Synthesis, Structure, Spectroscopy, and Reactivity of a Neutral Iridathiabenzene[1]

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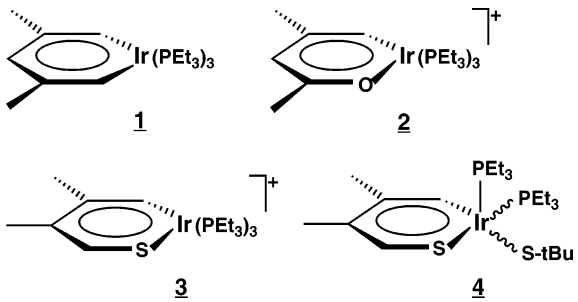
Received May 4, 2004

Treatment of the cationic iridathiabenzene $[\overline{CH{=}C(Me)C(Me){=}CHS{=}}Ir(PEt_3)_3]^+BF_4^-$ (**3**) with sodium *tert*-butylthiolate leads to the production of a stable neutral iridathiabenzene, $\overline{CH{=}C(Me)C(Me){=}CHS{=}}Ir(PEt_3)_2(S\text{-}t\text{-}Bu)$ (**4**). Compound **4** exists in solution as an equilibrating mixture of two square pyramidal isomers, "*cis*" **4a** and "*trans*" **4b**. When **4** is cooled to −30 °C in acetonitrile, it precipitates as an acetonitrile adduct, $\overline{CH{=}C(Me)C(Me){=}CHS}Ir(PEt_3)_2(S\text{-}t\text{-}Bu)(NCMe)$ (**6**), featuring an iridathiacyclohexa-1,3-diene ring system. Compound **6** reverts back to **4** upon redissolving and warming to room temperature. Treatment of **4** (or **6**) with excess PMe_3 results in addition of PMe_3 to the iridium center and replacement of the bulky PEt_3 ligands with PMe_3's, producing $\overline{CH{=}C(Me)C(Me){=}CHS}Ir(PMe_3)_3(S\text{-}t\text{-}Bu)$ (**7**) as a mixture of equilibrating isomers, "*cis*" **7a** and "*trans*" **7b**. Compound **7**, like **6**, includes a nonaromatic iridathiacyclohexa-1,3-diene ring. When **4** in acetonitrile solvent (or **6**) is reacted with trifluoromethanesulfonic acid, protonation occurs at the thiolate sulfur, causing loss of thiol. The resulting cationic fragment dimerizes to produce $\{[\overline{CH{=}C(Me)C(Me){=}CHS}Ir(PEt_3)_2(NCMe)]_2\}^{2+}(O_3SCF_3^-)_2$ (**8**), in which the two iridium centers are bridged by the two ring sulfurs. Finally, treatment of **4** (or **6**) with $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]^+O_3SCF_3^-$ results in production of the sandwich compound $\{\eta^5\text{-}[\overline{CH{=}C(Me)C(Me){=}CHS}Ir(PEt_3)_2(S\text{-}t\text{-}Bu)]Ru(\eta^5\text{-}C_5Me_5)\}^+O_3SCF_3^-$ (**9**), which exists in solution as an equilibrating mixture of isomers, "*cis*" **9a** and "*trans*" **9b**. Compounds **4a**, **7a**, **8**, and **9a** have been structurally characterized by X-ray diffraction.

Introduction

During the past decade, we have been exploring the chemistry of a novel family of iridacycles that exhibit aromatic physical and chemical properties. The first member of this family was "iridabenzene" (**1**), a neutral benzene analogue,[2] and more recent additions have included cationic iridapyrylium **2** [3] and iridathiabenzene **3**.[1] We now wish to report the synthesis of a new member of this unique compound class, the neutral iridathiabenzene **4**, shown below.[4,5] The structure and spectroscopy of this complex strongly imply the presence of an aromatic ring system in which metal d orbitals participate fully in ring π-bonding. However, the reaction chemistry of **4** demonstrates the fragile nature of the metalloaromaticity. Reactions with a variety of nucleophiles, electrophiles, and coordinating metal fragments lead to products in which the aromatic character of the ring is disrupted or destroyed.



Results and Discussion

A. Background. The idea for synthesizing a neutral iridathiabenzene was hatched during an earlier study of the iridathiacyclohexa-1,3-diene chloride complex, **5a** (see Scheme 1). We observed that when a crystalline sample of isomer **5a** was dissolved in polar solvents such

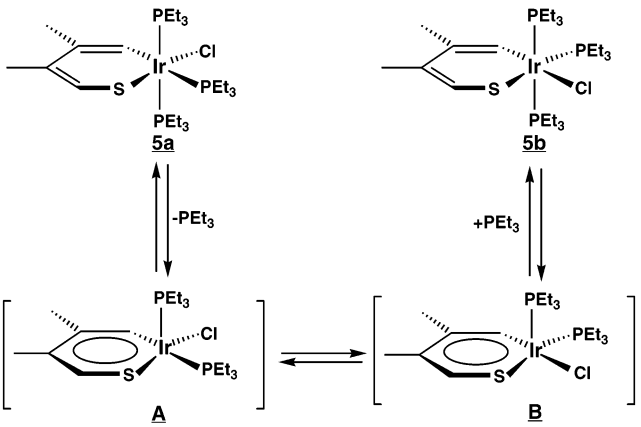
(1) Metallacyclohexadiene and Metallabenzene Chemistry. 18. Part 17: Bleeke, J. R.; Hinkle, P. V.; Rath, N. P. *Organometallics* **2001**, *20*, 1939. See also: Bleeke, J. R.; Hinkle, P. V. *J. Am. Chem. Soc.* **1999**, *121*, 595.

(2) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606. For a recent review of metallabenzenes, see: Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205.

(3) (a) Bleeke, J. R.; Blanchard, J. M. B.; Donnay, E. *Organometallics* **2001**, *20*, 324. (b) Bleeke, J. R.; Blanchard, J. M. B. *J. Am. Chem. Soc.* **1997**, *119*, 5443.

10.1021/om0400649 CCC: $27.50
Publication on Web 07/22/2004

Scheme 1



as acetone, it rapidly established an equilibrium with **5b**, the isomer in which PEt_3 and Cl^- have exchanged positions in the equatorial plane. At room temperature in acetone, the equilibrium ratio **5a**:**5b** was approximately 60:40.

We postulated that this isomerization proceeded through the intermediacy of transient iridathiabenzenes **A** and **B** as shown in Scheme 1. This, in turn, suggested that a *stable* neutral iridathiabenzene could perhaps be generated by replacement of the small chloride ligand in **A** and **B** with a bulkier anionic ligand.

B. Synthesis of a Neutral Iridathiabenzene (4). As shown in Scheme 2, treatment of cationic iridathiabenzene **3** with sodium *tert*-butyl thiolate in tetrahydrofuran produces neutral iridathiabenzene **4** as an equilibrium mixture of two isomers. In the "*cis*" isomer **4a**, the ring sulfur and the *tert*-butylthiolate ligand occupy adjacent basal sites in the square pyramidal coordination geometry, while in the "*trans*" isomer **4b**, the sulfur centers reside in opposite basal sites. Curiously, the relative ratio of **4a** to **4b** at equilibrium varies dramatically with the solvent. In polar solvents such as methanol, **4a** is favored, while in nonpolar solvents such as methylcyclohexane, **4b** predominates. Data for six different solvent systems are presented in Table 1.

A proposed mechanism for interconversion of the *cis* and *trans* isomers of **4** is shown within the "isomer wheel" in Scheme 3. On this wheel, the isomerization is represented by moving counterclockwise from **4a** at 12 o'clock through intermediates **C**, **D**, and **E** to **4b** at 8 o'clock. Note that in each of these interconversions *trans*-basal ligands in the square pyramidal species (**4a**, **D**, and **4b**) become *trans*-diaxial ligands in the trigonal bipyramidal intermediates (**C** and **E**) and vice versa. Square pyramidal intermediate **D** lies at higher energy than either **4a** or **4b** due to steric crowding of the large PEt_3 ligands, which reside in the adjacent basal coordination sites.

C. Spectroscopy of Neutral Iridathiabenzene 4. At room temperature (22 °C) in solution, isomers **4a** and **4b** rapidly interconvert, giving rise to averaged signals in the NMR. The $^{31}P\{^1H\}$ NMR spectrum in methanol-d_4, for example, shows a single broad hump centered at about δ 16.5 (relative to H_3PO_4). Similarly, the ^1H NMR spectrum shows a single very broad resonance for ring proton H1 at δ 10.4, a resonance for ring proton H4 at δ 7.95, ring methyl peaks at δ 2.35 (H5's) and 2.18 (H6's), and a *tert*-butylthiolate resonance at δ 1.40. The triethylphosphine resonances at δ 2.0 (CH_2's) and 1.0 (CH_3's) are uncomplicated, consistent with the fact that all of the phosphine ligands are exchanging at room temperature.[6]

However, as the sample of **4** in methanol-d_4 is cooled, dramatic changes in the NMR spectra begin to occur. At −10 °C, separate signals for the two isomers start to appear in the $^{31}P\{^1H\}$ and ^1H NMR spectra, and by −60 °C, the signals are sharp and well-separated (see Figure 1).

1. *"cis"* Isomer 4a. The $^{31}P\{^1H\}$ NMR spectrum of "*cis*" isomer **4a** in methanol-d_4 at −60 °C consists of a single sharp peak at δ 16.0, indicating that this isomer is fluxional and that the axial and basal phosphine ligands are rapidly exchanging positions. As the sample is cooled further, some broadening of this phosphine signal is observed, indicating a slowing of the exchange process. However, the resonance does not split into two peaks even upon cooling to −100 °C in $CDFCl_2$. Hence, the fluxional process has a very small free energy of activation.

In the ^1H NMR spectrum of **4a** at −60 °C, ring proton H1 resonates at δ 9.79 and appears as a binomial triplet due to coupling to two equivalent (exchanging) phosphines (J_{H-P} = 7.7 Hz). Similarly, ring proton H4 resonates at δ 8.13 and is split into a binomial triplet (J_{H-P} = 5.2 Hz) by the equivalent exchanging phosphines. These downfield ^1H NMR chemical shifts are indicative of an aromatic ring current. The ring methyl groups resonate at δ 2.31 (H5's) and 2.16 (H6's). In the $^{13}C\{^1H\}$ NMR spectrum of **4a** at −60 °C, the ring carbons resonate at δ 152.9 (C1), 139.1 (C2), 132.4 (C3), and 128.3 (C4) and are all singlets.

2. *"trans"* Isomer 4b. The $^{31}P\{^1H\}$ NMR spectrum of "*trans*" isomer **4b** in methanol-d_4 at −60 °C consists of two sharp peaks at δ 25.0 and −8.7, indicating that this isomer (unlike **4a**) is not fluxional at this temperature. Both signals are singlets; the axial and basal phosphines do not couple to one another. In the ^1H NMR spectrum, ring protons H1 and H4 appear at δ 11.02 and 7.88, respectively, again signaling the presence of an aromatic ring current. The H1 signal exhibits weak doublet coupling (J_{H-P} = 5.4 Hz) to the basal phosphine. The ring methyls resonate at δ 2.35 (H5's) and 2.16

(4) Several other examples of metallathiabenzenes have been reported: (a) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (b) Chen, J.; Daniels, L. M.; Angelici, R. J. *Polyhedron* **1990**, *9*, 1883. (c) Chin, R. M.; Jones, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 357. (d) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9851. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731. (f) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sanchez-Delgado, R. *J. Am. Chem. Soc.* **1994**, *116*, 4370.

(5) Several platinacycles (references a−c) and nickelacycles (references d, e) that are closely related to the metallathiabenzenes cited in ref 4 have been reported. However, spectroscopic and structural data suggest that these molecules are better described as metallathiacyclohexa-1,3-dienes. See: (a) Garcia, J. J.; Mann, B. E.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 2179. (b) Garcia, J. J.; Arevalo, A.; Capella, S.; Chehata, A.; Hernandez, M.; Montiel, V.; Picazo, G.; Del Rio, F.; Toscano, R. A.; Adams, H.; Maitlis, P. M. *Polyhedron* **1997**, *16*, 3185. (c) Arevalo, A.; Bernes, S.; Garcia, J. J.; Maitlis, P. M. *Organometallics* **1999**, *18*, 1680. (d) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855. (e) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606.

(6) In addition to the isomerization process discussed in Results and Discussion section B, isomers **4a** and **4b** undergo *intra*molecular fluxional processes that exchange the PEt_3 ligands (vide infra).

Scheme 2

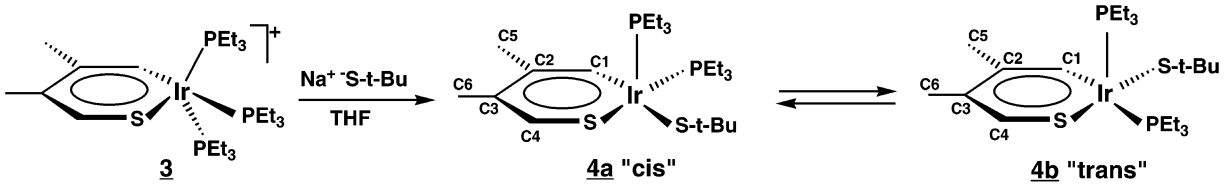


Table 1. Relative Ratios of "*cis*" Isomer (4a) to "*trans*" Isomer (4b) in Various Deuterated Solvent Systems

solvent	4a	4b	temp (°C)
$CDFCl_2$	76.3	23.7	−40
CD_3OD	56.9	43.1	−30
CD_2Cl_2	34.6	65.4	−30
$(CD_3)_2CO$	34.4	65.6	−30
$C_6D_5CD_3$	17.0	83.0	−30
$C_6D_{11}CD_3$	8.0	92.0	−40

(H6's). In the $^{13}C\{^1H\}$ NMR spectrum, C1 appears at δ 171.6 and is strongly coupled (J_{C-P} = 83.4 Hz) to the basal phosphine, which is situated *trans* to it. The other ring carbons resonate at δ 140.7 (C2), 132.2 (C3), and 126.0 (C4) and are all singlets.

3. Explanation for the Difference in Fluxional Behavior Exhibited by 4a and 4b. As described above, the "*cis*" isomer of **4** (**4a**) undergoes intramolecular phosphine ligand exchange much more rapidly than its "*trans*" isomer **4b**. This behavior reflects a difference in the energies of the intermediates that must be accessed in order for exchange to occur. These intermediates possess mirror-plane symmetry, and they have trigonal bipyramidal (tbp) coordination geometries. As shown on the isomer wheel in Scheme 3, the tbp intermediate required for intramolecular phosphine exchange in **4a** is **F** (1 o'clock). This intermediate has ring carbon C1 and the thiolate ligand assuming *trans*-diaxial positions, while the ring sulfur resides in the equatorial plane along with the phosphines (which are now equivalent by symmetry). Intermediate **F** is apparently quite readily accessible and leads to the facile fluxionality of **4a**.[7] It is interesting to note that tbp intermediate **F** bears a strong resemblance to the *ground-state structure* of cationic iridathiabenzene **3**, which has been characterized by X-ray crystallography.[1]

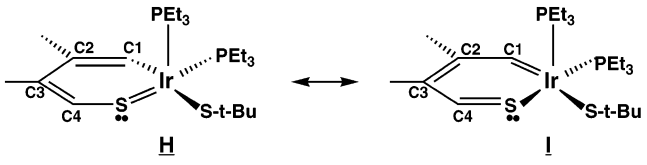
The tbp intermediate required for phosphine exchange in **4b** (**G**, 7 o'clock in Scheme 3) has the ring sulfur and the thiolate ligands in *trans*-diaxial positions, while carbon C1 and the symmetry-related phosphines occupy the equatorial sites. This ligand arrangement is apparently less favorable than that in **F**, leading to the much higher observed barrier for intramolecular phosphine exchange.[7]

Why is the tbp intermediate **G** less stable than **F**? It probably results from the fact that the ring sulfur, a good π-donor ligand, occupies an axial site in **G** but an equatorial site in **F**. Hoffmann[8] and others have shown that in tbp coordination compounds equatorial π-bonding is, in general, more favorable than axial. Calculations by Harris[9] on molecules closely related to **3** also show that an equatorial ring sulfur can π-bond strongly with the metal center.

D. X-ray Crystal Structure of "*cis*" Isomer 4a. When a saturated solution of **4** in methanol was cooled to −30 °C, dark green (almost black) blocks of isomer **4a** crystallized out. Single-crystal X-ray diffraction led to the solid state structure of **4a**, which is presented in Figure 2; selected bond distances and angles are given in the figure caption. The structure confirms the square pyramidal coordination geometry with PEt_3 phosphorus P2 occupying the unique axial site and ring sulfur S1, ring carbon C1, thiolate sulfur S2, and PEt_3 phosphorus P1 occupying the four basal sites. The two sulfur atoms reside *cis* to one another (S1−Ir−S2 = 93.30(10)°).

The metallacyclic ring (C1/C2/C3/C4/S1/Ir) is nearly planar with a mean deviation from the best plane of 0.076 Å. However, the nonmetal atoms of the ring (C1/C2/C3/C4/S1) make an even better plane (mean deviation = 0.050 Å), and the Ir atom sits 0.27 Å out of that plane. The dihedral angle between the C1/C2/C3/C4/S1 plane and the S1/Ir/C1 plane is 9.9°. This slight displacement of the metal center has been observed in related metallacycles[2] and may result from steric interactions between the basal ligands and the ring.

The Ir−S1 distance of 2.263(3) Å is considerably shorter than a typical single bond (cf., the Ir−S2 distance of 2.470(3) Å), reflecting substantial π-bonding between these ring atoms. Similarly, the Ir−C1 distance of 1.993(9) Å is consistent with partial bond character.[10] The carbon−carbon bond distances within the ring lie between the extremes of typical single and double bonds, but C1−C2 (1.391(15) Å) and C3−C4 (1.336(15) Å) are somewhat shorter than C2−C3 (1.455(16) Å), perhaps reflecting a greater contribution by resonance structure **H** to the bonding picture than that of resonance structure **I**. Overall, the bond distances within the metallacycle reflect the delocalization expected for an aromatic ring.



E. Reactivity of Iridathiabenzene 4: Addition of Nucleophiles. While resonance structures **H** and **I** are key to understanding the detailed structural features of **4**, a third resonance structure, **J**, helps to explain its reactivity. In structures **H** and **I**, the iridium center possesses 18 valence electrons, while in **J** it possesses only 16. This is because the electrons in the Ir−S π-bond (resonance structure **H**) have been localized at sulfur. As a result of the contribution from 16e$^-$ resonance

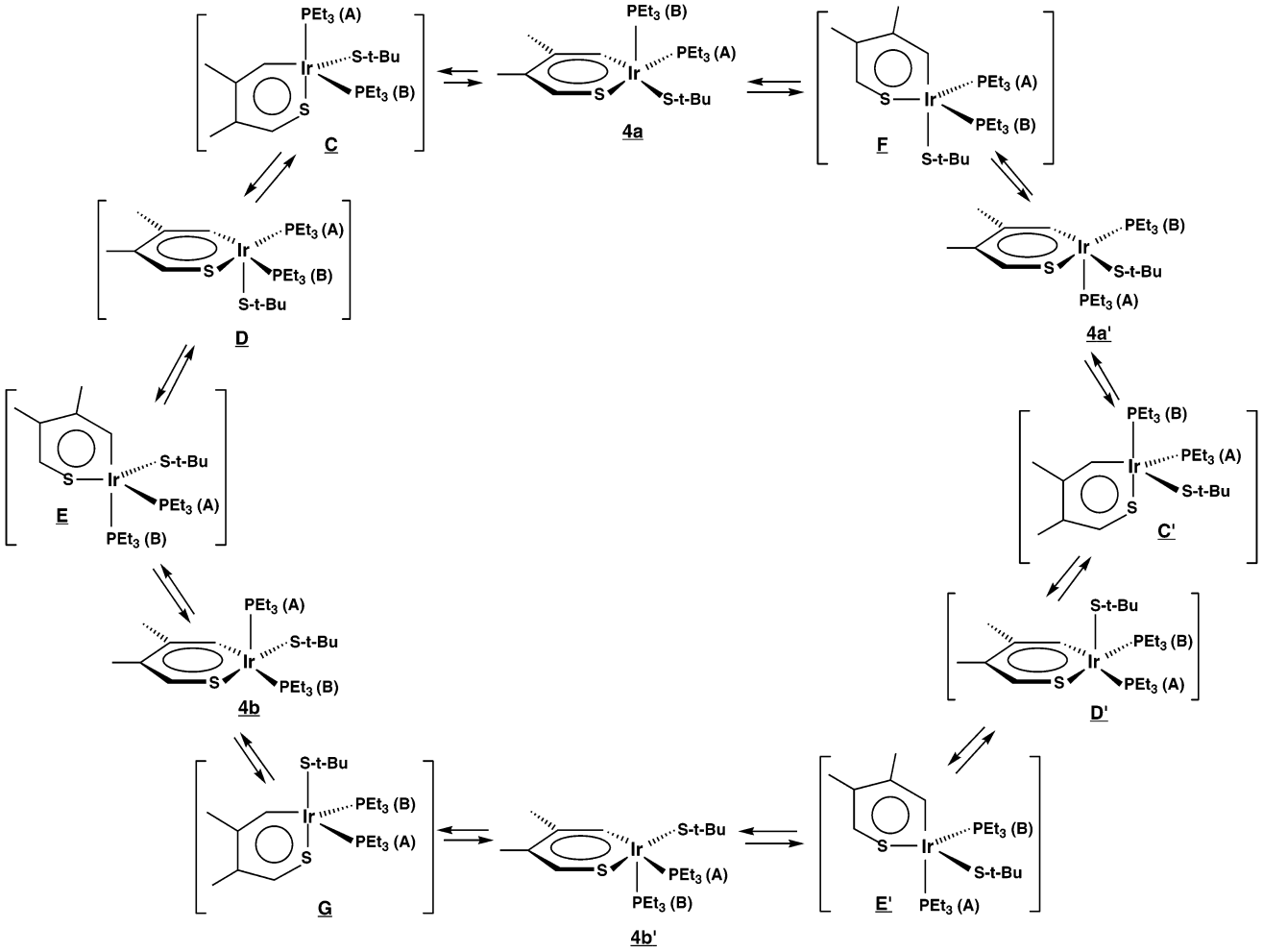
(7) As shown in Scheme 3, the fluxional processes lead to enantiomeric products in each case (**4a** → **4a′** and **4b** → **4b′**).

(8) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

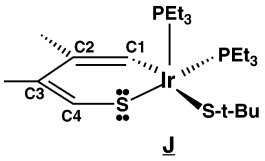
(9) (a) Palmer, M.; Carter, K.; Harris, S. *Organometallics* **1997**, *16*, 2448. (b) Harris, S. *Organometallics* **1994**, *13*, 2628.

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

Scheme 3



structure **J**, the iridium atom in **4** is reactive toward 2e⁻ donors, leading to the formation of six-coordinate iridathiacyclohexa-1,3-diene compounds.



J

1. Treatment of 4 with Acetonitrile. When dark green **4** is dissolved in acetonitrile and cooled to −30 °C, a flaky tan precipitate of the acetonitrile adduct, **6** (see Scheme 4), is produced. If this precipitate is redissolved and warmed back to room temperature, the solution color changes from light tan to dark green, signaling the re-formation of **4**.[11] The precipitation of **6**, followed by redissolution and warming, represents a convenient procedure for purifying compound **4**.

Compound **6** is sparingly soluble in acetonitrile at −10 °C, and under these conditions, only a small amount of **4** is present. Therefore, we have carried out the NMR characterization of **6** in acetonitrile-d_3 at −10 °C. The $^{31}P\{^1H\}$ NMR spectrum of **6** is a sharp singlet, indicating that the two PEt_3 ligands are situated *trans* to one another and hence equivalent by symmetry. In the ^1H NMR spectrum, ring protons H1 and H4 appear as singlets at δ 7.03 and 5.32, substantially upfield from their positions in **4** (vide supra). This upfield shift is due to the absence of an aromatic ring current in the iridacyclohexa-1,3-diene ring of **6**. The acetonitrile protons appear at the chemical shift position for free (uncoordinated) acetonitrile, δ 1.93. This strongly suggests that CH_3CN ligands have been replaced by CD_3CN solvent molecules; that is, acetonitrile exchange is facile even at −10 °C.

In the $^{13}C\{^1H\}$ NMR spectrum, the ring carbons are shifted upfield from their positions in **4**, appearing at δ 128 (C2), 125 (C3), 116.3 (C1), and 115.6 (C4). These are all typical chemical shift positions for carbons in an unsaturated, nonaromatic ring system. The *trans*-diaxial arrangement of the phosphine ligands is confirmed by the observation of a virtual triplet for the phosphine methylene carbons at δ 12.4.

Unfortunately, the relative orientation of the *tert*-butylthiolate and acetonitrile ligands cannot be definitively established from the NMR spectra. The absence of a NOESY cross-peak between H1 of the ring and the *tert*-butyl group of the thiolate ligand supports the "*cis*" structure wherein the two sulfur centers reside *cis* to one another in the equatorial plane. However, it is also possible that *both* isomers ("*cis*" and "*trans*") are present

(11) In solvents other than acetonitrile, the conversion of **6** back to **4** is essentially complete at room temperature. In acetonitrile, a mixture of **4** and **6** (~50:50) is observed at room temperature.

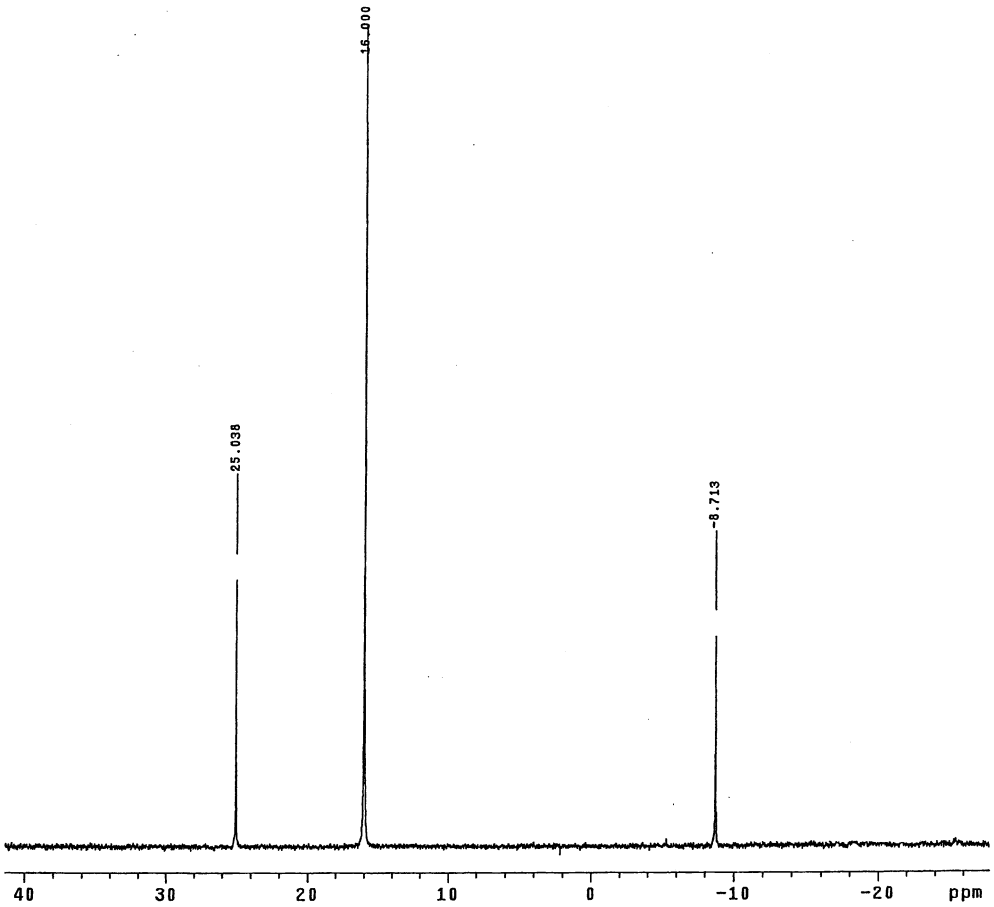


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of compound **4** in methanol-d_4 at −60 °C. The two smaller peaks are due to the phosphines in "*trans*" isomer **4b**, which is not fluxional at this temperature. The large peak is due to the exchanging phosphines in fluxional "*cis*" isomer **4a**. The ratio of **4a** to **4b** under these conditions is approximately 2:1.

but rapidly equilibrating via acetonitrile dissociation/reassociation.

2. Treatment of 4 with Excess PMe_3. Treatment of **4**[12] with excess trimethylphosphine at 22 °C leads to PMe_3 addition at the iridium center *and* replacement of the two bulky PEt_3 ligands with PMe_3's, generating the octahedral tris(PMe_3) product **7** (see Scheme 5).[13] A pair of isomers, "*cis*" **7a** and "*trans*" **7b**, are produced in an approximate 2:1 ratio.

In the $^{31}P\{^1H\}$ NMR spectrum of **7**, both isomers give rise to doublet/triplet patterns. The doublets (intensity 2) are due to the *trans*-diaxial phosphines, and the triplets (intensity 1) are due to the equatorial phosphines. However, the two isomers can be readily distinguished on the basis of their ^1H and ^{13}C NMR spectra. In general, for octahedral iridacycles,[1−3] H1 couples strongly only to a ^{31}P nucleus situated *cis* to it in the equatorial plane, while C1 couples strongly only to a ^{31}P nucleus located *trans* to it. Coupling to the axial phosphines is weak.

Hence, in major isomer **7a**, ring proton H1 appears as a strongly coupled doublet ($J_{H-P\,cis\,eq}$ = 14.7 Hz) at δ 6.95, while ring carbon C1 is a weakly coupled quartet. This weak coupling indicates that C1 resides *cis* to all

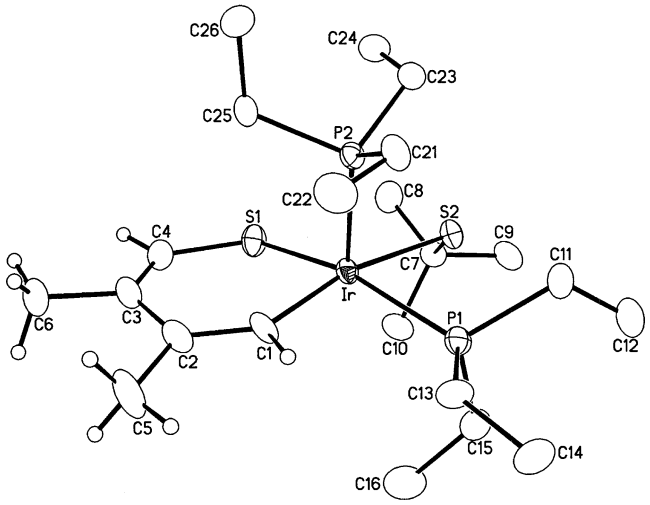
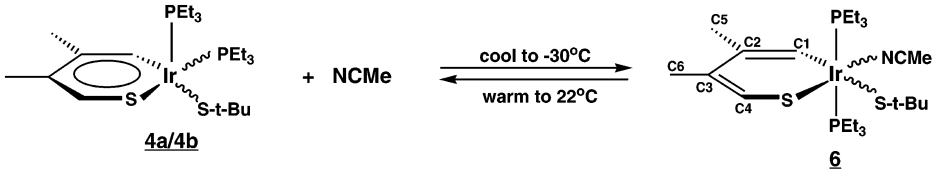


Figure 2. ORTEP drawing of **4a**, using thermal ellipsoids at the 30% probability level. Selected bond distances (Å): Ir−P1 2.311(3), Ir−P2 2.205(3), Ir−S2 2.470(3), Ir−S1 2.263(3), Ir−C1 1.993(9), S1−C4 1.711(11), S2−C7 1.844-(10), Cl−C2 1.391(15), C2−C3 1.455(16), C2−C5 1.502(16), C3−C4 1.336(15), C3−C6 1.521(15). Selected bond angles (deg): P2−Ir−P1 98.56(11), P2−Ir−S2 95.62(10), P2−Ir−S1 100.86(10), P2−Ir−C1 94.3(3), P1−Ir−S2 79.66(10), P1−Ir−S1 159.91(11), P1−Ir−C1 92.3(3), S2−Ir−S1 93.30-(10), S2−Ir−C1 168.1(3), S1−Ir−C1 91.4(3), Ir−C1−C2 134.2(9), C1−C1−C3 124.7(10), C2−C3−C4 124.3(10), C3−C4−S1 130.8(9), C4−S1−Ir 112.4(4), Ir−S2−C7 118.0(4).

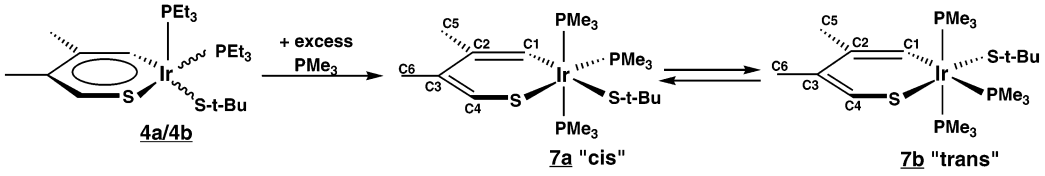
(12) In this reaction, **4** is produced in situ by dissolving the acetonitrile adduct **6** in pentane: see Experimental Section.

(13) In a similar vein, the cationic iridathiabenzene, $[\overline{CH{=}C(Me)C(Me){=}CHS{=}Ir(PEt_3)_3}]^+BF_4^-$ (**3**), reacts with excess PMe_3 to produce $[\overline{CH{=}C(Me)C(Me){=}CHSIr(PMe_3)_4}]^+BF_4^-$: See ref 1.

Scheme 4



Scheme 5



three phosphorus nuclei. In the minor isomer, **7b**, ring proton H1 resonates at δ 8.76 and is only weakly coupled to the *trans* equatorial and axial phosphines. Meanwhile, C1 appears as a doublet of triplets with strong coupling to the *trans*-equatorial PMe_3 ligand ($J_{C1-P\,trans\,eq} = 79.5$ Hz) and weak coupling to the axial PMe_3's ($J_{C1-Pax} = 13.0$ Hz).

Major isomer **7a** crystallizes as pink-orange prisms from a saturated toluene solution of **7a**/**7b** at −30 °C, and its structure has been confirmed by X-ray diffraction (see Figure 3 and caption). The coordination geometry around the iridium center is octahedral with the ring sulfur and the thiolate sulfur residing *cis* to one another. The ring is essentially planar (mean deviation = 0.025 Å) and exhibits the expected alternation in C−C bond lengths (C1−C2 = 1.361(6) Å; C2−C3 = 1.474(6) Å; C3−C4 = 1.344(6) Å). The Ir−S1 and Ir−C1 bonds have both lengthened with respect to their values in iridathiabenzene **4a** (Ir−S1 = 2.3844(11) Å; Ir−C1 = 2.072(4) Å vs Ir− S1 = 2.263(3) Å; Ir−C1 = 1.993(9) Å in **4a**).

When the crystals of **7a** are dissolved in toluene-d_8 at −70 °C, only the signals due to **7a** are observed in the $^{31}P\{^1H\}$ NMR spectrum. However, as the sample is warmed, the signals due to **7b** begin to appear at about −10 °C. And at room temperature, the usual 2:1 ratio of **7a**:**7b** is observed. These results indicate an equilibration of isomers that is slow on the NMR time scale but rapid on the laboratory time scale at room temperature. The mechanism for this equilibration, like that described earlier for **5a**/**5b** (Scheme 1), probably involves phosphine dissociation, rearrangement of the resulting five-coordinate intermediate (an iridathiabenzene), and reassociation of phosphine.

F. Reactivity of Iridathiabenzene 4: Addition of an Electrophile. Treatment of **4** with triflic acid (HO_3SCF_3) in acetonitrile solvent at −30 °C leads to an immediate color change from dark green to light orange, signaling the production of the dimeric compound **8** (see Scheme 6). The same product is obtained when **6**, the acetonitrile adduct of **4** (vide supra), is dissolved in diethyl ether and treated with triflic acid.

In these reactions, the triflic acid protonates the *tert*-butylthiolate sulfur, causing *tert*-butylthiol to dissociate from the iridium center. It is replaced by a much smaller acetonitrile ligand, and the resulting sterically destabilized iridathiabenzene (**K**, Scheme 6) then dimerizes to **8**.[14] Note that these dimerizing iridium fragments are enantiomers of one another and that the dimer itself possesses inversion symmetry.

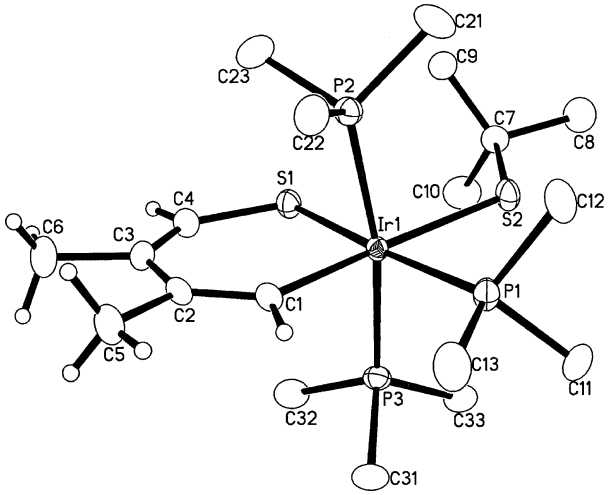


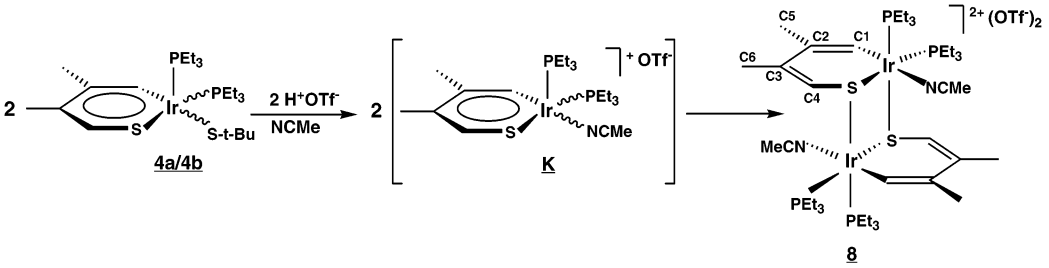
Figure 3. ORTEP drawing of **7a**, using thermal ellipsoids at the 50% level. Selected bond distances (Å): Ir1−P1 2.3225(11), Ir1−P2 2.3519(12), Ir1−P3 2.3417(12), Ir1−S1 2.3844(11), Ir1−S2 2.4990(10), Ir1−C1 2.072(4), S1−C4 1.728(5), S2−C7 1.847(5), C1−C2 1.361(6), C2−C3 1.474(6), C2−C5 1.522(6), C3−C4 1.344(6), C3−C6 1.534(6). Selected bond angles (deg): P1−Ir1−P2 92.79(4), P1−Ir1−P3 93.06(4), P1−Ir1−S1 174.51(4), P1−Ir1−S2 79.88(4), P1−Ir1−C1 93.48(13), P2−Ir1−P3 169.48(4), P2−Ir1−S1 88.47(4), P2−Ir1−S2 93.67(4), P2−Ir1−C1 84.31(12), P3−Ir1−S1 86.54(4), P3−Ir1−S2 95.97(4), P3−Ir1−C1 86.61(12), S1−Ir1−S2 94.71(4), S1−Ir1−C1 91.96(13), S2−Ir1−C1 172.97(13), Ir1−C1−C2 133.1(4), C1−C2−C3 126.0(4), C2−C3−C4 126.2(4), C3−C4−S1 132.7(4), C4−S1−Ir1 109.60(16), Ir1−S2−C7 120.34(15).

This symmetry is reflected in the $^{31}P\{^1H\}$ NMR spectrum of **8**, which exhibits two "filled-in" doublets, consistent with an AA′XX′ spin system. The doublet coupling, which represents the sum of J_{AX} and $J_{AX'}$, is 15.9 Hz.[15] Because of the inversion symmetry, the two metallacyclic rings are identical by NMR. In the ^1H

(14) In a previous paper,[1] we postulated that the dimerization of a similar fragment, $\overline{CH{=}C(Me)C(Me){=}CHS}{=}Ir(PEt_3)_2(Cl)$ (**B** in Scheme 1), is a key step in the production of the monochloro-bridged dimer $\{[\overline{CH{=}C(Me)C(Me){=}CHS}Ir(PEt_3)_2]_2(\mu\text{-}Cl)\}^+O_3SCF_3^-$.

(15) (a) Wilberg, K. B.; Nist, B. J. *Interpretation of NMR Spectra*; W. A. Benjamin, Inc.: New York, 1982. (b) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-resolution Nuclear Magnetic Resonance*; McGraw-Hill Book Company, Inc.: New York, 1959.

Scheme 6



NMR in methanol-d_4, ring proton H1 resonates at δ 8.02 and is a doublet due to strong coupling to the *cis*-equatorial PEt_3 ligand ($J_{H-P\,cis\,eq} = 13.0$ Hz), while ring proton H4 resonates at δ 5.00. These chemical shift positions are consistent with a nonaromatic iridathiacyclohexa-1,3-diene ring system. The acetonitrile ligand appears as a singlet at δ 2.67, substantially downfield from "free" (uncoordinated) acetonitrile (δ 1.93). When **8** is dissolved in $NCCD_3$, the ^{1}H NMR signal at δ 2.67 (coordinated $NCCH_3$) disappears and is replaced by a signal at δ 1.93 (free $NCCH_3$). This indicates that the acetonitrile ligands are weakly coordinated and readily undergo exchange in acetonitrile solvent at room temperature.

In the $^{13}C\{^1H\}$ NMR in methanol-d_4, the four ring carbons resonate in the normal region for a nonaromatic iridathiacyclohexa-1,3-diene ring, while the coordinated acetonitrile carbons are shifted slightly downfield from their positions in "free" acetonitrile. The methylene (CH_2) carbons of the PEt_3 ligands appear as "filled-in" doublets, an effect that results from long-range coupling to the phosphines on the adjacent iridium.

The structure of **8** has been confirmed by single-crystal X-ray diffraction and is presented in Figure 4; key bond distances and angles are listed in the figure caption. As expected, the dimer is linked through the two ring sulfur atoms and displays inversion symmetry.[16] The linking Ir−S bonds are only slightly longer than the Ir−S bonds within the metallacycles (2.4408(8) vs 2.3941(8) Å). The iridium centers display approximate octahedral coordination geometry, with the acetonitrile ligands residing *cis* to the ring sulfur atoms (and *trans* to the ring C1 carbons), as predicted by the NMR data.

As in **7a** (vide supra), the iridathiacyclohexa-1,3-diene ring in **8** shows the expected alternation in carbon−carbon bond lengths: C1−C2 = 1.342(5) Å; C2−C3 = 1.468(6) Å; C3−C4 = 1.366(6) Å. However, unlike **7a**, the metallacyclic ring is nonplanar. A rotation about bond C2−C3 has displaced ring carbon C4 and ring sulfur S1 out of the Ir/C1/C2/C3 plane by 0.43 and 0.98 Å, respectively. This twisting results in a dihedral angle of 19.3° between plane C1/C2/C5 and plane C3/C4/C6. Furthermore, the sum of the six internal angles within the metallacyclohexa-1,3-diene ring is only 708.6°, substantially less than the 720° required for a planar six-membered ring.

G. Reactivity of Iridathiabenzene 4: Coordination to a Metal Fragment. Treatment of iridathiabenzene **4**[12] with $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]^+O_3SCF_3^-$ [17] leads to clean acetonitrile displacement from Ru and

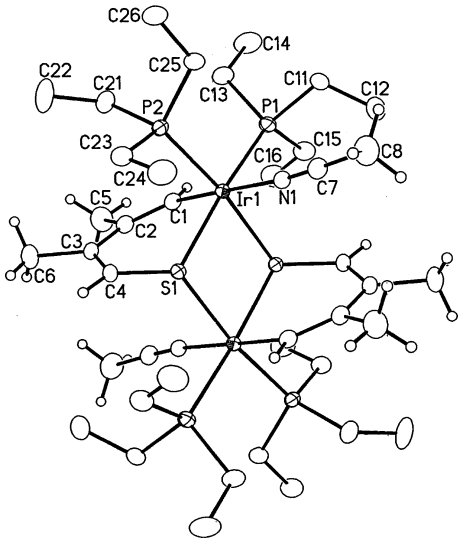


Figure 4. ORTEP drawing of the dication in **8**, using thermal ellipsoids at the 25% probability level. Starred atoms (S1* and Ir1*) belong to the symmetry-related portion of the dimer. Selected bond distances (Å): Ir1−P1 2.3405(9), Ir1−P2 2.3363(9), Ir1−N1 2.115(3), Ir1−S1* 2.4408(8), Ir1−S1 2.3941(8), Ir1−C1 2.030(3), S1−C4 1.725(4), C1−C2 1.342(5), C2−C3 1.468(6), C2−C5 1.524(6), C3−C4 1.366(6), C3−C6 1.527(5). Selected bond angles (deg): P1−Ir1−P2 95.43(3), P1−Ir1−N1 91.08(8), P1−Ir1−S1* 93.20(3), P1−Ir1−S1 172.36(3), P1−Ir1−C1 87.55(10), P2−Ir1−N1 88.78(8), P2−Ir1−S1* 171.15(3), P2−Ir1−S1 91.47(3), P2−Ir1−C1 93.10(10), N1−Ir1−S1* 93.02(8), N1−Ir1−S1 92.35(8), N1−Ir1−C1 177.76(13), S1*−Ir1−S1 79.80(3), S1*−Ir1−C1 85.30(10), S1−Ir1−C1 88.81(10), Ir1−C1−C2 133.5(3), C1−C2−C3 125.0(4), C2−C3−C4 124.6(3), C3−C4−S1 129.2(3), C4−S1−Ir1 107.45(13), C4−S1−Ir1* 110.43(13), Ir1−S1−Ir1* 100.20(3).

production of the "sandwich" compound **9** (Scheme 7). Two isomers are observed, but the major isomer, "*cis*" **9a**, accounts for about 85% of the product.

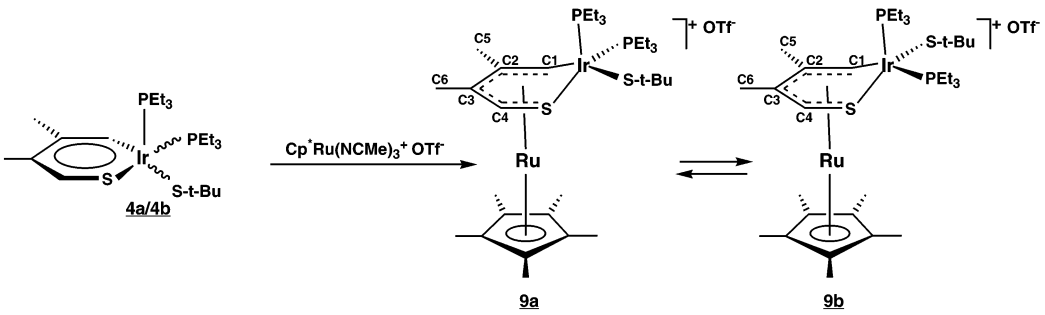
In the $^{31}P\{^1H\}$ NMR spectrum, the major isomer **9a** gives rise to two doublets at δ 39.8 and −7.5 ($J_{P-P} = 15.9$ Hz). In contrast, the minor isomer **9b** gives rise to two singlets at δ 44.1 and −16.2. This absence of P−P coupling strongly supports the assignment of **9b** as the "*trans*" form. Recall that the "*trans*" isomer of neutral iridathiabenzene **4** (**4b**) also showed no P−P coupling (see Results and Discussion section C.2).

In the ^{1}H NMR spectrum, the ring protons of the major isomer, **9a**, resonate at δ 7.72 (H1) and 5.99 (H4), substantially upfield from their positions in **4**. This upfield shift is usually observed when arenes coordinate to metal fragments. H1 is strongly coupled to phospho-

(16) Analogous structures have been reported for dimeric rhodathiacycles[4d] and platinathiacycles.[5a,c]

(17) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

Scheme 7



rus (J_{H1-P} = 12.5 Hz), confirming that it resides *cis* to a PEt_3 ligand. In the $^{13}C\{^1H\}$ NMR spectrum of the major isomer, C1 is a singlet, confirming that it resides *trans* to the thiolate ligand, not a PEt_3. The chemical shifts of the ring carbons of **9a** are δ 101.6 (C1), 107.0 (C2), 99.4 (C3), and 75.7 (C4), substantially upfield shifted as compared to **4a**.

In the minor isomer, **9b**, the ring protons resonate at δ 8.97 (H1) and 5.66 (H4) and are singlets, while C1 is strongly coupled to phosphorus (J_{C1-P} = 76.6 Hz). This coupling pattern confirms that H1 lies *cis* to the thiolate ligand while C1 lies *trans* to a PEt_3 ligand.

A pure sample of isomer **9a** crystallized as dark green plates from tetrahydrofuran−diethyl ether at −30 °C. The solid state structure, obtained from an X-ray diffraction study, is presented in Figure 5; important bond distances and angles are listed in the caption. The most striking feature of the structure is that the ruthenium atom is *not* bonded to iridium. It is, in fact, bonded in an η^5-fashion to C1, C2, C3, C4, and S1 of the metallacycle. These five atoms are essentially coplanar, exhibiting a mean deviation of only 0.03 Å. The iridium atom, on the other hand, is pushed up and out of the plane by 0.71 Å. The dihedral angle between C1/C2/C3/C4/S1 and C1/Ir/S1 is 26.1°. Recall that the analogous dihedral angle in the parent iridathiabenzene **4a** was 9.9°.

The η^5-bonding of the iridathiacycle in **9a** contrasts with the structure of $\{\eta^6$-[CH=C(Me)C(Me)=CHS=Ir-$(PEt_3)_3]Mo(CO)_3\}^+BF_4^-$, in which Ir and Mo are bonded.[1,18] Similarly, Angelici has shown that that the iridathiabenzene, [C(Me)=CH−CH=C(Me)S=Ir(η^5-C_5Me_5)]$^+$, coordinates in an η^6-fashion to a variety of metal fragments, including $M(CO)_3$ (M = Cr, Mo, W) and [Fe-$(\eta^5$-$C_5H_5)]^+$.[19] The large displacement of the iridium center in **9a** up and out of the ring plane is probably a response to unfavorable steric interactions between the η^5-C_5Me_5 ligand on Ru and the PEt_3 and *tert*-butylthiolate ligands on Ir.

The iridium center in **9a** has retained its square pyramidal coordination geometry in which PEt_3 phosphorus P2 occupies the unique axial site and ring sulfur S1, ring carbon C1, thiolate sulfur S2, and PEt_3 phosphorus P1 occupy the four basal sites. The sulfur atoms reside *cis* to one another (S1−Ir−S2 = 93.13(5)°). Within the metallacycle, the Ir−S1 and Ir−C1 bonds have lengthened somewhat compared to their values in iridathiabenzene **4a**, reflecting a shift toward single-bond character. In **9a**, these distances are 2.3079(13) and 2.054(6) Å, respectively, versus 2.263(3) and 1.993-(9) Å in **4a**. The bonding within the remaining portion of the metallacycle is at least partially delocalized with C1−C2 = 1.414(8) Å, C2−C3 = 1.445(8) Å, C3−C4 = 1.390(8) Å, and C4−S1 = 1.742(6) Å. Overall, the bonds within this portion of the ring are lengthened slightly over their values in **4a**.

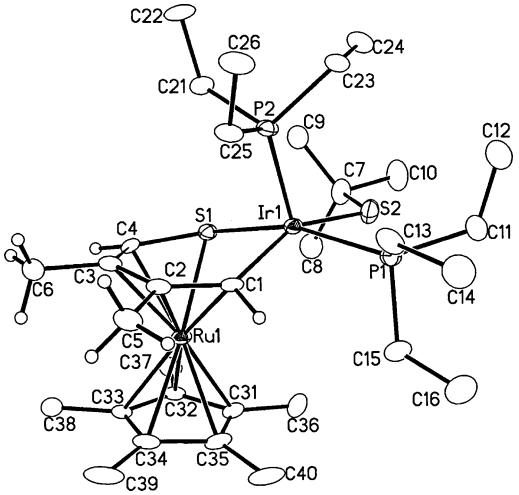


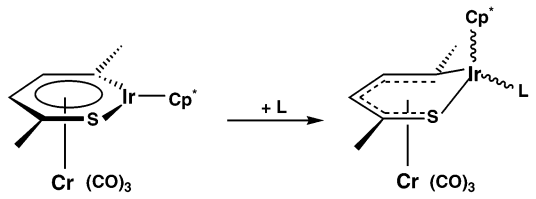
Figure 5. ORTEP drawing of the cation in **9a**, using the thermal ellipsoids at the 25% probability level. Selected bond distances (Å): Ru1−C1 2.240(5), Ru1−C2 2.236(5), Ru1−C3 2.254(6), Ru1−C4 2.154(5), Ru1−S1 2.4316(15), Ir1−P1 2.3365(15), Ir1−P2 2.2215(14), Ir1−S2 2.3961(18), Ir1−S1 2.3079(13), Ir1−C1 2.054(6), S1−C4 1.742(6), S2−C7 1.866(7), C1−C2 1.414(8), C2−C3 1.445(8), C2−C5 1.507(8), C3−C4 1.390(8), C3−C6 1.505(8), Ir1−Ru1 3.196-(nonbonded). Selected bond angles (deg): P2−Ir1−P1 97.79(6), P2−Ir1−S2 113.15(6), P2−Ir1−S1 100.05(5), P2−Ir1−C1 92.78(15), P1−Ir1−S2 83.99(7), P1−Ir1−S1 161.58-(5), P1−Ir1−C1 89.39(16), S2−Ir1−S1 93.13(5), S2−Ir1−C1 153.85(16), S1−Ir1−C1 85.24(15), Ir1−C1−C2 134.4(4), C1−C2−C3 123.4(5), C2−C3−C4 122.7(5), C3−C4−S1 129.2(4), C4−S1−Ir1 113.84(18), Ir1−S2−C7 120.8(2).

Further comparison of the bond distances in **9a** and **4a** shows that the Ir−S2 (thiolate) bond in **9a** has shortened significantly (by 0.074 Å) as compared to its value in **4a**. This suggests that while the Ir−S1 (ring) interaction has lost most of its π-character, some new double-bond character has developed between Ir and S2 in order to stabilize the otherwise 16e$^-$ iridium center. On the basis of the observed bond distances, the best description of the bonding in **9a** appears to be resonance structure **L**. By using two carbon−carbon double bonds

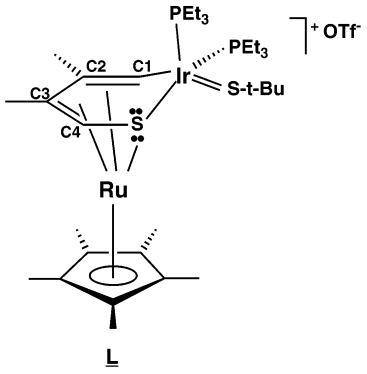
(18) The Ir−Mo distance is 3.0180(16) Å, compared to a Ir−Ru distance of 3.196 Å in **9a**.

(19) Chen, J.; Young,V. G., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 6362.

Scheme 8



and a sulfur lone pair, the iridacycle serves as a 6e$^-$ neutral ligand for the ruthenium center.



To our knowledge, **9a** represents the first example of a stable, isolable metallathiabenzene coordinating to a second metal in an η^5-fashion. However, Angelici has observed a similar bonding mode by treating the (η^6-iridathiabenzene)Cr(CO)$_3$ complex shown in Scheme 8 with 2e$^-$ ligands (L) such as CO or PEt$_3$.[20] These ligands add to the iridium center, effectively converting the iridathiabenzene to an iridathiacyclohexa-1,3-diene, which coordinates in an η^5-fashion to chromium, as shown. Bimetallic compounds containing η^5-coordinated metallathiacycles have also been isolated by Sweigart[21] and Angelici[22] from reactions involving thiophenes or coordinated thiophenes.

When crystals of **9a** are dissolved in cold (−78 °C) acetone-d_6 and analyzed by low-temperature ^{31}P{^{1}H} NMR, only the pair of doublets due to **9a** is observed. However, if the sample is warmed while monitoring the ^{31}P{^{1}H} NMR, the pair of singlets due to isomer **9b** first appears at about −10 °C and then grows to about 15% of the total integrated intensity at room temperature. These observations indicate that the two isomers of **9** can interconvert readily on the laboratory time scale at room temperature. This interconversion of isomers probably involves trigonal bipyramidal (at iridium) intermediates such as those discussed earlier for **4a** and **4b**. These intermediates are accessible only because the iridium center is *not* coordinated to ruthenium, and hence it retains its five-coordinate character.

It should be noted that while **9a** and **9b** are able to interconvert in solution, their isomerization *rate* is considerably slower than that exhibited by **4a** and **4b**. Isomers **4a** and **4b** interconvert rapidly on the NMR time scale at room temperature, as evidenced by their broad NMR line shapes. Only upon cooling to −10 °C do the separate signals for **4a** and **4b** appear in the ^{31}P-{^{1}H} NMR spectrum. In contrast, the ^{31}P NMR lines for **9a** and **9b** are sharp even at room temperature.

Concluding Remarks

We have synthesized a new neutral iridathiabenzene (**4**) by treating cationic iridathiabenzene **3** with anionic *tert*-butylthiolate. The steric bulk of the *tert*-butylthiolate ligand prevents **4** from dimerizing. In solution, **4** exists as an equilibrating mixture of square pyramidal isomers. Nucleophiles such as NCMe and PMe$_3$ react associatively with **4** at the iridium center, generating six-coordinate products with the iridathiacyclohexa-1,3-diene ring skeleton. This reactivity results from the fact that the electrons in the iridium−ring sulfur π-bond of **4** can be localized on sulfur, rendering the iridium atom a reactive 16e$^-$ center. Compound **4** also reacts with electrophiles such as HO_3SCF_3. In this case, protonation occurs at the thiolate sulfur, leading to release of thiol and production of a reactive fragment, which dimerizes through its ring sulfur atom. Finally, **4** behaves more like a conventional arene in its reaction with [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$]$^+$O$_3$SCF$_3^-$, forming a new sandwich compound by displacement of the acetonitrile ligands from the Ru center. But surprisingly, the iridium center is bent severely out of the arene ring plane and away from ruthenium, probably in order to minimize unfavorable steric contacts.

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. NMR solvents were obtained in sealed vials and used as received. The following reagents were used as obtained from the supplier indicated: sodium *tert*-butylthiolate (Aldrich), trimethylphosphine (Strem), trifluoromethanesulfonic acid (Aldrich). "Iridathiabenzene" ([CH=C(Me)C(Me)=CHS=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$, **3**)[1] and [(η^5-C$_5$Me$_5$)Ru(NCMe)$_3$]$^+$O$_3$SCF$_3^-$ [17] were synthesized by literature procedures.

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 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. 2D NOESY experiments provided spacial information.

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)C(Me)=CHS=Ir(PEt$_3$)$_2$(S-t-Bu) (4). Compound **3**, [CH=C(Me)C(Me)=CHS=Ir(PEt$_3$)$_3$]$^+$BF$_4^-$ (0.066 g, 0.089 mmol), was dissolved in 10 mL of tetrahydrofuran (THF) in a vial and stirred at room temperature. Sodium

(20) (a) Chen, J.; Angelici, R. J. *Inorg. Chim. Acta* **2002**, *334*, 204. (b) Chen, J.; Young, V. G., Jr.; Angelici, R. J. *Organometallics* **2002**, *21*, 5951.

(21) (a) Dullaghan, C. A.; Sun, S.; Carpenter, G. B.; Weldon, B.; Sweigart, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 212. (b) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Choi, D. S.; Lee, S. S.; Chung, Y. K. *Organometallics* **1997**, *16*, 5688. (c) Dullaghan, C. A.; Zhang, S.; Green, D. L.; Carpenter, G. B.; Sweigart, D. A.; Camiletti, C.; Rajaseelan, E. *Organometallics* **1998**, *17*, 3316.

(22) Reynolds, M. A.; Guzei, I. A.; Angelici, R. J. *Organometallics* **2001**, *20*, 1071.

tert-butylthiolate (approximately 0.020 g, 0.18 mmol) was added into the reaction vial by rinsing it from a spatula using 10 mL of THF. The solution color quickly changed from burgundy to dark green, and the solution was stirred at room temperature for 1 h, followed by filtration. The solvent was removed in vacuo, and the green oily residue extracted with pentane and filtered. Compound **4a** was crystallized as green-black plates or rods from concentrated solutions of methanol at −30 °C. Yield: 0.047 g (84%). Anal. Calcd for $C_{22}H_{47}IrP_2S_2$: C, 41.94; H, 7.54. Found: C, 41.84; H, 7.49.

Major "*cis*" Isomer (4a). Note: this isomer is fluxional at −60 °C. ^{1}H NMR (methanol-d_4, −60 °C, 300 MHz): δ 9.79 (t, J_{H-P} = 7.7 Hz, 1, H1), 8.13 (t, J_{H-P} = 5.2 Hz, 1, H4), 2.31 (s, 3, H5's), 2.16 (s, 3, H6's), 1.95 (complex overlapping m's, 12, PEt_3 CH_2's), 1.53 (s, 9, thiolate CH_3's), 0.94 (br d of t, J_{H-P} = 15.6 Hz, J_{H-H} = 6.6 Hz, 18, PEt_3 CH_3's). ^{13}C{^{1}H} NMR (methanol-d_4, −60 °C, 150 MHz): δ 152.9 (s, C1), 139.1 (s, C2), 132.4 (s, C3), 128.3 (s, C4), 43.0 (s, thiolate *C*$(CH_3)_3$), 38.1 (s, thiolate C(*C*$H_3)_3$'s), 28.8 (s, C5), 26.4 (s, C6), 18.7 (m, PEt_3 CH_2's), 9.1 (s, PEt_3 CH_3's). ^{31}P{^{1}H} NMR (methanol-d_4, −60 °C, 121 MHz): δ 16.0 (s, 2, PEt_3's).

Minor "*trans*" Isomer (4b). ^{1}H NMR (methanol-d_4, −60 °C, 300 MHz): δ 11.02 (d, J_{H-P} = 5.4 Hz, 1, H1), 7.88 (s, 1, H4), 2.35 (s, 3, H5's), 2.16 (s, 3, C6's), 1.95 (complex overlapping m's, 12, PEt_3 CH_2's), 1.27 (s, 9, thiolate CH_3's), 1.07 (br d of t, J_{H-P} = 14.1 Hz, J_{H-H} = 7.5 Hz, 9, PEt_3 CH_3's), 0.75 (br d of t, J_{H-P} = 17.0 Hz, J_{H-H} = 7.5 Hz, 9, PEt_3 CH_3's). ^{13}C{^{1}H} NMR (methanol-d_4, −60 °C, 150 MHz): δ 171.6 (br d, J_{C-P} = 83.4 Hz, C1), 140.7 (s, C2), 132.2 (s, C3), 126.0 (s, C4), 41.8 (s, thiolate *C*$(CH_3)_3$), 37.9 (s, thiolate C(*C*$H_3)_3$'s), 27.9 (br s, C5), 26.3 (s, C6), 22.7 (d, J_{C-P} = 41.7 Hz, PEt_3 CH_2's), 9.3 (s, PEt_3 CH_3's). (Note: one PEt_3 CH_2 peak is obscured.) ^{31}P{^{1}H} NMR (methanol-d_4, −60 °C, 121 MHz): δ 25.0 (s, 1, axial PEt_3), −8.7 (s, 1, basal PEt_3).

Synthesis of $\overline{CH{=}C(Me)C(Me){=}CHSIr(PEt_3)_2}$(S-t-Bu)(NCMe) (6). Compound **4**, $\overline{CH{=}C(Me)C(Me){=}CHS{=}Ir(PEt_3)_2}$(S-t-Bu) (0.35 g, 0.55 mmol), was dissolved in 15 mL of acetonitrile and cooled to −30 °C. Overnight, compound **6** precipitated from the solution as light tan thin plates and was collected by filtration. Yield: 0.21 g (57%). Note: the isolated tan plates of **6** gradually took on a greenish cast due to slow loss of NCMe. This behavior thwarted our attempts to obtain an accurate elemental analysis. ^{1}H NMR (acetonitrile-d_3, −10 °C, 300 MHz): δ 7.03 (s, 1, H1), 5.32 (s, 1, H4), 2.46 (br m, 6, PEt_3 CH_2's), 1.93 (s, 3, $NCCH_3$), 1.74 (br m, 6, PEt_3 CH_2's), 1.74 (s, 3, H5's), 1.72 (s, 3, H6's), 1.34 (s, 9, thiolate CH_3's), 1.01 (d of t, J_{H-P} = 14.4 Hz, J_{H-H} = 7.2 Hz, 18, PEt_3 CH_3's). (Note: the acetonitrile peak at δ 1.93 is due to free $NCCH_3$. Coordinated acetonitrile is not observed.) ^{13}C{^{1}H} NMR (acetonitrile-d_3, −10 °C, 150 MHz): δ 128 (C2), 125 (C3), 116.3 (s, C1), 115.6 (s, C4), 39.5 (thiolate *C*$(CH_3)_3$), 36.6 (s, thiolate C(*C*$H_3)_3$'s), 27.0 (s, C5), 25.8 (s, C6), 12.4 (virtual t, J_{C-P} = 30.2 Hz, PEt_3 CH_2's), 7.7 (s, PEt_3 CH_3's). (Note: coordinated acetonitrile is not observed.) ^{31}P{^{1}H} NMR (acetonitrile-d_3, −10 °C, 121 MHz): δ −25.9 (s, 2, PEt_3's).

Synthesis of $\overline{CH{=}C(Me)C(Me){=}CHSIr(PMe_3)_3}$(S-t-Bu) (7). Compound **6**, $\overline{CH{=}C(Me)C(Me){=}CHSIr(PEt_3)_2}$(S-t-Bu)(NCMe) (0.014 g, 0.021 mmol), was dissolved in 5 mL of pentane to form a deep green solution and then cooled to −30 °C. Excess PMe_3 (0.32 g, 4.2 mmol) was likewise cooled to −30 °C and added to the green solution, causing the color to change to pale yellow. After warming to room temperature and stirring for 30 min, the solution was filtered and the volatiles were removed in vacuo. The residue was dissolved in a minimal quantity of toluene and cooled to −30 °C, causing **7** to crystallize as pink-orange prisms. Yield: 0.012 g (92%). High-resolution FAB-MS: calcd for M^+ ($C_{19}H_{44}{}^{193}IrP_3S_2$), 622.1727; found, 622.1746.

Major "*cis*" Isomer (7a). ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): δ 6.95 (br d, J_{H-P} = 14.7 Hz, 1, H1), 6.15 (d, J_{H-P} = 14.4 Hz, 1, H4), 2.15 (s, 3, H5's), 2.06 (s, 3, H6's), 1.87 (s, 9, thiolate CH_3's), 1.33 (virtual t, J_{H-P} = 6.6 Hz, 18, axial PMe's), 1.09 (d, J_{H-P} = 9.0 Hz, 9, equatorial PMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 22 °C, 150 MHz): δ 127.1 (s, C3), 126.6 (s, C2), 120.2 (s, C4), 113.6 (br quartet, C1), 40.0 (d, J_{C-P} = 8.1 Hz, thiolate *C*$(CH_3)_3$), 37.3 (s, thiolate C(*C*$H_3)_3$'s), 28.9 (s, C5), 26.1 (s, C6), 13.3−14.3 (complex m, PMe_3's). ^{31}P{^{1}H} NMR (benzene-d_6, 22 °C, 121 MHz): δ −45.0 (d, J_{P-P} = 22.4 Hz, 2, axial PMe_3's), −50.0 (t, J_{P-P} = 22.4 Hz, 1, equatorial PMe_3).

Minor "*trans*" Isomer (7b). ^{1}H NMR (benzene-d_6, 22 °C, 300 MHz): δ 8.76 (d of t, J_{H-P} = 7.5 Hz, 3.7 Hz, 1, H1), 6.01 (s, 1, H4), 2.27 (br t, J_{H-P} = 3.0 Hz, 3, H5's), 2.04 (s, 3, H6's), 1.68 (s, 9, thiolate CH_3's), 1.38 (virtual t, J_{H-P} = 7.2 Hz, 18, axial PMe_3's), 0.99 (d, J_{H-P} = 7.5 Hz, 9, equatorial PMe_3). ^{13}C{^{1}H} NMR (benzene-d_6, 22 °C, 150 MHz): δ 129.2 (s, C2), 127.1 (s, C3), 121.6 (d of t, J_{C-P} = 79.5 Hz, 13.0 Hz, C1), 115.8 (s, C4), 37.5 (d, thiolate *C*$(CH_3)_3$), 36.9 (s, thiolate C(*C*$H_3)_3$'s), 27.1 (d, J_{C-P} = 11.1 Hz, C5), 25.7 (s, C6), 13.3−14.3 (complex m, PMe_3's). ^{13}P{^{1}H} NMR (benzene-d_6, 22 °C, 121 MHz): δ −48.2 (d, J_{P-P} = 20.4 Hz, 2, axial PMe_3's), −61.6 (t, J_{P-P} = 20.4 Hz, 1, equatorial PMe_3).

Synthesis of {$\overline{[CH{=}C(Me)C(Me){=}CHSIr(PEt_3)_2(NC-Me)]}$}$^{2+}$($O_3SCF_3^-$)$_2$ (8). Compound **6**, $\overline{CH{=}C(Me)C(Me){=}CHSIr(PEt_3)_2}$(S-t-Bu)(NCMe) (0.12 g, 0.18 mmol), was dissolved in diethyl ether at −30 °C, forming a dark green solution. Excess HO_3SCF_3 (0.12 g, 0.80 mmol) was then added via syringe, causing the solution color to change to light orange. After warming to room temperature and stirring for 15 min, the solution was filtered and the volatiles were removed in vacuo. The light orange residue was washed with cold pentane, redissolved in a minimal quantity of methanol, and cooled to −30 °C, causing compound **8** to crystallize as orange prisms. Yield: 0.12 g (92%). Anal. Calcd for $C_{42}H_{82}F_6Ir_2N_2O_6P_4S_4$: C, 34.51; H, 5.67. Found: C, 34.48; H, 5.57. ^{1}H NMR (methanol-d_4, 22 °C, 500 MHz): δ 8.02 (d, J_{H-P} = 13.0 Hz, 1, H1), 5.00 (d, J_{H-P} = 8.5 Hz, 1, H4), 2.67 (s, 3, $NCCH_3$), 2.15 (s, 3, H5's), 1.98 (s, 3, H6's), 2.1−1.8 (complex m's, 12, PEt_3 CH_2's), 1.20 (d of t, J_{H-P} = 14.0 Hz, J_{H-H} = 7.0 Hz, 9, PEt_3 CH_3's), 1.10 (d of t, J_{H-P} = 14.5 Hz, J_{H-H} = 7.0 Hz, 9, PEt_3 CH_3's). ^{13}C{^{1}H} NMR (methanol-d_4, 22 °C, 125 MHz): δ 149.2 (s, C2), 132.1 (s, C3), 124.4 (s, N*C*CH_3), 118.3 (s, C1), 111.2 (s, C4), 26.6 (s, C5), 24.0 (s, C6), 17.2 (filled-in d, J_{C-P} = 32.9 Hz, PEt_3 CH_2's), 16.6 (filled-in d, J_{C-P} = 32.2 Hz, PEt_3 CH_2's), 9.2 (s, PEt_3 CH_3's), 8.3 (s, PEt_3 CH_3's), 3.6 (s, $NCCH_3$). ^{31}P{^{1}H} NMR (methanol-d_4, 22 °C, 121 MHz): −11.6 (filled-in d, J = 15.9 Hz, 1, PEt_3), −17.9 (filled-in d, J = 15.9 Hz, 1, PEt_3). Note: for an AA′XX′ spin system, $J = J_{AX} + J_{AX'}$.

Synthesis of {η^5-$\overline{[CH{=}C(Me)C(Me){=}CHSIr(PEt_3)_2}$(S-t-Bu)]Ru($\eta^5$-$C_5Me_5$)}$^+$$O_3SCF_3^-$ (9). Compound **6**, $\overline{CH{=}C(Me)C(Me){=}CHSIr(PEt_3)_2}$(S-t-Bu)(NCMe) (0.16 g, 0.25 mmol), was dissolved in 10 mL of pentane to form a dark green solution and then cooled to −25 °C. This solution was then added to a −25 °C stirred solution of [(η^5-C_5Me_5)Ru$(NCMe)_3]^+O_3SCF_3^-$ (0.13 g, 0.25 mmol) in 10 mL of acetone. The resulting solution was warmed to ambient temperature and stirred for an additional 1 h, during which time the color changed from dark green to a lighter emerald green. The volatiles were removed in vacuo, resulting in an oily green film. After washing with cold diethyl ether, the residue was dissolved in a 1:1 mixture of THF and diethyl ether and cooled to −30 °C, causing dark green plates of **9** to crystallize. Alternatively, this compound can be crystallized from methanol at −30 °C. Yield: 0.20 g (79%). High-resolution FAB-MS: calcd for M^+($C_{32}H_{62}{}^{193}IrP_2RuS_2$), 867.2441; found, 867.2452.

Major "*cis*" Isomer (9a). ^{1}H NMR (acetone-d_6, −10 °C, 500 MHz): δ 7.72 (d, J_{H-P} = 12.5 Hz, 1, H1), 5.99 (d, J_{H-P} = 8.5

Table 2. X-ray Diffraction Structure Summary

	4a	**7a**	**8**	**9a**·THF[b]
formula	$C_{22}H_{47}IrP_2S_2$	$C_{19}H_{44}IrP_3S_2$	$C_{42}H_{82}F_6Ir_2N_2O_6P_4S_4$	$C_{37}H_{70}F_3IrO_4P_2RuS_3$
fw	629.86	621.77	1461.62	1087.32
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	10.7228(2)	9.3451(1)	9.9719(4)	11.7669(3)
b, Å	16.5065(4)	17.8049(3)	12.1386(4)	13.9381(4)
c, Å	16.3439(3)	15.5957(2)	23.8566(8)	14.7584(4)
α, deg	90.0	90.0	90.0	97.640(2)
β, deg	107.488(1)	100.073(1)	94.801(2)	103.4200(10)
γ, deg	90.0	90.0	90.0	105.870(2)
V, Å^3	2759.1(1)	2554.95(6)	2877.59(18)	2214.20(10)
Z	4	4	2	2
cryst dimens, mm	0.30 × 0.15 × 0.10	0.29 × 0.10 × 0.08	0.35 × 0.26 × 0.23	0.30 × 0.10 × 0.06
calcd density, g/cm^3	1.516	1.616	1.687	1.631
radiation; λ, Å	0.71073	0.71073	0.71073	0.71073
temp, K	218(2)	155(2)	295(2)	150(2)
θ range, deg	1.80−25.05	1.75−28.00	1.88−30.00	1.88−28.00
data collected				
h	−12 to +12	−12 to 12	−13 to 14	−15 to 15
k	−19 to +19	−23 to 23	−16 to 16	−18 to 18
l	−19 to +19	−20 to 20	−33 to 33	−19 to 19
total decay	none obsd	none obsd	none obsd	none obsd
no. of data collected	45 897	58 663	70 921	27 671
no. of unique data	4889	6162	8160	10 406
Mo Kα linear abs coeff, mm^{-1}	5.113	5.580	4.938	3.605
abs corr applied	empirical, SADABS	empirical, SADABS	empirical, SADABS	empirical, SADABS
data-to-param ratio	19.2:1	27.3:1	24.9:1	20.9:1
final R indices (obsd data)[a]				
R1	0.0693	0.0384	0.0322	0.0521
wR2	0.1325	0.0652	0.0635	0.0853
R indices (all data)				
R1	0.0992	0.0450	0.0377	0.0818
wR2	0.1440	0.0666	0.0650	0.0932
goodness of fit	1.170	1.288	1.223	1.057

[a] $I > 2\sigma(I)$. [b] A molecule of tetrahydrofuran (THF) cocrystallizes with **9a**.

Hz, 1, H4), 2.27 (s, 3, H6's), 2.15 (s, 3, H5's), 1.84 (s, 15, cyclopentadienyl CH_3's), 1.53 (s, 9, thiolate CH_3's), 2.50−1.75 (complex m's, 12, PEt_3 CH_2's), 1.29 (d of t, J_{H-P} = 14.0 Hz, J_{H-H} = 7.5 Hz, 9, PEt_3 CH_3's), 0.92 (d of t, J_{H-P} = 16.5 Hz, J_{H-H} = 8.0 Hz, 9, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR (acetone-d_6, −10 °C, 125 MHz): δ 107.0 (s, C2), 101.6 (s, C1), 99.4 (s, C3), 95.5 (s, cyclopentadienyl C's), 75.7 (s, C4), 37.2 (s, thiolate $C(CH_3)_3$), 36.3 (s, thiolate $C(CH_3)_3$'s), 23.7 (s, C5), 23.1 (d, J_{C-P} = 39.5 Hz, PEt_3 CH_2's), 20.3 (s, C6), 16.7 (d, J_{C-P} = 32.6 Hz, PEt_3 CH_2's), 10.6 (s, cyclopentadienyl CH_3's), 10.0 (d, J_{C-P} = 5.8 Hz, PEt_3 CH_3's), 9.0 (d, J_{C-P} = 4.7 Hz, PEt_3 CH_3's). $^{31}P\{^1H\}$ NMR (acetone-d_6, 22 °C, 121 MHz): δ 39.8 (d, J_{P-P} = 15.9 Hz, 1, PEt_3), −7.5 (d, J_{P-P} = 15.9 Hz, 1, PEt_3).

Minor "*trans*" Isomer (9b) (selected peaks). ^1H NMR (acetone-d_6, −10 °C, 500 MHz): δ 8.97 (s, 1, H1), 5.66 (s, 1, H4). $^{13}C\{^1H\}$ NMR (acetone-d_6, −10 °C, 125 MHz): δ 110.1 (d, J_{C-P} = 76.6 Hz, C1), 76.6 (d, J_{C-P} = 4.6 Hz, C4). $^{31}P\{^1H\}$ NMR (acetone-d_6, 22°C, 121 MHz): δ 44.1 (s, 1, PEt_3), −16.2 (s, 1, PEt_3).

X-ray Diffraction Studies of Compounds 4a, 7a, 8, and 9a. Single crystals of compounds **4a**, **7a**, **8**, and **9a** were mounted on glass fibers under a nitrogen atmosphere. Diffraction data were obtained using a Bruker SMART charge coupled device (CCD) detector system. 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).[23] 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. Minor disorders involving the trifluoromethanesulfonate anions in **8** and **9a** and the tetrahydrofuran molecule of crystallization in **9a** were successfully modeled.

Crystal data and details of both collection and structure analysis are listed in Table 2.

Acknowledgment. Support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Washington University's High Resolution NMR Service Facility was funded in part by NIH Support Instrument Grants (RR-02004, RR-05018, and RR-07155). Mass spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR00954).

Supporting Information Available: Structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **4a**, **7a**, **8**, and **9a.** This material is available free of charge via the Internet at http://pubs.acs.org.

OM0400649

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