

## Synthesis, Structure, Spectroscopy, and Reactivity of a Metallathiabenzene<sup>1</sup>

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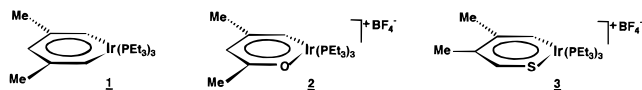
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During the past decade, we have been studying the chemistry of “iridabenzene” **1**,<sup>2</sup> a rare<sup>3,4</sup> metal-containing analogue of benzene. Our synthetic approach to this novel aromatic molecule involves the use of a pentadienide reagent to supply the ring carbon atoms. The key ring-forming step is the metal-mediated activation of a pentadienyl C–H bond. Using a similar synthetic strategy, we have recently succeeded in producing an oxygen-containing relative of **1**, iridapyrylium **2**,<sup>5</sup> and we now report the synthesis, structure, spectroscopy, and preliminary reaction chemistry of a sulfur-containing member of this unique aromatic family, iridathiabenzene **3**.<sup>6</sup>



As shown in Scheme 1, treatment of (Cl)Ir(PEt<sub>3</sub>)<sub>3</sub> with lithium 2,3-dimethyl-5-thiapentadienide<sup>7</sup> leads to the production of a six-membered metallacycle, iridathiacyclohexadiene **4**, via C–H1 bond activation in 16e<sup>-</sup> intermediate **A**. The presence of a methyl group at C2 is crucial, because in its absence, activation at C–H2 is preferred, leading ultimately to the production of a five-membered metallacycle.<sup>8</sup>

The <sup>1</sup>H NMR spectrum of **4** exhibits downfield signals for ring protons H1 and H4 at δ 7.05 and δ 5.78, respectively, while the metal-hydride signal appears far upfield at δ -16.10. In the <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum, the ring carbons resonate at δ 118.8 (C1), 127.3 (C2), 127.3 (C3), and 120.9 (C4). The signal for C1 is a characteristic doublet (*J*<sub>C–P</sub> = 72.0 Hz) of triplets (*J*<sub>C–P</sub> = 15.0 Hz) due to coupling to the <sup>31</sup>P nuclei of the trans and cis phosphines, respectively. The X-ray crystal structure of **4**, to be reported in detail in a future paper, exhibits *localized* single and double bonds within the metallacycle.<sup>9</sup>

(1) Metallacyclohexadiene and Metallabenzene Chemistry. 15. For Part 14, see: Bleeker, J. R.; Behm, R. *J. Am. Chem. Soc.* **1997**, *119*, 8503.

(2) Bleeker, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M.; Robinson, K. R.; Beatty, A. M. *Organometallics* **1997**, *16*, 606.

(3) Only one other stable metallabenzene has been reported: Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

(4) Detection of a thermally unstable metallabenzene at low temperature has recently been reported: Yang, J.; Jones, W. M.; Dixon, J. K.; Allison, N. *J. Am. Chem. Soc.* **1995**, *117*, 9776.

(5) Bleeker, J. R.; Blanchard, J. M. B. *J. Am. Chem. Soc.* **1997**, *119*, 5443.

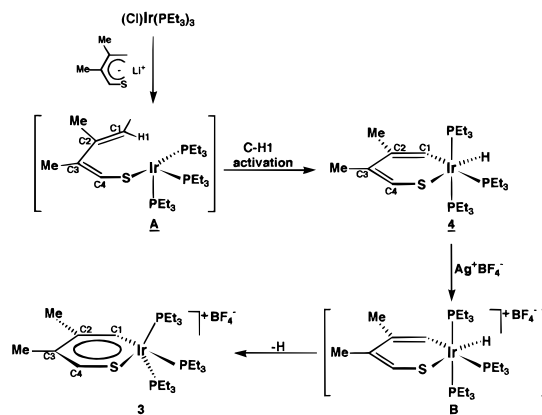
(6) Several other examples of metallathiabenzenes have been reported. In each case the key ring-forming step involved activation of a thiophene C–S bond. (a) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (b) Chin, R. M.; Jones, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 357. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731.

(7) This reagent is synthesized by treating 2,5-dihydro-3,4-dimethylthiophene with *n*-butyllithium in hexane/tetrahydrofuran.

(8) (a) Bleeker, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740. (b) Bleeker, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813.

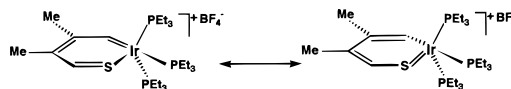
(9) Bond distances within the ring (Å) are as follows: Ir–C1, 2.093(10); C1–C2, 1.340(14); C2–C3, 1.456(18); C3–C4, 1.380(19); C4–S, 1.731(12); S–Ir, 2.433(3).

## Scheme 1



Treatment of yellow-orange iridathiacyclohexadiene **4** with silver tetrafluoroborate in tetrahydrofuran leads to the immediate production of deep red iridathiabenzene **3**, presumably through the intermediacy of the 17e<sup>-</sup> oxidation product **B** (Scheme 1).<sup>10</sup> The <sup>1</sup>H NMR spectrum of **3** shows downfield shifting for ring protons H1 and H4, consistent with its formulation as an aromatic species. Proton H1 resonates at δ 10.36 and is a quartet (*J*<sub>H–P</sub> = 8.4 Hz) due to coupling to three equivalent <sup>31</sup>P nuclei (vide infra), while H4 resonates at δ 8.61. The ring carbons resonate at δ 165.1 (C1), 143.6 (C2), 134.9 (C3), and 130.0 (C4), and C1 (like H1) appears as a phosphorus-coupled quartet (*J*<sub>C–P</sub> = 21.6 Hz). The <sup>31</sup>P{<sup>1</sup>H} NMR signal for **3**, like that for analogues **1**<sup>2</sup> and **2**,<sup>5</sup> is a singlet at room temperature, indicating that the three phosphine ligands are exchanging rapidly in solution. However, upon cooling to -90 °C, the <sup>31</sup>P{<sup>1</sup>H} NMR signal broadens and ultimately resolves into two sharp resonances with an intensity ratio of 2:1. Simulation of the variable-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectra<sup>11</sup> yields a Δ*G*<sup>‡</sup> of 9.5 kcal/mol for this intramolecular phosphine exchange process.

The X-ray crystal structure of **3**<sup>12</sup> (see Figure 1) shows delocalized bonding around the ring, consistent with an aromatic system in which both 6π electron resonance structures shown below are contributing. Carbon–carbon bond distances C1–C2,



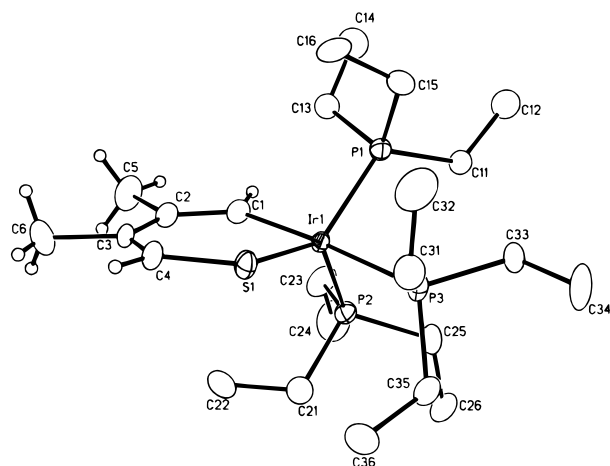
C2–C3, and C3–C4 have moved toward equalization, while bonds Ir–C1 and Ir–S1 have both shortened substantially (vs their lengths in **4**),<sup>9</sup> indicating significant metal participation in the ring π-bonding. The nonmetal portion of the ring (C1/C2/C3/C4/S1) is very nearly planar (mean deviation 0.015 Å), while the iridium center lies 0.185 Å out of this plane. The dihedral angle between planes C1/C2/C3/C4/S1 and C1/Ir1/S1 is 7.0°. Consistent with the low-temperature <sup>31</sup>P NMR spectrum described above, the coordination geometry around iridium is trigonal bipyramidal, with C1 and P3 occupying the axial positions and S1, P1, and P2 occupying the equatorial sites. This contrasts with the square-pyramidal coordination geometry adopted by **1**.<sup>2</sup>

As summarized in Scheme 2, iridathiabenzene **3** is reactive toward a variety of substrates. Treatment of **3** with PPN<sup>+</sup>Cl<sup>-</sup> or with excess PMe<sub>3</sub> at room temperature results in direct ligand addition at the metal center, generating six-coordinate products

(10) The fate of the metal-bound hydrogen is not yet known.

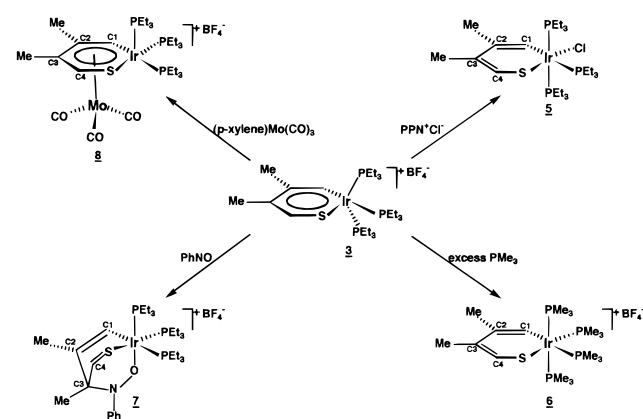
(11) Johnson, C. S., Jr. *Am. J. Phys.* **1967**, *35*, 929.

(12) Crystal data for **3**: red prism; monoclinic, space group *P2<sub>1</sub>/c*, *a* = 14.483(7) Å, *b* = 10.331(5) Å, *c* = 21.842(7) Å, β = 93.85(3)°, *V* = 3261(2) Å<sup>3</sup>, *Z* = 4; *R* = 4.03%, *R<sub>w</sub>* = 5.53%, GOF = 1.00.



**Figure 1.** ORTEP drawing of  $\text{CH}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{CH}-\text{S}=\text{Ir}(\text{PEt}_3)_3^+ \text{BF}_4^-$  (**3**). Selected bond distances (Å): Ir1–S1, 2.249(3); Ir1–C1, 2.019(10); S1–C4, 1.713(12); C1–C2, 1.396(16); C2–C3, 1.415(15); C3–C4, 1.361(16). Selected bond angles (deg): S1–Ir1–C1, 89.3(3); Ir1–C1–C2, 134.1(8); C1–C2–C3, 126.7(10); C2–C3–C4, 125.0(11); C3–C4–S1, 127.7(9); C4–S1–Ir1, 116.4(4).

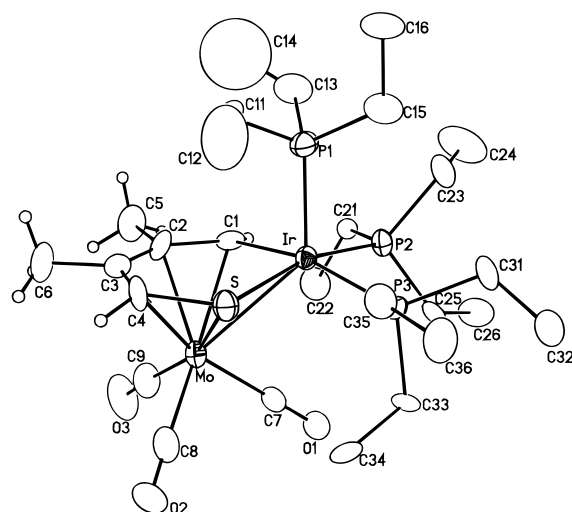
### Scheme 2



**5** and **6**, respectively. The NMR data for **5** and **6** are strikingly similar to those for compound **4** and confirm the presence of the iridathiacyclohexa-1,3-diene ring system. Note that the  $\text{PMe}_3$  addition reaction is accompanied by the rapid and complete replacement of all three bulky  $\text{PEt}_3$  ligands with smaller  $\text{PMe}_3$  ligands. This reaction contrasts with the room-temperature reaction of iridabenzene **1** with excess  $\text{PMe}_3$ ,<sup>2</sup> which results in replacement of only one  $\text{PEt}_3$  ligand with  $\text{PMe}_3$  and retention of the aromatic ring system.<sup>13</sup>

When **3** is treated with nitrosobenzene, the [4+2] cycloaddition product **7** is generated. The iridathiacyclohexa-1,4-diene ring in **7** is characterized by a relatively upfield chemical shift position for  $\text{sp}^3$  carbon C3 ( $\delta$  50.8) and downfield shift positions for thioaldehyde carbon C4 ( $\delta$  154.2) and hydrogen H4 ( $\delta$  8.31).

Finally, treatment of **3** with  $(\eta^6\text{-}p\text{-xylene})\text{Mo}(\text{CO})_3$  in tetrahydrofuran leads to arene exchange and clean production of the deep violet iridathiabenzene adduct, **8**. The NMR signals for the ring protons and carbons in **8** shift upfield from their positions in **3**, as is normally observed when arenes  $\pi$ -coordinate to transition metals. Protons H1 and H4 in **8** resonate at  $\delta$  8.27 and 6.59, respectively, while carbons C1, C2, C3, and C4 resonate at  $\delta$  129.0, 117.6, 109.5, and 89.0, respectively. Unlike **3**, which undergoes intramolecular phosphine exchange in solution (vide supra), **8** is stereochemically rigid. Hence, the  $^{31}\text{P}\{^1\text{H}\}$  NMR



**Figure 2.** ORTEP drawing of  $[\eta^6\text{-CH}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{CH}-\text{S}=\text{Ir}(\text{PEt}_3)_3]\text{Mo}(\text{CO})_3^+ \text{BF}_4^-$  (**8**). Compound **8** crystallized with two independent molecules in the unit cell; molecule 1 is reported here. Selected bond distances (Å): Ir–S, 2.312(4); Ir–C1, 2.049(15); S–C4, 1.766(16); C1–C2, 1.42(2); C2–C3, 1.40(3); C3–C4, 1.42(2); Mo–Ir, 3.0180(16); Mo–S, 2.544(5); Mo–C1, 2.459(16); Mo–C2, 2.382(19); Mo–C3, 2.399(18); Mo–C4, 2.382(17). Selected bond angles (deg): S–Ir–C1, 89.6(6); Ir–C1–C2, 135.5(15); C1–C2–C3, 126.5(17); C2–C3–C4, 125.3(16); C3–C4–S, 128.1(13); C4–S–Ir, 114.0(7).

spectrum at room temperature consists of three discrete signals for the three inequivalent phosphine ligands. However, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **8** exhibits a single peak for the three carbonyl ligands, indicating that the iridathiabenzene ring is rotating freely with respect to the  $\text{Mo}(\text{CO})_3$  moiety.

The X-ray crystal structure of **8** (see Figure 2)<sup>14</sup> shows that the molybdenum atom is strongly  $\pi$ -complexed to all six atoms of the iridathiabenzene ring and that the bonding within this ring is still delocalized. The coordination geometry at the iridium center in **8** approximates a square pyramid, in contrast to the trigonal bipyramidal coordination geometry exhibited by **3**. Atoms C1, S, P2, and P3 define the basal ligand set while phosphorus atom P1 occupies the unique axial site. This shift in coordination geometry is undoubtedly a response to the steric demands of the  $\text{Mo}(\text{CO})_3$  moiety.

In summary, we have synthesized a new iridathiabenzene complex, using thiapentadienide as the source of ring carbon and sulfur atoms and exploiting C–H bond activation in the key ring forming step. The X-ray crystal structure of this species, its solution-phase NMR spectra, and its ability to undergo arene exchange with  $(p\text{-xylene})\text{Mo}(\text{CO})_3$  are all consistent with the presence of an aromatic ring system in which the metal center participates in ring  $\pi$ -bonding. However, the aromaticity is evidently quite “fragile”, being readily disrupted by direct ligand addition to the metal center or by cycloadduct formation.

**Acknowledgment.** We thank the National Science Foundation for support (Grant CHE-9303516), Johnson Matthey Alfa/Aesar for a loan of  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ , and Robert Behm (Washington University) for assistance with the X-ray crystal structure of compound **3**.

**Supporting Information Available:** Syntheses and full NMR spectral data for compounds **3–8** and structure determination summary tables and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **3** and **8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) The reaction of **1** with  $\text{PMe}_3$  proceeds by a dissociative mechanism, while the reaction of **3** with  $\text{PMe}_3$  probably involves a series of associative steps.

(14) Crystal data for **8**: deep violet plate; orthorhombic, space group  $Pca2_1$ ,  $a = 19.6927(2)$  Å,  $b = 10.4724(1)$  Å,  $c = 36.9242(2)$  Å,  $V = 7614.87(11)$  Å<sup>3</sup>,  $Z = 8$ ;  $R = 6.19\%$ ,  $R_w = 13.00\%$ , GOF = 1.03.