

## Communications to the Editor

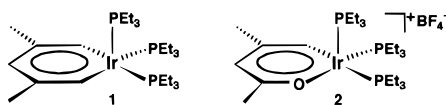
Synthesis and Reactivity of a Metallapyrylium<sup>1</sup>

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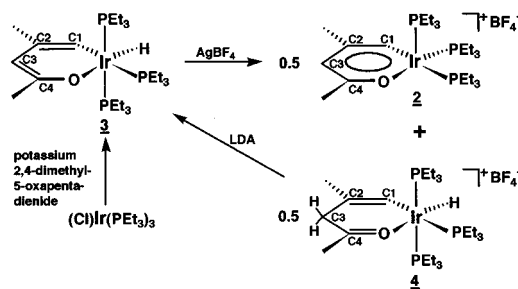
During the past several years, we have investigated the chemistry of “iridabenzene” (**1**),<sup>2</sup> a rare example of a stable metallabenzene complex.<sup>3,4</sup> We have found that the physical and chemical properties of **1** are consistent with the presence of a genuine—albeit fragile—aromatic ring system. We now report the synthesis, spectroscopy, and preliminary reaction chemistry of the oxygen-containing analog of **1**, “iridapyrylium” (**2**), which, to our knowledge, is the first example of a stable metallaioxabenzene.<sup>5</sup> Highlighted in this paper are some of the similarities and differences that are evident in the chemical behavior of compounds **1** and **2**.



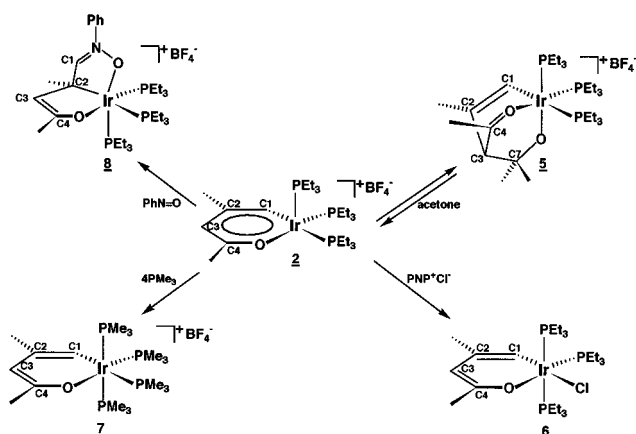
The synthesis of iridapyrylium (**2**) is accomplished by the series of steps shown in Scheme 1. Treatment of (Cl)Ir(PEt<sub>3</sub>)<sub>3</sub> with potassium 2,4-dimethyl-5-oxapentadienide generates the iridaoxacyclohexa-1,3-diene compound **3** via C–H bond activation.<sup>6</sup> This species is then treated dropwise with 1 equiv of Ag<sup>+</sup>BF<sub>4</sub><sup>−</sup> in tetrahydrofuran at −47 °C. When the reaction is warmed to room temperature, a clean 1:1 mixture of iridapyrylium (**2**) and the protonated ring compound **4** is isolated.<sup>7,8</sup> Treatment of the mixture of **2** and **4** with 0.5 equiv of lithium diisopropylamide in tetrahydrofuran leads to selective deprotonation of **4** and regeneration of 0.5 equiv of **3**. This neutral species can then be extracted with pentane and reused, leaving behind clean iridapyrylium (**2**) as a deep purple solid.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **2**, like that of **1**,<sup>2</sup> consists of a sharp singlet, which does not broaden significantly even upon cooling to −90 °C. This behavior is indicative of a low-energy

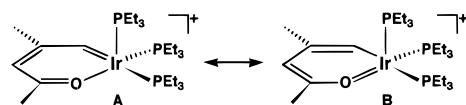
## Scheme 1



## Scheme 2



fluxional process that exchanges the phosphine ligands.<sup>9</sup> In the <sup>1</sup>H NMR spectrum of **2** (in CD<sub>2</sub>Cl<sub>2</sub>), ring protons H1 and H3 are shifted downfield to δ 9.35 and 6.45, respectively,<sup>10</sup> indicating metal orbital participation in ring π-bonding and contributions from resonance structures **A** and **B**. The H1 signal is split into a quartet (*J* = 6.0 Hz) by the <sup>31</sup>P nuclei of the three exchanging phosphine ligands. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the ring carbons resonate at δ 170.7 (C4), 162.2 (C1), 147.3 (C2), and 112.2 (C3). The C1 signal is split into a phosphorus-coupled quartet (*J* = 22.7 Hz).



When iridapyrylium (**2**) is dissolved in acetone-*d*<sub>6</sub> at room temperature, its <sup>31</sup>P NMR signal broadens dramatically and three new broad humps appear upfield in the <sup>31</sup>P NMR spectrum. As the sample is cooled to −40 °C, the iridapyrylium signal disappears and the upfield humps sharpen into three clean doublet-of-doublet signals, indicating the formation of a low-temperature adduct with a static, *facial* arrangement of PEt<sub>3</sub> ligands. This cooling process is accompanied by a color change from deep purple (**2**) to light yellow (adduct) and is fully reversible. The NMR spectra of the adduct, recorded at −40 °C in acetone-*d*<sub>6</sub>, clearly demonstrate that it is the [4 + 2] cycloaddition product **5**, as shown in Scheme 2. In particular, the signals for H3 and C3 shift upfield to δ 3.95 and 74.9,

(9) If compound **2** is isostructural with **1** (square pyramidal), the phosphine exchange probably occurs via a Berry-type process involving trigonal bipyramidal intermediates.

(10) In precursor **3**, H1 and H3 resonate at δ 5.76 and 4.02, respectively, in CD<sub>2</sub>Cl<sub>2</sub>.

(1) *Metallacyclohexadiene and Metallabenzene Chemistry*. 13. For Part 12, see: Bleeker, J. R.; Behm, R.; Beatty, A. M. *Organometallics* **1997**, *16*, 1103.

(2) (a) Bleeker, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606. (b) Bleeker, J. R.; Behm, R.; Xie, Y.-F.; Clayton, T. W., Jr.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093. (c) Bleeker, J. R. *Acc. Chem. Res.* **1991**, *24*, 271.

(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.

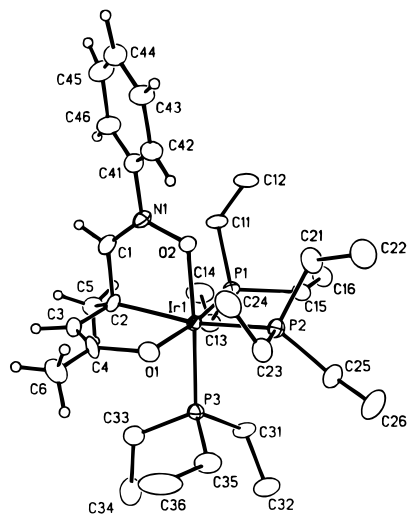
(4) Detection of a thermally unstable metallabenzene at low temperature has recently been reported: Yang, J.; Jones, W. M.; Dixon, J. K.; Allison, N. *J. Am. Chem. Soc.* **1995**, *117*, 9776.

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

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

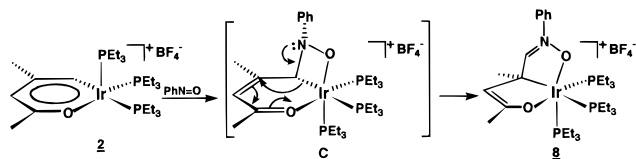
(7) Although the mechanistic details of this reaction are not known, one reasonable pathway involves (a) 1e<sup>−</sup> oxidation of 0.5 equiv of **3** to 17e<sup>−</sup> **3**<sup>+</sup>, (b) transfer of H<sup>+</sup> from **3**<sup>+</sup> to the remaining 0.5 equiv of **3**, producing 0.5 equiv of **4** and 0.5 equiv of neutral iridapyrylium, and (c) oxidation of the neutral iridapyrylium to 0.5 equiv of **2**. Introduction of an external base (e.g., NEt<sub>3</sub>) has no effect on the reaction.

(8) Compound **4** can be synthesized independently by protonation of **3** with HBF<sub>4</sub>·OEt<sub>2</sub>.



**Figure 1.** ORTEP drawing of the cation in compound **8** with 20% thermal ellipsoids. Hydrogens on the PEt<sub>3</sub> ligands are omitted for clarity. Selected bond distances (Å): Ir1–O1, 2.089(9); Ir1–O2, 2.112(9); Ir1–C2, 2.178(13); O2–N1, 1.323(14); N1–C1, 1.320(20); C1–C2, 1.517(22); C2–C3, 1.496(25); C3–C4, 1.347(23); C4–O1, 1.337(20). Selected bond angles (deg): O1–Ir1–O2, 85.7(4); C2–Ir1–O2, 81.5(4); Ir1–O2–N1, 112.6(8); O2–N1–C1, 120.1(12); N1–C1–C2, 122.2(12); C1–C2–Ir1, 102.4(9); C1–C2–C3, 98.5(12); C2–C3–C4, 118.9(14); C3–C4–O1, 120.9(15); C4–O1–Ir1, 113.1(9); O1–Ir1–C2, 80.9(5); Ir1–C2–C3, 105.3(9).

### Scheme 3



respectively, indicating that these atoms are no longer aromatic or olefinic. Furthermore, the C4 signal shifts far downfield to  $\delta$  224.5, as expected for a carbonyl carbon, while the central carbon of the acetone moiety, C7, resonates at  $\delta$  64.9, consistent with alkoxide character. The connectivity of the molecule is further demonstrated by the observation of coupling between C3 and C7 ( $J = 30.3$  Hz) when <sup>13</sup>C-labeled acetone is used in the experiment.<sup>11</sup>

When compound **2** is treated with PNP<sup>+</sup>Cl<sup>−</sup> or with excess PMe<sub>3</sub> at room temperature, ligand addition occurs directly at the metal center, generating yellow six-coordinate iridaoxacyclohexa-1,3-diene products, compounds **6** and **7**, respectively (Scheme 2). The chloride addition product **6** bears a close resemblance to compound **3**, except that the chloride ligand in **6** resides *trans* to ring carbon C1, while the hydride ligand in **3** lies *trans* to oxygen. This ligand arrangement is evident from

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

the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **6**, where ring carbon C1 exhibits only weak coupling ( $J_{CP} = 7.7$  Hz) to the <sup>31</sup>P nuclei of the three PEt<sub>3</sub> ligands. The PMe<sub>3</sub> addition reaction is accompanied by the rapid and complete replacement of all three bulky PEt<sub>3</sub> ligands with smaller PMe<sub>3</sub> ligands, generating the tetrakis(PMe<sub>3</sub>) product **7**. This reaction contrasts sharply with the room temperature reaction of iridabenzene **1** with excess PMe<sub>3</sub>, which results in replacement of only one PEt<sub>3</sub> ligand with PMe<sub>3</sub> and retention of the aromatic ring system.<sup>12</sup>

When iridapyrylium **2** is treated with nitrosobenzene, a novel adduct containing two fused five-membered metallacycles, compound **8** (Scheme 2), is generated. From the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **8**, it is clear that ring carbon C1 is no longer bonded to the iridium center (no C–P coupling), while neighboring carbon C2 is ( $J_{CP} = 78.7$  Hz). Furthermore, the chemical shift of C2 ( $\delta$ 42.7) indicates that it is no longer aromatic or olefinic. In contrast, the signals for ring carbons C1, C3, and C4 remain in the olefinic region of the spectrum ( $\delta$  156.8, 102.0, and 172.3, respectively). The structure of **8** has been confirmed by single-crystal X-ray diffraction and is shown in Figure 1; selected bond distances and angles are reported in the caption. Although the mechanism of this reaction is not known, the connectivity of the final product (i.e., nitrogen bonded to C1) suggests that the initial interaction may be a [2 + 2] cycloaddition involving the NO double bond of nitrosobenzene and the metal–carbene bond of **2**. Rearrangement of this cycloadduct, as shown in Scheme 3, could lead to the observed product **8**. It is interesting to note that iridabenzene (**1**) also reacts with nitrosobenzene, but the product in this case is a [4 + 2] cycloadduct which undergoes no further rearrangement.<sup>2</sup>

In summary, we have synthesized the first example of a stable metallapyrylium complex. The <sup>1</sup>H NMR spectrum of this species shows that the ring proton signals are shifted significantly downfield, indicating that the metal center participates in ring  $\pi$ -bonding. However, these metal  $\pi$ -interactions are evidently quite weak, being readily disrupted by cycloadduct formation or by direct ligand addition to the metal center.

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**Supporting Information Available:** Detailed synthetic procedures and spectroscopic data for compounds **2**, **4**–**7**, and **8** and structure determination summary and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compound **8** (16 pages). See any current masthead page for ordering and Internet access instructions.

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(12) The reaction of **1** with PMe<sub>3</sub> proceeds by a dissociative mechanism (ref 2), while the reaction of **2** with PMe<sub>3</sub> probably involves a series of associative steps.