization has not been explored, it seems likely that a C3-η^1-silapentadienyl intermediate is involved. Rotation about the C3−C4 single bond in that intermediate would lead to the observed *Z* to *E* isomerization.

(B) Reactions of Butadienylsilanes with (η^2-Cyclooctene)-(Me)Ir(PMe_3)$_3$. In order to investigate alternative bonding modes for silapentadienyl ligands and also to explore the possibility of using silapentadienyl−metal complexes as precursors to novel metallacycles, we needed a reliable and irreversible way to create coordinative unsaturation at iridium. One promising approach was to replace the chloro ligand with methyl in our starting material, followed by treatment with butadienylsilanes. The resulting silapentadienyl products, containing *cis* methyl and hydride ligands, could then be heated to reductively eliminate methane.

To this end, (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ was reacted with MeLi to produce (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$, a previously unreported compound. A saturated pentane solution, cooled to −30 °C, yielded beautiful yellow crystals, which were characterized by X-ray diffraction. As shown in Figure 1, the compound adopts a *fac* geometry with two phosphines *trans* to the η^2-cyclooctene ligand and the remaining phosphine *trans* to the methyl ligand. The cyclooctene double bond (C1═C2) is coordinated so that the bulky alkyl substituents (C3 and C8) are directed "up" toward the methyl group (C9), while the hydrogen substituents are directed "down" toward the PMe_3 ligand. In solution at room temperature cyclooctene slowly dissociates to produce 16e$^-$ (Me)Ir(PMe_3)$_3$.

As shown in Scheme 2, the reaction of (η^2-cyclooctene)-(Me)Ir(PMe_3)$_3$ with (*E*-butadienyl)dimethylsilane produces *fac*-(η^1-*E*-dimethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ (***fac*-2E**), while treatment of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with (*Z*-butadienyl)dimethylsilane generates ***fac*-2Z**. No isomerization of either compound is observed even upon stirring for several days.[7] The detailed NMR spectra for ***fac*-2E** and ***fac*-2Z** are reported in the Experimental Section and have already been discussed in our prior communication.[1]

(C) Heating of (η^1-Dimethylsilapentadienyl)(H)(Me)-Ir(PMe_3)$_3$ Complexes. As discussed above, **2E** and **2Z** are attractive precursors because coordinative unsaturation can

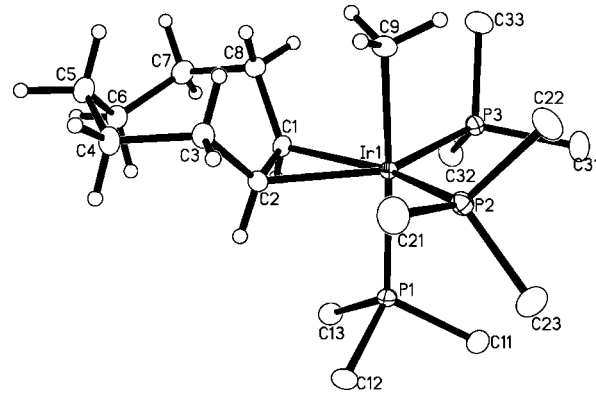
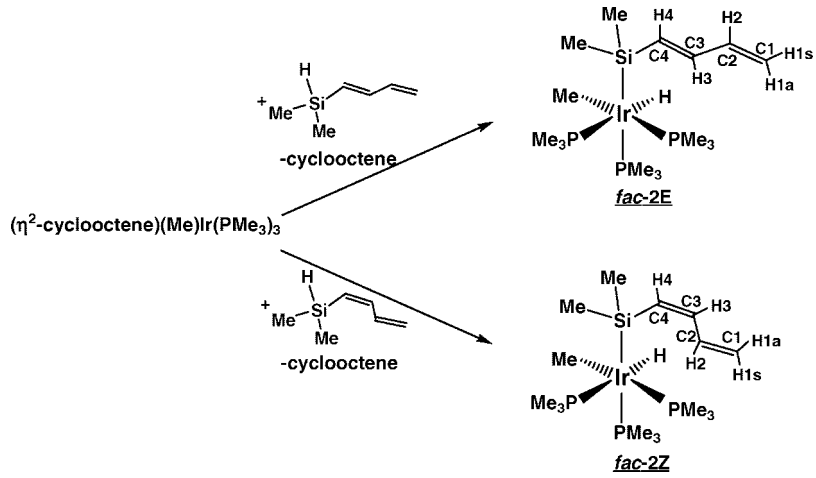


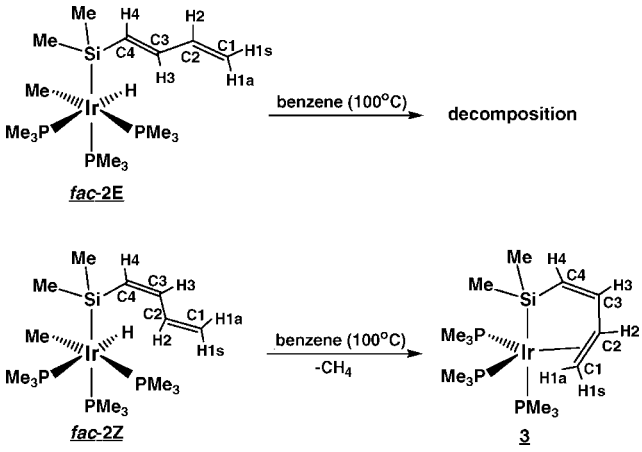
Figure 1. ORTEP drawing of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown. Selected bond distances (Å): Ir1−P1, 2.2938(4); Ir1−P2, 2.2946(4); Ir1−P3, 2.2838(4); Ir1−C9, 2.1637(14); Ir1−C1, 2.1494(14); Ir1−C2, 2.1664(13); C1−C2, 1.459(2).

(6) Milstein has used a similar Si−H bond activation strategy to produce silyl−iridium complexes. Milstein's starting material is (Me)Ir(PMe_3)$_4$, which loses PMe_3 to produce "(Me)Ir(PMe_3)$_3$". See: (a) Aizenberg, M.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 317–319. (b) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456–6464.

Scheme 2



Scheme 3



potentially be created by reductive elimination of methane. This, in turn, could lead to the observation of new silapentadienyl bonding modes or the formation of novel metallasilacycles. Unfortunately, as shown in Scheme 3, when **2E** is heated in benzene at 100 °C (under pressure), it decomposes to intractable products. However, under exactly the same conditions, compound **2Z** cleanly converts to (η^1, η^2-dimethylsilapentadienyl)-Ir(PMe_3)$_3$ (**3**) by loss of methane and coordination of the terminal double bond of the silapentadienyl ligand. The decomposition of **2E** can be readily understood by noting that the *E* stereochemistry at C3=C4 prevents C1=C2 from coordinating to iridium. In addition, **2E** possesses no attractive targets for C−H bond activation; the only bond that presents itself to the iridium center is C3−H3, which, if activated, would lead to a highly strained four-membered ring.

The full NMR data for **3** are reported in the Experimental Section and have been discussed in our prior communication.[1] Likewise, the X-ray crystal structure of **3** was reported previously[1] and is therefore not reproduced here.

(D) Reactions of (2,3-Dimethylbutadienyl)dimethylsilanes with (η^2-Cyclooctene)(Cl)Ir(PMe_3)$_3$. In previous work with pentadienyl−iridium[8] and heteropentadienyl−iridium[9,10] complexes, we have observed significant changes in structure and reactivity upon introduction of methyl substituents onto the pentadienyl or heteropentadienyl chain. We therefore sought to synthesize analogues of butadienyldimethylsilane in which the butadienyl substituent was selectively methylated. Our synthetic approach is outlined in Scheme 4. Treatment of commercially available 2-methyl-1-buten-3-yne with ethylmagnesium bromide and dimethylchlorosilane produces (2-methyl-1-buten-3-ynyl)dimethylsilane. Further treatment of this species with $AlMe_3$/Cp_2ZrCl_2,[11] followed by aqueous workup, produces (2,3-dimethylbutadienyl)dimethylsilane, predominantly as the *E* isomer. Ultraviolet photolysis in the presence of duroquinone as a photosensitizer results in substantial double-bond isomerization from *E* to *Z*.[12] The two isomers can be easily distinguished by ^{1}H NOESY experiments. The *E* isomer exhibits a NOESY correlation between H4 and the hydrogens on methyl C5 (bonded to chain carbon C2), while the *Z* isomer shows a strong correlation between H4 and the hydrogens on methyl C6 (which is bonded to C3).

As shown in Scheme 5 (upper path), the reaction of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ with (*E*-2,3-dimethylbutadienyl)dimethylsilane produces *mer*-(η^1-*E*-2,3,5,5-tetramethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$ (***mer*-4E**), the analogue of ***mer*-1E** (*vide supra*). The *mer* coordination geometry is evident from the characteristic ^{31}P NMR signals: a doublet for the mutually *trans* phosphines and a triplet for the unique *cis* phosphine. In the ^{1}H NMR, the hydride shows strong coupling to ^{31}P (J_{H-P} = 133.8 Hz), indicating that it lies *trans* to a phosphine ligand. Therefore, the chloro ligand must reside *trans* to the silapentadienyl ligand.[13] The η^1-bonding mode of the silapentadienyl ligand is confirmed by the downfield chemical shifts of H4 (δ6.23), H1 (δ5.18), and H1 (δ5.01), while the *E* stereochemistry is confirmed by a correlation between H4 and the hydrogens on C5 in the ^{1}H NOESY spectrum.

When compound ***mer*-4E** is dissolved in acetone, it isomerizes to *fac*-(η^1-*E*-2,3-dimethylbutadienyl)(H)($SiMe_2Cl$)Ir(PMe_3)$_3$ (***fac*-5**, Scheme 5). The *fac* geometry of **5** is evident from the three dd patterns in the ^{31}P NMR spectrum. In the ^{1}H NMR

(7) The observation that **2Z** does *not* convert to **2E** suggests that the rapid conversion of **1Z** to **1E** (*vide supra*) may involve reversible chloride dissociation.

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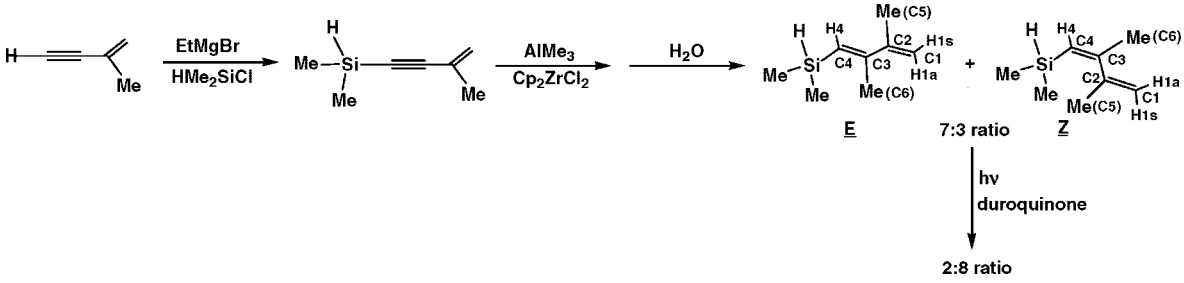
(9) (a) Bleeke, J. R.; Haile, T.; Chiang, M. Y. *Organometallics* **1991**, *10*, 19–21. (b) Bleeke, J. R.; Haile, T.; New, P. R.; Chiang, M. Y. *Organometallics* **1993**, *12*, 517–528.

(10) (a) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740–2743. (b) Bleeke, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813–2826.

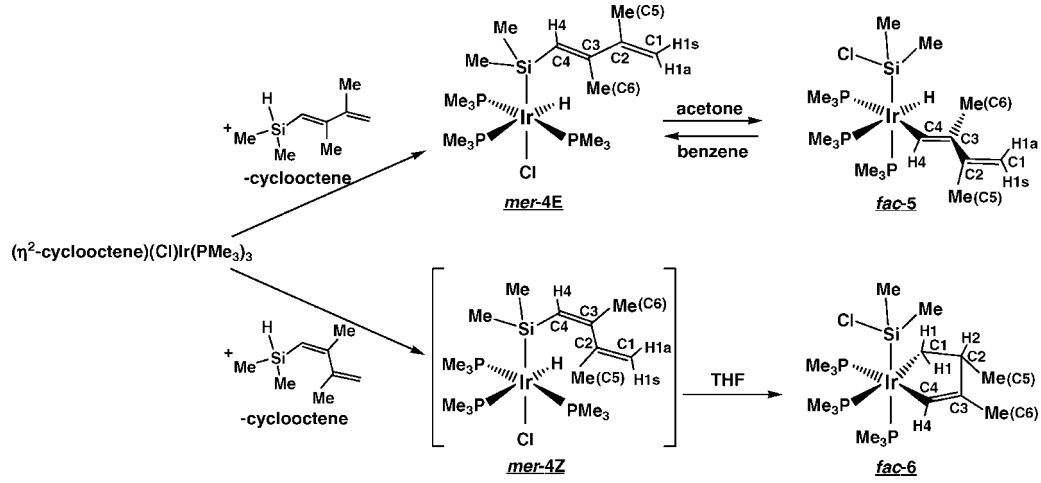
(11) Paquette, L. A., Editor-in-Chief. *Encyclopedia of Reagents for Organic Synthesis*; John Wiley and Sons: Chichester, 1995; Vol. 7, pp 5192−5195, and references therein.

(12) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197–3217.

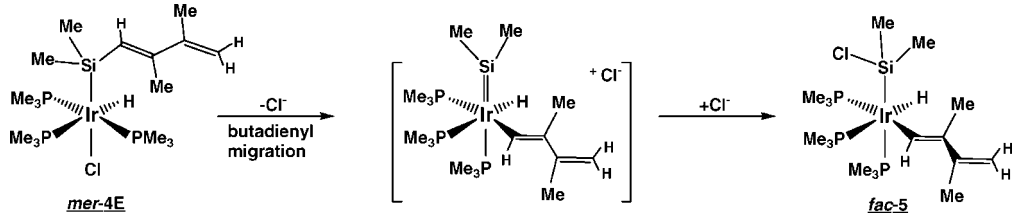
Scheme 4



Scheme 5



Scheme 6



spectrum, the signals for H4, $H1_{anti}$, and $H1_{syn}$ still appear in the downfield region (as in ***mer*-4E**), but H4 is now strongly coupled to phosphorus (J_{H-P} = 18.6 Hz). This coupling is due to the ^{31}P nucleus that lies *cis* to and coplanar with the butadienyl group. In the ^{13}C NMR spectrum of ***fac*-5**, C4 is strongly coupled to the ^{31}P nucleus that resides *trans* to it (J_{C-P} = 67.9 Hz).

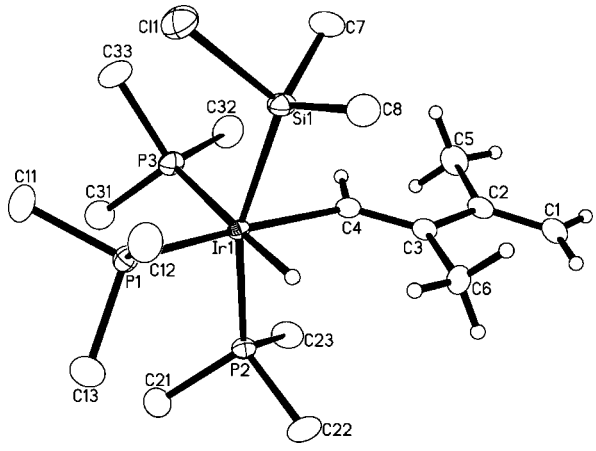


Figure 2. ORTEP drawing of ***fac*-5**-acetone, using thermal ellipsoids at the 50% level. PMe_3 methyl H's and the acetone solvate are not shown. Selected bond distances (Å): Ir1−P1, 2.3046(5); Ir1−P2, 2.3573(5); Ir1−P3, 2.3383(5); Ir1−Si1, 2.3609(5); Ir1−H1, 1.60(2); Ir1−C4, 2.1033(17); C1−C2, 1.342(3); C2−C3, 1.485(2); C2−C5, 1.509(3); C3−C4, 1.349(3); C3−C6, 1.504(2); Si1−Cl(1), 2.1582(7); Si1−C7, 1.885(2); Si1−C8, 1.877(2).

The structure of ***fac*-5** has been confirmed by X-ray crystallography and is presented in Figure 2. The coordination geometry about iridium is a distorted octahedron. The *trans*-diaxial silyl and phosphine ligands are noticeably tilted (angle Si1−Ir1−P2 = 161.362(18)°), apparently to avoid steric contacts with the other phosphines. The facial arrangement of the phosphines allows for a direct comparison of the *trans* influence of the three opposing ligands. On the basis of the iridium−phosphorus bond distances (see caption to Figure 2), the opposing ligands exert a *trans* influence in the following order: alkyl < H < silyl.[14] The butadienyl−iridium moiety adopts a W-shape with torsional angle C1−C2−C3−C4 equal to 176.10(17)° and torsional angle C2−C3−C4−Ir1 equal to 175.77(13)°. The butadienyl group lies essentially in the equatorial plane of the molecule; the mean deviation of atoms C1, C2, C3, C4, Ir1, P1, and P3 from the plane is 0.04 Å.

A likely mechanism for the formation of ***fac*-5** from ***mer*-4E** is presented in Scheme 6. Dissociation of chloride from ***mer*-4E** creates coordinative unsaturation at iridium, which is relieved by a 1,2-migration of the 2,3-dimethylbutadienyl group from

silicon to iridium. The resulting electrophilic silylene ligand is then attacked by chloride to produce neutral ***fac*-5**. Similar 1,2-migrations of alkyl and aryl groups from silicon to metal have been previously observed by Burger and Bergman[15] in iridium−silyl complexes and more recently by Tobita et al. in tungsten−silyl complexes.[16] Interestingly, the reaction shown in Scheme 5 (upper path) is reversible.[17] Hence, when crystals of ***fac*-5** are redissolved in benzene and heated to 100 °C (under pressure), they convert slowly back to ***mer*-4E**.

It is striking that ***mer*-4E** undergoes rearrangement to ***fac*-5**, while its close analogue ***mer*-1E** is stable under the same conditions. This difference reflects a higher silicon-to-iridium migratory aptitude for the 2,3-dimethylbutadienyl moiety versus the unmethylated butadienyl moiety, which, in turn, could be attributed to the enhanced electron richness and nucleophilicity of the dimethylated butadienyl group.

The reaction of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ with the *Z* isomer of (2,3-dimethylbutadienyl)dimethylsilane yields a rather different result. As shown in the lower path of Scheme 5, the expected *Z*-2,3,5,5-tetramethylsilapentadienyl−iridium product, ***mer*-4Z**, cannot be isolated. Rather, the iridacyclopentene complex, ***fac*-6**, is obtained via a rather complicated rearrangement (*vide infra*). The detailed structure of ***fac*-6** can be readily inferred from its NMR spectra. The *fac* geometry is clear from the three dd patterns in the ^{31}P NMR. While H4 still resonates in the downfield region (δ 6.00), the H1's have shifted far upfield into the aliphatic region (δ 2.04 and 1.64) and are joined by a new signal (H2) at δ 2.18. In addition, there are no hydride signals, strongly suggesting that the hydride has migrated to C2. In the ^{13}C NMR, carbons C3 and C4 resonate in the downfield region (δ 150.1 and 125.7, respectively), and C4 is strongly coupled to phosphorus (J_{C-P} = 74.3 Hz), suggesting that it is directly bonded to iridium. Carbons C2 and C1 are shifted upfield (to δ 48.2 and 12.7, respectively), and C1 also displays strong phosphorus coupling (J_{C-P} = 66.7 Hz), indicating that it too is bonded directly to iridium.[18]The metallacyclic structure of ***fac*-6** has been confirmed by X-ray crystallography, and its ORTEP drawing is presented in Figure 3. The iridacyclopentene ring exhibits a slight puckering with C2 displaced 0.37 Å out of the plane made by Ir1, C1, C3, and C4. The bond distances within the ring are fully consistent with the metallacyclopentene formulation (see caption to Figure 3). As in the structure of ***fac*-5**, the *trans*-diaxial silyl and phosphine ligands are tilted with angle Si1−Ir1−P1 = 167.33(3)°.

A likely mechanism for the formation of ***fac*-6** is presented in Scheme 7. From the putative *Z*-2,3,5,5-tetramethylsilapentadienyl−iridium intermediate, ***mer*-4Z**, loss of chloride creates an open coordination site, allowing coordination of double bond C1═C2 (intermediate **B**). Migration of the hydride ligand from iridium to C2 then produces the 16e$^-$ iridasilacyclohexene ring complex, **C**. Migration of ring carbon C4 from silicon to iridium restores the 18e$^-$ count at iridium, while generating the silylene/iridacyclopentene intermediate, **D**. Finally, chloride addition to the electrophilic silylene ligand yields the observed product, ***fac*-6**.

(E) Reactions of (2,3-Dimethylbutadienyl)dimethylsilanes with (η^2-Cyclooctene)(Me)Ir(PMe_3)$_3$. As shown in Scheme 8, treatment of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with (*E*-2,3-dimethylbutadienyl)dimethylsilane produces *fac*-(η^1-*E*-2,3,5,5-tetramethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ (***fac*-7E**). Similarly, treatment of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with the *Z* isomer of (2,3-dimethylbutadienyl)dimethylsilane produces the *Z* isomer of compound **7** (***fac*-7Z**). The *fac* geometry of both compounds is evident from the three dd signals in their ^{31}P NMR spectra, and they show no tendency to isomerize to the *mer* geometry. The η^1-bonding modes of the silapentadienyl ligands are confirmed by the downfield shifts of chain hydrogens H4, H1$_{anti}$, and H1$_{syn}$ and chain carbons C1−C4. The *E* and *Z* isomers can be distinguished by their ^{1}H NOESY spectra. In the *E* isomer, a NOESY correlation is observed between H4 and the hydrogens of methyl C5 (bonded to C2). In the *Z* isomer, on the other hand, a NOESY correlation is observed between H4 and the hydrogens of methyl C6 (bonded to C3).

The X-ray crystal structure of ***fac*-7E** has been obtained and is presented in Figure 4. As in the structure of ***mer*-1E**, described earlier,[1] the silapentadienyl ligand in ***fac*-7E** is W-shaped with torsional angle C1−C2−C3−C4 equal to 175.4(2)° and torsional angle C2−C3−C4−Si1 equal to 172.03(15)°. In addition, the five chain atoms (C1/C2/C3/C4/Si1) are essentially coplanar (mean deviation equals 0.049 Å). However, unlike the structure of ***mer*-1E**, the silapentadienyl ligand in ***fac*-7E** does *not* lie in the molecule's equatorial plane. Instead, rotation about Si1−C4 causes it to be severely canted with respect to that plane (torsional angle C3−C4−Si1−Ir1 equals 70.5(2)°). Most likely, this rotation reflects a relaxation of steric constraints on going from the *mer* geometry of **1E** to the *fac* geometry of **7E**.

(F) Heating of (η^1-2,3,5,5-Tetramethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ Complexes. As shown in Scheme 9 (upper path), heating of *fac*-(η^1-*E*-2,3,5,5-tetramethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ (***fac*-7E**) in toluene at reflux leads to reductive elimination of methane, followed by oxidative addition across

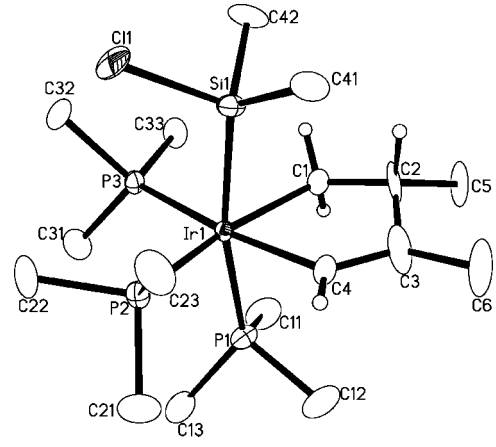


Figure 3. ORTEP drawing of ***fac*-6**, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown. Selected bond distances (Å): Ir1−P1, 2.3776(15); Ir1−P2, 2.3176(6); Ir1−P3, 2.3361(5); Ir1−Si1, 2.3698(16); Ir1−C1, 2.140(2); Ir1−C4, 2.1150(19); C1−C2, 1.493(9); C2−C3, 1.489(12); C2−C5, 1.584(15); C3−C4, 1.389(3); C3−C6, 1.470(3); Si1−Cl(1), 2.189(3); Si1−C41, 1.886(15); Si1−C42, 1.895(5).

(13) NMR monitoring of the reaction also shows the presence of a second *mer* isomer in which the chloride ligand lies *trans* to the hydride. This species gradually converts to ***mer*-4E**.

(14) A similar trend has been observed by Aizenberg and Milstein: see ref 6.

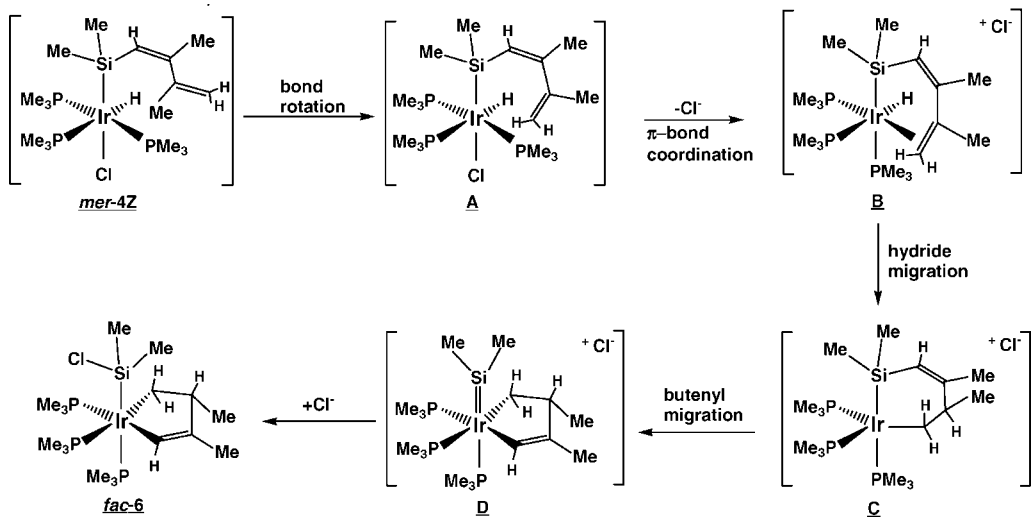
(15) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462–10463.

(16) Suzuki, E.; Okazaki, M.; Tobita, H. *Chem. Lett.* **2005**, *34*, 1026–1027.

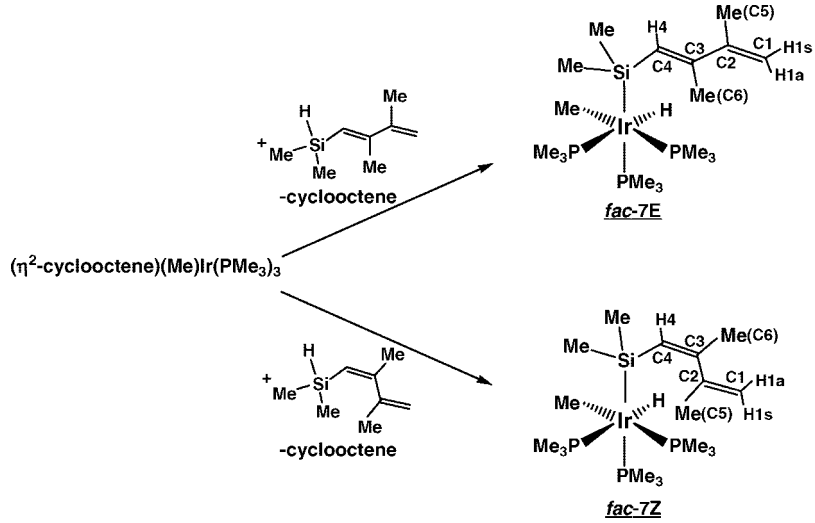
(17) For further examples of the reverse reaction, see ref 16 and: Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816–1817.

(18) A second (minor) *fac* isomer of **6** is also observed by NMR. While most of this isomer's NMR peaks overlap those of the major isomer, the signals for H2 and C2 are shifted (to δ 2.71 and 47.3, respectively) and are hence easily identifiable in the ^{1}H and ^{13}C NMR spectra. This suggests that the two isomers may differ only in the stereochemistry at ring carbon C2.

Scheme 7



Scheme 8



a C−H bond of methyl group C6, producing the isopropenyl-substituted iridasilacyclopentene ring, ***fac*-8**. The ^{31}P NMR spectrum of ***fac*-8** consists of three dd signals, confirming the *fac* coordination geometry. In the ^{1}H NMR spectrum, the signals for H4 (δ 6.51), H1 (δ 5.59), and H1 (δ 5.13) remain in the downfield region, but one of the chain methyl singlets is missing, and in its place are two multiplets at δ 2.66 and 2.16, which integrate to one H apiece. These multiplets are due to the two inequivalent H6's (see atom labeling in Scheme 9), which lie above and below the metallacyclic plane. In the ^{13}C NMR spectrum, carbon C6 shifts upfield to δ 5.2 and is strongly coupled to phosphorus (J_{C-P} = 66.6 Hz), indicating that it is directly bonded to iridium. Carbon atoms C1 to C4 remain in the downfield region (δ 164.6 to 110.8).

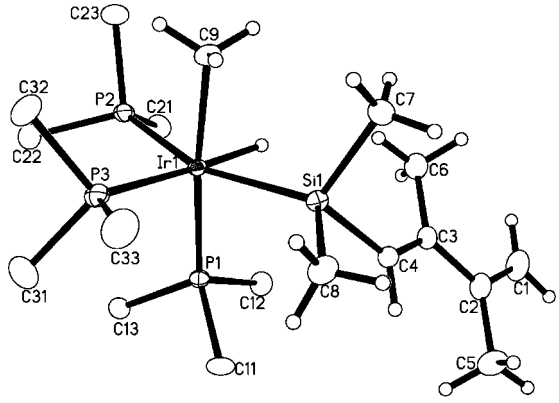
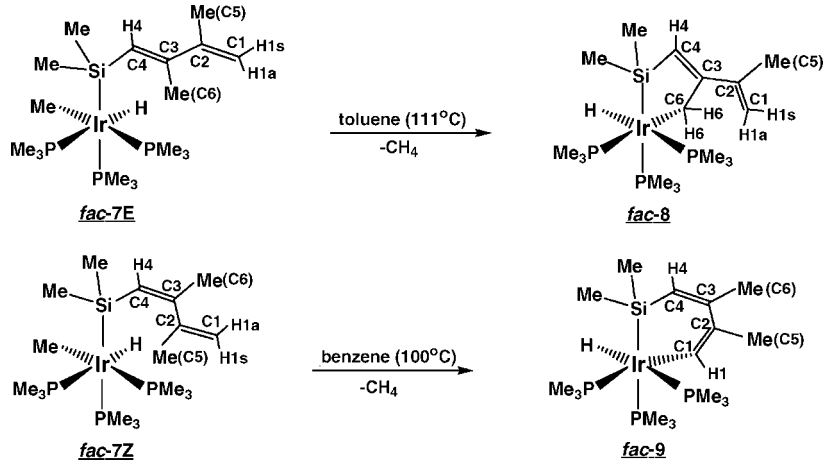


Figure 4. ORTEP drawing of ***fac*-7E**, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown. Selected bond distances (Å): Ir1−P1, 2.3014(5); Ir1−P2, 2.3372(6); Ir1−P3, 2.3229(5); Ir1−C9, 2.1688(19); Ir1−H1, 1.55(3); Ir1−Si1, 2.4166(6); Si1−C4, 1.909(2); Si1−C7, 1.903(2); Si1−C8, 1.905(2); C1−C2, 1.336(3); C2−C3, 1.482(3); C2−C5, 1.507(3); C3−C4, 1.346(3); C3−C6, 1.505(3).

This cyclometalation reaction is closely related to the cyclometalation of an η^1-tetramethylsilaallyl ligand, which we reported earlier.[1] In that reaction, heating of *fac*-(η^1-1,1,3,3-tetramethylsilaallyl)(H)(Me)Ir(PMe_3)$_3$ in toluene at reflux led to methane loss and oxidative addition across a C−H bond in one of the terminal methyl groups. The resulting iridasilacyclopentene product was identical to ***fac*-8** except for a methyl group in place of ***fac*-8**'s isopropenyl group.[19]

(19) For other examples of cyclometalations to form iridasilacycles, see ref 6 and: (a) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472–5474. (b) Aizenberg, M.; Milstein, D. *Organometallics* **1996**, *15*, 3317–3322.

Scheme 9



As shown in Scheme 9 (lower path), heating of *fac*-(η^1-*Z*-2,3,5,5-tetramethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ (***fac*-7Z**) in benzene at 100 °C (under pressure) results in reductive elimination of methane, followed by oxidative addition across C−H1$_{anti}$, producing the iridasilacyclohexadiene complex, ***fac*-9**. The ^{31}P NMR of ***fac*-9** consists of three dd patterns, confirming the *fac* octahedral coordination geometry. In the ^{1}H NMR, H1 and H4 appear in the downfield region of the spectrum at δ 7.10 and 5.74, respectively, and the H1 signal is a widely spaced doublet (J = 23.7 Hz) due to strong coupling to the phosphine that lies *cis* to it in the ring plane. In the ^{13}C NMR, the four ring carbons (C1−C4) all resonate in the downfield region (δ 152.4 to 121.0). Carbon C1 is strongly coupled to the *trans* phosphine (J_{C-P} = 74.3 Hz).

It is interesting to compare the thermal reaction of *fac*-(η^1-*Z*-2,3,5,5-tetramethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ (***fac*-7Z**) with that of its close analogue, *fac*-(η^1-*Z*-dimethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ (***fac*-2Z**). Recall from Scheme 3 that heating of ***fac*-2Z** in benzene at 100 °C (under pressure) releases methane and produces (η^1,η^2-dimethylsilapentadienyl)Ir(PMe_3)$_3$, **3**. No C−H bond activation is observed. We suspect that a transient η^1,η^2-silapentadienyl intermediate may also form when ***fac*-7Z** is heated in benzene. However, in this case, the methylation of the silapentadienyl chain weakens the olefin−metal interaction, allowing C1═C2 to dissociate. The resulting 16e$^-$ iridium center then oxidatively adds across C1−H1 to produce the observed iridasilacyclohexadiene.

Similar behavior is observed in the all-carbon pentadienyl−iridium−phosphine system.[8] Hence, when (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ is treated with unmethylated pentadienide, (η^1,η^2-pentadienyl)Ir(PMe_3)$_3$ is produced. However, the same reaction involving 2,4-dimethylpentadienide generates an equilibrium mixture of the η^1,η^2-pentadienyl compound and the iridacyclohexadiene.

Summary. Using a Si−H bond activation strategy, we have synthesized the first examples of (silapentadienyl)metal complexes. Treatment of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ or (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with *E*- or *Z*-butadienyldimethylsilane results in the production of (η^1-dimethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$ or (η^1-dimethylsilapentadienyl)-(H)(Me)Ir(PMe_3)$_3$ complexes in high yield. Upon heating, (η^1-*Z*-dimethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ undergoes methane loss and coordination of the terminal silapentadienyl π-bond, producing an η^1,η^2-silapentadienyl−iridium derivative. Similarly, treatment of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ or (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ with *E*- or (*Z*-2,3-dimethylbutadienyl)dimethylsilane leads to (η^1-2,3,5,5-tetramethylsilapentadienyl)(H)(Cl)Ir(PMe_3)$_3$ or (η^1-2,3,5,5-tetramethylsilapentadienyl)(H)(Me)Ir(PMe_3)$_3$ complexes. The chloro-containing compounds undergo novel rearrangements, including 1,2-migrations of the 2,3-dimethylbutadienyl groups from silicon to iridium. The methyl derivatives, on the other hand, undergo reductive elimination of methane (upon heating), followed by oxidative addition across a silapentadienyl C−H bond to produce five- or six-membered iridasilacycles. Among the products isolated is the first example of a metallasilacyclohexadiene. We are currently investigating the possible conversion of this and related compounds to stable iridasilabenzenes.

Experimental Section

General Comments on Experimental Techniques. 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 in sealed vials and used as received. The following reagents were used as obtained from the supplier indicated: 1.6 M methyllithium in diethyl ether (Aldrich), 2-methyl-1-buten-3-yne (Aldrich), 3.0 M ethylmagnesium bromide in diethyl ether (Aldrich), chlorodimethylsilane (Aldrich), 2.0 M trimethylaluminum in hexanes (Aldrich), and Cp_2ZrCl_2 (Aldrich). (η^2-Cyclooctene)(Cl)Ir(PMe_3)$_3$[5] was prepared by the literature method, while *E*- and (*Z*-butadienyl)dimethylsilanes were prepared as previously described.[1]

Photolyses were performed in Pyrex vessels using a 450 W Conrad-Hanovia medium-pressure vapor lamp.

NMR experiments were performed on a Varian Unity Plus-300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz), a Varian Mercury-300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz), a Varian Unity Plus-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz), or a Varian Unity-600 spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz; ^{31}P, 242 MHz). ^{1}H and ^{13}C spectra were referenced to tetramethylsilane, while ^{31}P spectra were referenced to external H_3PO_4. HMQC (^{1}H-detected multiple quantum coherence) and HMBC (heteronuclear multiple bond correlation) experiments aided in assigning some of the ^{1}H and ^{13}C peaks. ^{1}H NOESY experiments were, in some cases, used to assign double-bond stereochemistry. Butadienylsilane and silapentadienyl chain carbons are numbered C1−C4, with C1 on the end of the chain opposite silicon.

High-resolution EI mass spectra were obtained on a VG ZAB-T four-sector tandem mass spectrometer, while high-resolution ESI mass spectra were obtained using a Micromass ATOF-Ultima quadrupole-TOF mass spectrometer with electrospray ionization.

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

Synthesis of (η^2-Cyclooctene)(Me)Ir(PMe_3)$_3$. To a cold solution of (η^2-cyclooctene)(Cl)(Ir)(PMe_3)$_3$ (0.51 g, 0.90 mmol) in THF was added 1.6 M methyllithium in diethyl ether (0.56 mL, 0.90 mmol) dropwise by syringe. The solution was stirred at room temperature for 2 h, producing a brownish-red solution. After removal of the solvent under vacuum, the brown residue was extracted with pentane and filtered, yielding a yellow solution. Yellow crystals were obtained upon cooling a saturated pentane solution to −30 °C. Yield: 0.33 g (67%). In the solid state, the crystals gradually lost cyclooctene, producing (Me)Ir(PMe_3)$_3$. Anal. Calcd for 55% (η^2-cyclooctene)(Me)(Ir)(PMe_3)$_3$ ($IrP_3C_{18}H_{44}$) and 45% (Me)Ir(PMe_3)$_3$ ($IrP_3C_{10}H_{30}$): C, 34.86; H, 7.67. Found: C, 34.86; H, 7.55. ^{1}H NMR (acetone-d_6, 22 °C): δ 1.7−1.5 (br m's, 14, cyclooctene), 1.38 (filled-in d, J_{H-P} = 6.6 Hz, 18, PMe_3's *trans* to cyclooctene), 1.28 (d, J_{H-P} = 6.9 Hz, 9, PMe_3 *trans* to Me), −0.41 (triplet of doublets, J_{H-P} = 10.2 Hz, 5.1 Hz, 3, IrMe). ^{31}P{^{1}H} NMR (acetone-d_6, 22 °C): δ −54.6 (t, J_{P-P} = 16.0 Hz, 1, PMe_3 *trans* to Me), −58.2 (d, J_{P-P} = 16.0 Hz, 2, PMe_3's *trans* to cyclooctene). In solution, cyclooctene slowly dissociated (∼80% complete in 1 h), producing (Me)Ir(PMe_3)$_3$. ^{1}H NMR (acetone-d_6, 22 °C): δ 1.55 (d, J_{H-P} = 7.8 Hz, 9, PMe_3), 1.48 (virtual t, J_{H-P} = 6.6 Hz, 18, mutually *trans* PMe_3's), −0.08 (triplet of doublets, J_{H-P} = 8.2 Hz, 4.8 Hz, 3, IrMe). ^{31}P{^{1}H} NMR (acetone-d_6, 22 °C): δ −49.6 (d, J_{P-P} = 21.4 Hz, 2, mutually *trans* PMe_3's), −55.8 (t, J_{P-P} = 21.4 Hz, 1, PMe_3).

Synthesis of (2-Methyl-1-buten-3-ynyl)dimethylsilane, CH_2=C(Me)C≡CSiMe_2H. To a cold (0 °C) solution of 2-methyl-1-buten-3-yne (1.96 g, 0.03 mol) in 50 mL of THF was added dropwise a 3.0 M solution of ethylmagnesium bromide in diethyl ether (20 mL, 0.06 mol). The resulting mixture was stirred at 0 °C for 1 h and then at room temperature for another hour. After cooling the solution to 0 °C, chlorodimethylsilane (5.68 g, 0.06 mol) was added dropwise, and this mixture was stirred at 0 °C for 1 h and at room temperature for 2 h. After dropwise addition of 70 mL of 3.0 M HCl at 0 °C, the resulting pale yellow solution was transferred to a 250 mL separatory funnel and the aqueous layer was discarded. The organic layer was washed once with 20 mL of water, four times with 20 mL of $NaHCO_3$-saturated water, and twice with 20 mL of NaCl-saturated water. The organic solvent was removed *in vacuo*, and the remaining residue was purified by trap-to-trap vacuum distillation (at room temperature, 1×10^{-2} Torr) to yield the colorless product. Yield: 2.05 g (55%). HREI MS: calcd for $SiC_7H_{12}^+$ 124.0703, found 124.0692. Note: The purified product contained a small quantity of THF. ^{1}H NMR (chloroform-*d*, 22 °C): δ 5.29 (s, 1, H1), 5.19 (s, 1, H1), 4.11 (septet, 3.6 Hz, 1, SiH), 1.81 (s, 3, Me), 0.18 (d, J_{Me-SiH} = 3.6 Hz, 6, SiMe's). ^{13}C{^{1}H} NMR (chloroform-*d*, 22 °C): δ 126.5 (s, C2), 123.1 (s, C1), 107.5 (s, C3), 89.7 (s, C4), 23.0 (s, Me), −3.2 (s, SiMe's).

Synthesis of (*E*-2,3-Dimethylbutadienyl)dimethylsilane, *E*-CH_2=C(Me)C(Me)=CHSiMe_2H. A 250 mL Schlenk flask was charged with CH_2Cl_2 (30 mL), Cp_2ZrCl_2 (5.8 g, 0.02 mol), and a solution of 2.0 M $AlMe_3$ in hexanes (20 mL, 0.04 mol). To the resulting yellow solution was added (2-methyl-1-buten-3-ynyl)dimethylsilane (2.5 g, 0.02 mol). After it had been stirred for 15 h at room temperature, the orange solution was cooled to 0 °C and quenched with cold water. The white precipitate was removed by filtration, and the yellow solution was collected. Solvents were removed *in vacuo*, and the remaining residue was purified by trap-to-trap vacuum distillation (at room temperature, 1×10^{-2} Torr) to yield colorless (2,3-dimethylbutadienyl)dimethylsilane with *E*:*Z* mol ratio of 7:3. Yield: 2.1 g (75%). HREI MS: calcd for $SiC_8H_{16}^+$ 140.1016, found 140.1022. Note: The purified product contained a small quantity of hexanes. ^{1}H NMR (chloroform-*d*, 22 °C): δ 5.62 (d, J_{H4-SiH} = 4.2 Hz, 1, H4), 5.12 (s, 1, H1), 5.01 (s, 1, H1), 4.29 (d of heptets, J_{SiH-H4} = 4.2 Hz, J_{SiH-Me} = 3.9 Hz, 1, SiH), 2.02 (s, 3, H6's), 1.92 (s, 3, H5's), 0.18 (d, J_{Me-SiH} = 3.9 Hz, 6, SiMe's). ^{13}C{^{1}H} NMR (chloroform-*d*, 22 °C): δ 153.5 (s, C3), 146.3 (s, C2), 124.5 (s, C4), 114.1 (s, C1), 21.9 (s, C5), 20.3 (s, C6), −2.3 (s, SiMe's).

Synthesis of (*Z*-2,3-Dimethylbutadienyl)dimethylsilane, *Z*-CH_2=C(Me)C(Me)=CHSiMe_2H. A 0.3 mL sample of (2,3-dimethylbutadienyl)dimethylsilane (*E*:*Z* ratio = 7:3 from previous synthesis) was diluted with 1 mL of benzene, and a small quantity of duroquinone was added as a photosensitizer. The resulting yellowish solution was irradiated with ultraviolet light for 2 h, yielding a pale green solution of (2,3-dimethylbutadienyl)dimethylsilane with *E*:*Z* mol ratio of 2:8. ^{1}H NMR (chloroform-*d*, 22 °C): δ 5.24 (d, J_{H4-SiH} = 3.9 Hz, 1, H4), 4.84−4.81 (complex m, 2, H1's), 4.10 (d of heptets, J_{SiH-H4} = 3.9 Hz, J_{SiH-Me} = 3.9 Hz, 1, SiH), 1.93 (s, 3, H6's), 1.83 (s, 3, H5's), 0.11 (d, J_{Me-SiH} = 3.9 Hz, 6, SiMe's). ^{13}C{^{1}H} NMR (chloroform-*d*, 22 °C): δ 159.9 (s, C3), 149.1 (s, C2), 123.8 (s, C4), 113.6 (s, C1), 27.2 (s, C6), 22.7 (s, C5), −1.7 (s, SiMe's).

Synthesis of *mer*-(H)(Cl)(PMe_3)$_3$Ir(SiMe_2CH=CHCH=CH_2) (*mer*-1E). To a solution of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ (0.25 g, 0.44 mmol) in 30 mL of THF was added (*E*-butadienyl)dimethylsilane (0.049 g, 0.44 mmol). After stirring for 4 h at room temperature, the solvent was removed *in vacuo*. The resulting oily yellow residue was extracted with pentane, concentrated, and cooled to −30 °C, causing yellow crystals of ***mer*-1E** to form overnight. Yield: 0.21 g (84%). Anal. Calcd for $IrClP_3SiC_{15}H_{39}$: C, 31.70; H, 6.93. Found: C, 31.21; H, 7.05. ^{1}H (benzene-d_6, 22 °C): δ 6.63 (dd, J_{H3-H4} = 17.7 Hz, J_{H3-H2} = 10.2 Hz, 1, H3), 6.47 (ddd, $J_{H2-H1anti}$ = 16.8 Hz, J_{H2-H3} = 10.2 Hz, $J_{H2-H1syn}$ = 9.9 Hz, 1, H2), 6.30 (d, J_{H4-H3} = 17.7 Hz, 1, H4), 5.20 (d, $J_{H1anti-H2}$ = 16.8 Hz, 1, $H1_{anti}$), 5.01 (d, $J_{H1syn-H2}$ = 9.9 Hz, 1, $H1_{syn}$), 1.51 (virtual t, J_{H-P} = 7.2 Hz, 18, mutually *trans* PMe_3's), 1.23 (d, J_{H-P} = 7.5 Hz, 9, PMe_3), 0.51 (s, 6, SiMe's), −10.46 (doublet of triplets, J_{H-P} = 133.8 Hz, 21.0 Hz, 1, IrH). ^{13}C{^{1}H} NMR (benzene-d_6, 22 °C): δ 148.5 (s, C4), 141.5 (s, C2), 140.6 (s, C3), 115.4 (s, C1), 21.6 (virtual t, J_{C-P} = 40.7 Hz, mutually *trans* PMe_3's), 19.6 (d, J_{C-P} = 27.1 Hz, PMe_3), 9.4 (s, SiMe's). ^{31}P{^{1}H} NMR (benzene-d_6, 22 °C): −54.7 (d, J_{P-P} = 20.8 Hz, 2, mutually *trans* PMe_3's), −57.2 (t, J_{P-P} = 20.8 Hz, 1, PMe_3).

Observation of *fac*-(H)(Cl)(PMe_3)$_3$Ir(SiMe_2CH=CHCH=CH_2) (*fac*-1E). Immediate workup of the previous reaction allowed spectroscopic observation of the initially formed *fac* isomer, ***fac*-1E**. ^{1}H NMR (benzene-d_6, 22 °C): δ 6.91−6.74 (complex second-order m, 2, H3 and H4), 6.57 (ddd, $J_{H2-H1anti}$ = 16.8 Hz, $J_{H2-H1syn}$ = 9.9 Hz, J_{H2-H3} = 9.0 Hz, 1, H2), 5.20 (dd, $J_{H1anti-H2}$ = 16.8 Hz, $J_{H1anti-H1syn}$ = 1.8 Hz, 1, $H1_{anti}$), 5.00 (dd, $J_{H1syn-H2}$ = 9.9 Hz, $J_{H1syn-H1anti}$ = 1.8 Hz, 1, $H1_{syn}$), 1.28 (d, J_{H-P} = 7.8 Hz, 9, PMe_3), 1.21 (d, J_{H-P} = 6.9 Hz, 9, PMe_3), 1.20 (d, J_{H-P} = 10.8 Hz, 9, PMe_3), 0.97 (d, J = 1.8 Hz, 3, SiMe), 0.92 (d, J = 2.4 Hz, 3, SiMe), −10.66 (ddd, J_{H-P} = 145.5 Hz, 22.5 Hz, 17.1 Hz, 1, IrH). ^{31}P{^{1}H} (benzene-d_6, 22 °C): δ −44.5 (dd, J_{P-P} = 11.0 Hz, 9.4 Hz, 1, PMe_3), −50.9 (dd, J_{P-P} = 24.0 Hz, 11.0 Hz, 1, PMe_3), −55.7 (dd, J_{P-P} = 24.0 Hz, 9.4 Hz, 1, PMe_3).

Synthesis of *fac*-(H)(Me)(PMe_3)$_3$Ir(SiMe_2CH=CHCH=CH_2) (*fac*-2E). To a stirred solution of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ (0.29 g, 0.53 mmol) in 30 mL of THF was added (*E*-butadienyl)dimethylsilane (0.060 g, 0.53 mmol). After stirring for 30 min at room temperature, the solvent was removed *in vacuo*, and the orange residue was extracted with pentane. Removal of the pentane left ***fac*-2E** as a pure orange solid. Yield: 0.23 g (79%). Anal. Calcd for $IrP_3SiC_{16}H_{42}$: C, 35.08; H, 7.74. Found: C, 34.89; H, 7.68. ^{1}H NMR (benzene-d_6, 22 °C): δ 6.80 (dd, J_{H3-H4} = 18.0 Hz, J_{H3-H2} = 8.4 Hz, 1, H3), 6.73 (d, J_{H4-H3} = 18.0 Hz, 1, H4), 6.61 (ddd, $J_{H2-H1anti}$ = 16.8 Hz, $J_{H2-H1syn}$ = 9.6 Hz, J_{H2-H3} = 8.4 Hz, 1, H2), 5.20 (dd, $J_{H1anti-H2}$ = 16.8 Hz, $J_{H1anti-H1syn}$ = 2.1 Hz, 1, $H1_{anti}$), 4.99 (dd, $J_{H1syn-H2}$ = 9.6 Hz, $J_{H1syn-H1anti}$ = 2.1 Hz, $H1_{syn}$), 1.32 (d, J_{H-P} = 7.8 Hz, 9, PMe_3), 1.13 (d, J_{H-P} = 7.8 Hz, 9, PMe_3), 1.11 (d, J_{H-P} = 6.9 Hz, 9, PMe_3), 0.81 (d, J = 1.8 Hz, 3, SiMe), 0.75 (d,

J = 2.1 Hz, 3, SiMe), 0.30 (complex m, 3, IrMe), −12.18 (ddd, J_{H-P} = 132.6 Hz, 17.5 Hz, 17.5 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (benezene-d_6, 22 °C): δ 151.7 (s, C4), 142.2 (s, C2), 138.8 (s, C3), 113.0 (s, C1), 25.9 (d, J_{C-P} = 27.2 Hz, PMe_3), 21.4 (d, J_{C-P} = 25.2 Hz, PMe_3), 20.4 (d, J_{C-P} = 23.4 Hz, PMe_3), 7.7 (s, SiMe), 5.9 (s, SiMe), −30.8 (ddd, J_{C-P} = 62.2 Hz, 7.8 Hz, 7.8 Hz, IrMe). $^{31}P\{^1H\}$ NMR (benezene-d_6, 22 °C): δ −57.5 (dd, J_{P-P} = 16.7 Hz, 16.0 Hz, 1, PMe_3), −58.5 (dd, J_{P-P} = 21.3 Hz, 16.0 Hz, 1, PMe_3), −61.5 (dd, J_{P-P} = 21.3 Hz, 16.7 Hz, 1, PMe_3).

Synthesis of *fac*-(H)(Me)(PMe_3)$_3$Ir($SiMe_2CH{=}CHCH{=}CH_2$) (*fac*-2Z). A procedure identical to that described above was employed, except that (*Z*-butadienyl)dimethylsilane replaced the (*E*-butadienyl)dimethylsilane. Yield: 0.22 g (75%). Anal. Calcd for $IrP_3SiC_{16}H_{42}$: C, 35.08; H, 7.74. Found: C, 34.89; H, 7.68. ^1H NMR (benzene-d_6, 22 °C): δ 7.46 (ddd, $J_{H2-H1anti}$ = 16.8 Hz, J_{H2-H3} = 11.0 Hz, $J_{H2-H1syn}$ = 10.5 Hz, 1, H2), 6.95 (dd, J_{H3-H4} = 14.1 Hz, J_{H3-H2} = 11.0 Hz, 1, H3), 6.55 (d, J_{H4-H3} = 14.1 Hz, 1, H4), 5.26−5.18 (complex m, 2, H1's), 1.42 (d, J_{H-P} = 8.1 Hz, 9, PMe_3), 1.33 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 1.20 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 0.90 (d, J = 2 Hz, 3, SiMe), 0.83 (d, J = 2 Hz, 3, SiMe), 0.22 (complex m, 3, IrMe), −11.96 (ddd, J_{H-P}= 132.9 Hz, 18.9 Hz, 18.9 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 151.3 (s, C4), 139.6 (s, C2), 139.0 (s, C3), 115.2 (s, C1), 26.0−25.5 (m, PMe_3's), 21.5 (d, J_{C-P} = 25.0 Hz, PMe_3), 9.0 (s, SiMe), 8.2 (s, SiMe), −30.6 (ddd, J_{C-P} = 62.2 Hz, 7.8 Hz, 7.8 Hz, IrMe). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −57.3 (dd, J_{P-P} = 17.5 Hz, 16.7 Hz, 1, PMe_3), −58.3 (dd, J_{P-P} = 19.8 Hz, 16.7 Hz, 1, PMe_3), −62.1 (dd, J_{P-P}= 19.8 Hz, 17.5 Hz, 1, PMe_3).

Synthesis of (PMe_3)$_3$Ir($SiMe_2CH{=}CHCH{=}CH_2$) (3). A solution of *fac*-(H)(Me)(PMe_3)$_3$Ir($SiMe_2CH{=}CHCH{=}CH_2$) (***fac*-2Z**) (0.25 g, 0.46 mmol) in benzene was heated in a sealed NMR tube at 100 °C for 20 h. The solvent was removed *in vacuo*, and the residue was extracted with pentane. After removal of the pentane under vacuum, the yellow residue was dissolved in a minimal quantity of acetone and cooled to −30 °C, resulting in the formation of yellow crystals of **3**. Yield: 0.20 g (82%). Anal. Calcd for $IrP_3SiC_{15}H_{38}$: C, 33.88; H, 7.22. Found: C, 33.68; H, 7.18. HRESI MS: calcd for $IrP_3SiOC_{15}H_{41}^+$ ($M + H_3O^+$) 551.1769, found 551.1750. ^1H NMR (benzene-d_6, 22 °C): δ 7.65 (apparent quintet, $J \approx$ 5.1 Hz, 1, H3), 5.88 (v br d, $J \approx$ 9 Hz, 1, H4), 2.52 (complex m, 1, H2), 1.76 (complex m, 1, H1), 1.63 (complex m, 1, H1), 1.40 (d, J_{H-P} = 7.5 Hz, 9, PMe_3), 1.32 (d, J_{H-P} = 7.5 Hz, 9, PMe_3), 0.86 (d, J_{H-P} = 6.6 Hz, 9, PMe_3), 0.65 (t, J = 1.8 Hz, 3, SiMe), 0.61 (d, J = 2.4 Hz, 3, SiMe). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 159.0 (s, C3), 133.1 (d, J_{C-P} = 7.9 Hz, C4), 39.0 (dd, J_{C-P} = 23.8 Hz, 7.8 Hz, C2), 25.9 (d, J_{C-P} = 25.4 Hz, PMe_3), 25.7 (d, J_{C-P} = 25.4 Hz, PMe_3), 24.1 (ddd, J_{C-P} = 31.2 Hz, 7.8 Hz, 3.9 Hz, C1), 17.9 (d, J_{C-P} = 21.5 Hz, PMe_3), 7.4 (d, J = 7.8 Hz, SiMe), 4.4 (t, J = 6.9 Hz, SiMe). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −55.8 (dd, J_{P-P} = 45.8 Hz, 22.8 Hz, 1, PMe_3), − 57.6 (dd, J_{P-P} = 45.8 Hz, 25.6 Hz, 1, PMe_3), −60.6 (dd, J_{P-P} = 25.6 Hz, 22.8 Hz, 1, PMe_3).

Synthesis of *mer*-(H)(Cl)(PMe_3)$_3$Ir($SiMe_2CH{=}C(Me)C(Me){=}CH_2$) (*mer*-4E). To a solution of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ (0.62 g, 1.1 mmol) in 40 mL of THF was added (*E*-2,3-dimethylbutadienyl)dimethylsilane (0.15 g, 1.1 mmol). After the solution was stirred for 4 h at room temperature, the solvent was removed *in vacuo*, and the yellow residue was extracted with pentane. Removal of the pentane left ***mer*-4E** as a pure yellow solid. Yield: 0.52 g (79%). Anal. Calcd for $IrClP_3SiC_{17}H_{43}$: C, 34.24; H, 7.28. Found: C, 34.54; H, 7.35. HRESI MS: calcd for $IrP_3SiOC_{17}H_{45}^+$ ($M - Cl + H_2O^+$) 579.2057, found 579.2082. ^1H NMR (benzene-d_6, 22 °C): δ 6.23 (s, 1, H4), 5.18 (s, 1, H1), 5.01 (s, 1, H1), 2.20 (s, 3, H6's), 2.01 (s, 3, H5's), 1.53 (virtual t, J_{H-P} = 7.2 Hz, 18, mutually *trans* PMe_3's), 1.25 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 0.61 (s, 6, SiMe's), −10.37 (d of t, J_{H-P} = 133.8 Hz, 21.0 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 146.4 (s, C2), 144.9 (s, C3), 141.2 (s, C4), 111.2 (s, C1), 21.9 (s, C5), 20.9 (virtual t, J_{C-P} = 38.5 Hz, mutually *trans* PMe_3's), 19.2 (d, J_{C-P} = 25.6 Hz, PMe_3), 18.9 (s, C6), 10.0 (s, SiMe's). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −44.2 (d, J_{P-P} = 22.0 Hz, 2, mutually *trans* PMe_3's), −47.8 (t, J_{P-P} = 22.0 Hz, 1, PMe_3).

Synthesis of *fac*-(H)($SiMe_2Cl$)(PMe_3)$_3$Ir($CH{=}C(Me)C(Me){=}CH_2$) (*fac*-5). A sample of *mer*-(H)(Cl)(PMe_3)$_3$Ir($SiMe_2CH{=}C(Me)C(Me){=}CH_2$) (***mer*-4E**) (0.5 g, 0.84 mmol) was dissolved in a small quantity of acetone and cooled to −30 °C, causing orange crystals of ***fac*-5**·acetone to form overnight. Yield: 0.24 g (44%). Anal. Calcd for $IrClP_3SiC_{17}H_{43}$: C, 34.24; H, 7.28. Found: C, 34.65; H, 7.37. ^1H NMR (benzene-d_6, 22 °C): δ 7.65 (d, J_{H-P} = 18.6 Hz, 1, H4), 5.11 (s, 1, H1), 5.03 (s, 1, H1), 2.28 (s, 3, H6's), 2.17 (s, 3, H5's), 1.41 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 1.23 (d, J_{H-P} = 7.8 Hz, 9, PMe_3), 1.16 (s, 3, SiMe), 0.96 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 0.83 (s, 3, SiMe), −11.64 (d of t, J_{H-P} = 132.0 Hz, 18.3 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 147.3 (s, C2), 138.9 (s, C3), 132.5 (d, J_{C-P} = 67.9 Hz, C4), 106.1 (s, C1), 24.6 (d, J_{C-P} = 29.6 Hz, PMe_3), 24.3 (s, C6), 22.9 (s, C5), 21.5 (d, J_{C-P} = 24.4 Hz, PMe_3), 19.4 (d, J_{C-P} = 27.0 Hz, PMe_3), 17.0 (s, SiMe), 11.1 (s, SiMe). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −56.0 (dd, J_{P-P} = 23.6 Hz, 16.9 Hz, 1, PMe_3), −58.2 (dd, J_{P-P} = 23.6 Hz, 18.2 Hz, 1, PMe_3),−58.5 (dd, J_{P-P} = 18.2 Hz, 16.9 Hz, 1, PMe_3).

Synthesis of *fac*-($SiMe_2Cl$)(PMe_3)$_3$Ir($CH{=}C(Me)C(Me)HCH_2$) (*fac*-6). To a stirred solution of (η^2-cyclooctene)(Cl)Ir(PMe_3)$_3$ (0.62 g, 1.1 mmol) in 30 mL of THF was added (*Z*-2,3-dimethylbutadienyl)dimethylsilane (0.15 g, 1.1 mmol). After stirring for 30 min at room temperature the solvent was removed *in vacuo*, and the resulting yellow residue was extracted with diethyl ether. After removing the diethyl ether under vacuum, the residue was dissolved in THF, concentrated, and cooled to −30 °C, causing yellow crystals of ***fac*-6** to form overnight. Yield: 0.48 g (73%). Anal. Calcd for $IrClP_3SiC_{17}H_{43}$: C, 34.24; H, 7.28. Found: C, 34.34; H, 7.38. ^1H NMR (benzene-d_6, 22 °C): δ 6.00 (apparent t, J_{H-P} = 7.8 Hz, 1, H4), 2.18 (br s, 1, H2), 2.04 (br, 1, H1), 1.89 (d, J= 4.2 Hz, 3, H6's), 1.64 (br, 1, H1), 1.41 (d, J = 7.2 Hz, 3, H5's), 1.32 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 1.27 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 1.00 (s, 3, SiMe), 0.94 (d, J_{H-P} = 6.0 Hz, 9, PMe_3), 0.92 (s, 3, SiMe). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 150.1 (dd, J_{C-P} = 11.5 Hz, 7.7 Hz, C3), 125.7 (ddd, J_{C-P} = 74.3 Hz, 11.5 Hz, 6.3 Hz, C4), 48.2 (d, J_{C-P} = 11.5 Hz, C2), 23.4 (dd, C6), 23.0 (d, J_{C-P} = 6.3 Hz, C5), 21.7 (d, J_{C-P} = 27.0 Hz, PMe_3), 20.3 (d, J_{C-P} = 27.0 Hz, PMe_3), 18.9 (d, J_{C-P} = 21.9 Hz, PMe_3), 12.7 (ddd, J_{C-P} = 66.7 Hz, 7.0 Hz, 5.1 Hz, C1), 10.2 (d, J_{C-P} = 6.3 Hz, SiMe), 9.2 (d, J_{C-P} = 3.9 Hz, SiMe). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −56.1 (dd, J_{P-P} = 17.4 Hz, 12.9 Hz, 1, PMe_3), −60.1 (dd, J_{P-P} = 19.1 Hz, 12.9 Hz, 1, PMe_3), −63.5 (dd, J_{P-P} = 19.1 Hz, 17.4 Hz, 1, PMe_3).

Synthesis of *fac*-(H)(Me)(PMe_3)$_3$Ir($SiMe_2CH{=}C(Me)C(Me){=}CH_2$) (*fac*-7E). To a stirred solution of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ (0.38 g, 0.70 mmol) in 30 mL of THF was added (*E*-2,3-dimethylbutadienyl)dimethylsilane (0.10 g, 0.71 mmol). After stirring for 30 min at room temperature, the solvent was removed *in vacuo*. The residue was extracted with pentane, and the solution was cooled to −30 °C overnight, causing yellow crystals of ***fac*-7E** to form. Yield: 0.34 g (83%). Anal. Calcd for $IrP_3SiC_{18}H_{46}$: C, 37.54; H, 8.07. Found: C, 37.16; H, 8.20. ^1H NMR (benzene-d_6, 22 °C): δ 6.48 (s, 1, H4), 5.18 (d, J_{H-H} = 1.8 Hz, 1, H1), 4.98 (d, J_{H-H} = 1.8 Hz, 1, H1), 2.34 (s, 3, H6's), 2.10 (s, 3, H5's), 1.33 (d, J_{H-P} = 7.5 Hz, 9, PMe_3), 1.16 (d, J_{H-P} = 6.9 Hz, 9, PMe_3), 1.13 (d, J_{H-P} = 6.9 Hz, 9, PMe_3), 0.81 (d, J_{H-P} = 1.8 Hz, 3, SiMe), 0.76 (d, J_{H-P} = 2.4 Hz, 3, SiMe), 0.26 (complex m, 3, IrMe), −12.14 (ddd, J_{H-P} = 131.4 Hz, 18.5 Hz, 16.2 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 147.1 (s, C2), 143.4 (s, C3), 143.3 (m, C4), 109.6 (s, C1), 25.6 (dt, J_{C-P} = 28.2 Hz, 3.9 Hz, PMe_3), 22.1 (s, C5), 21.5 (d, J_{C-P} = 21.7 Hz, PMe_3), 20.3 (dd, J_{C-P} = 24.3 Hz, 6.5 Hz, PMe_3), 19.0 (s, C6), 8.1 (t, J = 5.8 Hz, SiMe),

Table 1. X-ray Diffraction Structure Summary

	(cycloocetene)(Me)Ir(PMe_3)$_3$	***fac*-5**-acetone	***fac*-6**	***fac*-7E**
formula	$IrP_3C_{18}H_{44}$	$IrClP_3SiOC_{20}H_{49}$	$IrClP_3SiC_{17}H_{43}$	$IrP_3SiC_{18}H_{46}$
fw	545.64	654.24	596.16	575.75
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1$	$Pbca$
a, Å	15.2176(6)	9.3183(7)	9.3062(6)	15.8275(8)
b, Å	9.3278(4)	18.2326(15)	10.7212(7)	17.7785(10)
c, Å	17.7508(7)	17.2933(15)	12.1508(7)	17.9098(9)
α, deg	90	90	90	90
β, deg	114.744(2)	104.074(4)	94.122(3)	90
γ, deg	90	90	90	90
V, Å^3	2288.3(16)	2849.9(4)	1209.19(13)	5039.6(5)
Z	4	4	2	8
cryst dimens, mm	0.26 × 0.21 0.16	0.34 × 0.21 × 0.19	0.18 × 0.15 × 0.14	0.18 × 0.14 × 0.14
calcd density, g/cm^3	1.584	1.525	1.637	1.518
radiation; λ, Å	0.71073	0.71073	0.71073	0.71073
temp, K	100(2)	100(2)	100(2)	100(2)
θ range, deg	2.31−36.49	3.02−36.32	2.86−35.86	3.04−32.71
data collected				
h	−25 to 23	−15 to 10	−15 to 14	−23 to 23
k	−15 to 15	−30 to 29	−17 to 17	−26 to 26
l	−28 to 29	−26 to 28	−19 to 19	−27 to 27
total decay	none obsd	none obsd	none obsd	none obsd
no. of data collected	119 939	115 902	67 549	244 958
no. of unique data	11 202	13 806	11 139	9255
Mo Kα linear abs coeff, mm^{-1}	6.042	4.998	5.878	5.536
abs corr applied	numerical	numerical	semiempirical	numerical
data to param ratio	29.87	52.49	47.81	40.95
final R indices (obsd data)[a]				
R1	0.0198	0.0256	0.0261	0.0224
wR2	0.0344	0.0505	0.0446	0.0390
R indices (all data)				
R1	0.0283	0.0387	0.0317	0.0378
wR2	0.0360	0.0534	0.0460	0.0419
goodness of fit	1.031	1.038	1.034	1.030
largest dif peak/hole, e Å^{-3}	1.068, −0.826	1.137, −1.344	0.996, −1.017	0.646, −0.680

[a] $I > 2\sigma(I)$.

8.0 (s, SiMe), −31.0 (ddd, J_{C-P} = 62.8 Hz, 8.3 Hz, 8.3 Hz, 1, IrMe). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −56.8 (apparent t, J_{P-P} = 17.0 Hz, 1, PMe_3), −58.0 (dd, J_{P-P} = 19.8 Hz, 17.0 Hz, 1, PMe_3), −62.8 (dd, J_{P-P} = 19.8 Hz, 17.0 Hz, 1, PMe_3).

Synthesis of *fac*-(H)(Me)(PMe_3)$_3$Ir(SiMe$_2$CH=C(Me)C(Me)=CH$_2$) (*fac*-7Z). A procedure identical to that described above was employed, except (*Z*-2,3-dimethylbutadienyl)dimethylsilane replaced the *E* isomer. Yield: 0.31 g (77%). Anal. Calcd for $IrP_3SiC_{18}H_{46}$: C, 37.54; H, 8.07. Found: C, 37.16; H, 8.20. ^1H NMR (toluene-d_8, −20 °C): δ 6.02 (s, 1, H4), 5.25 (s, 1, H1), 4.99 (s, 1, H1), 2.09 (s, 3, H6's), 2.02 (s, 3, H5's), 1.31 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 1.11 (d, J_{H-P} = 7.2 Hz, 9, PMe_3), 1.06 (d, J_{H-P} = 6.9 Hz, 9, PMe_3), 0.75 (br s, 6, SiMe's), 0.20 (m, 3, IrMe), −12.14 (ddd, J_{H-P} = 131.4 Hz, 17.4 Hz, 17.4 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (toluene-d_8, −20 °C): δ 149.6 (s, C2), 146.8 (s, C3), 141.0 (s, C4), 112.4 (s, C1), 29.3 (s, C6), 25.9 (d, J_{C-P} = 28.3 Hz, PMe_3), 23.8 (s, C5), 21.6 (d, J_{C-P} = 21.7 Hz, PMe_3), 20.6 (d, partially obscured, PMe_3), 8.9 (s, SiMe), 8.4 (s, SiMe), −29.3 (d, J_{C-P} = 61.5 Hz, IrMe). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −57.4 (apparent t, J_{P-P} = 16.8 Hz, 1, PMe_3), −58.1 (dd, J_{P-P} = 21.4 Hz, 16.8 Hz, 1, PMe_3), −62.5 (dd, J_{P-P} = 21.4 Hz, 16.8 Hz, 1, PMe_3).

Synthesis of *fac*-(H)(PMe_3)$_3$Ir(SiMe$_2$CH=C(CMe=CH$_2$)CH$_2$) (*fac*-8). A solution of *fac*-(H)(Me)(PMe_3)$_3$Ir(SiMe$_2$CH=C(Me)-C(Me)=CH$_2$) (***fac*-7E**) (0.60 g, 1.0 mmol) in 50 mL of toluene was heated at reflux for 24 h under nitrogen. From the resulting orange solution, solvent was removed *in vacuo*, and the residue was extracted with pentane. The solvent was removed again under vacuum, and the residue was redissolved in acetone, concentrated, and cooled to −30 °C, causing yellow crystals of ***fac*-8** to form overnight. Yield: 0.51 g (88%). Anal. Calcd for $IrP_3SiC_{17}H_{42}$: C, 36.47; H, 7.58. Found: C, 36.74; H, 7.92. ^1H NMR (benzene-d_6, 22 °C): δ 6.51 (s, 1, H4), 5.59 (d, J_{H-H} = 3.0 Hz, 1, H1), 5.13 (d, J_{H-H} = 3.0 Hz, 1, H1), 2.66 (complex m, 1, H6), 2.26 (s, 3, H5's), 2.16 (complex m, 1, H6), 1.36 (d, J_{H-P} = 7.8 Hz, 9, PMe_3), 1.14 (d, J_{H-P} = 6.9 Hz, 9, PMe_3), 1.11 (d, J_{H-P} = 7.5 Hz, 9, PMe_3), 0.84 (d, J = 2.4 Hz, 3, SiMe), 0.61 (d, J = 2.7 Hz, 3, SiMe), −12.04 (ddd, J_{H-P} = 131.4 Hz, 16.8 Hz, 16.8 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 164.6 (d, J_{C-P} = 11.5 Hz, C3), 146.6 (d, J_{C-P} = 5.1 Hz, C2), 140.7 (d, J_{C-P} = 10.3 Hz, C4), 110.8 (d, J_{C-P} = 3.9 Hz, C1), 25.7 (d, J_{C-P} = 28.2 Hz, PMe_3), 24.1 (s, C5), 21.4 (d, J_{C-P} = 21.9 Hz, PMe_3), 19.7 (d, J_{C-P} = 29.6 Hz, PMe_3), 13.1 (apparent quartet, J_{C-P} = 6.5 Hz, SiMe), 6.9 (dd, J_{C-P} = 8.9 Hz, 3.8 Hz, SiMe), 5.2 (ddd, J_{C-P} = 66.6 Hz, 5.1 Hz, 5.1 Hz, C6). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −56.0 (dd, J_{P-P} = 21.4 Hz, 16.0 Hz, 1, PMe_3), −57.7 (dd, J_{P-P} = 18.3 Hz, 16.0 Hz, 1, PMe_3), −60.4 (dd, J_{P-P} = 21.4 Hz, 18.3 Hz, 1, PMe_3).

Synthesis of *fac*-(H)(PMe_3)$_3$Ir(SiMe$_2$CH=C(Me)C(Me)=CH) (*fac*-9). A solution of *fac*-(H)(Me)(PMe_3)$_3$Ir(SiMe$_2$CH=C(Me)-C(Me)=CH$_2$) (***fac*-7Z**) (0.31 g, 0.54 mmol) in benzene was heated in a sealed NMR tube at 100 °C for 2 h. The solvent was removed under vacuum, and the dark orange residue was extracted with pentane. Removal of pentane left ***fac*-9** as a pure orange product. Yield: 0.20 g (66%). Anal. Calcd for $IrP_3SiC_{17}H_{42}$: C, 36.47; H, 7.58. Found: C, 36.22; H, 7.46. HRESI MS: calcd for $IrP_3SiOC_{17}H_{43}^+$ (M + H_3O − H_2^+) 577.1926, found 577.1919. ^1H NMR (benzene-d_6, 22 °C): δ 7.10 (br d, J_{H-P} = 23.7 Hz, 1, H1), 5.74 (t, J = 1.2 Hz, 1, H4), 2.33 (d, J = 1.5 Hz, 3, H5's), 2.21 (s, 3, H6's), 1.28 (d, J_{H-P} = 7.5 Hz, 9, PMe_3), 1.19 (d, J_{H-P} = 6.9 Hz, 9, PMe_3), 1.14 (d, J_{H-P} = 6.6 Hz, 9, PMe_3), 0.92 (d, J = 1.8 Hz, 3, SiMe), 0.65 (d, J = 2.7 Hz, 3, SiMe), −11.95 (ddd, J_{H-P} = 123.9 Hz, 20.0 Hz, 18.9 Hz, 1, IrH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 152.4 (s, C2), 135.7 (br s, C3), 132.7 (filled-in d, J_{C-P} = 11.6 Hz, C4), 121.0 (d, J_{C-P} = 74.3 Hz, C1), 27.9 (d, J_{C-P} = 7.7 Hz, C5), 25.9 (d, J_{C-P} = 23.1 Hz, PMe_3), 25.8 (partially obscured,

C6), 21.5 (d, $J_{C-P} = 23.1$ Hz, PMe_3), 20.3 (d, $J_{C-P} = 20.5$ Hz, PMe_3), 10.8 (apparent quintet, $J = 7.0$ Hz, SiMe), 6.7 (dd, $J = 8.9$ Hz, 3.8 Hz, SiMe). $^{31}P\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −56.0 (dd, $J_{P-P} = 18.4$ Hz, 18.2 Hz, 1, PMe_3), −57.2 (dd, $J_{P-P} = 18.2$ Hz, 14.6 Hz, 1, PMe_3), −62.5 (dd, $J_{P-P} = 18.4$ Hz, 14.6 Hz, 1, PMe_3).

General Comments on X-ray Diffraction Studies. Single crystals of (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ and compounds ***fac*-5-**acetone, ***fac*-6**, and ***fac*-7E** were mounted on glass fibers under oil. X-ray data were collected on a Bruker SMART charge-coupled device (CCD) detector system at low temperature under nitrogen. 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 either refined isotropically or placed at idealized positions and assumed the riding model. The structure of ***fac*-6** exhibited a 2-fold disorder, which was fully resolved. Ring methyl C5 was refined with partial occupancies in both the "up" and "down" positions, as was ring carbon C2. Similarly, the *trans*-diaxial PMe_3 and $ClSiMe_2$ ligands exhibited partial occupancies in each site. An ORTEP drawing showing the disordered atoms is provided in the Supporting Information. Crystal data and details of both collection and structure analysis are listed in Table 1.

(20) Sheldrick, G. M. *SHELXTL-PLUS*; Bruker Analytical Division: Madison, WI, 1997.

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Supporting Information Available: Structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and torsional angles for (η^2-cyclooctene)(Me)Ir(PMe_3)$_3$ and compounds ***fac*-5-**acetone, ***fac*-6**, and ***fac*-7E**. This material is available free of charge via the Internet at http://pubs.acs.org.

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