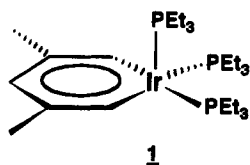


Cycloaddition Reactions of a Metallabenzene¹John R. Bleeke,* Robert Behm, Yun-Feng Xie,
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Metallabenzenes, *i.e.*, benzenoid compounds in which one CH group has been replaced by a transition metal and its associated ligands, are exceedingly rare. In fact, only two examples of such compounds have been isolated and characterized, an "osmabenzene" reported by Roper² and our "iridabenzene" **1**.³



Although compound **1** exhibits the delocalized bonding and downfield ¹H NMR chemical shifts characteristic of aromatic ring compounds, its reaction chemistry indicates that the aromaticity is rather fragile. In this communication, we describe a series of cycloaddition reactions which disrupt the aromaticity of **1** and lead to novel organometallic products containing multiple ring systems.

As shown in Scheme 1, **1** reacts with electron-poor olefins, heteroolefins, heterocumulenes, and 1,3-dipolar reagents. In each of these reactions, the substrate approaches the square pyramidal iridabenzene molecule from the open face. The key orbital interaction involves the "effective HOMO" of the electron-rich iridabenzene, pictured in Figure 1,⁴ and the LUMO of the substrate molecule. As can be seen from Figure 1, the effective HOMO of **1** is derived from a strong bonding interaction between the 3π orbital of the organic ring fragment and a hybrid metal d orbital (d_{xz}/d_{z^2}). As a result, the wave function has the same phase on Ir and C1/C5 but the opposite phase on C3. Although we cannot prove that these cycloaddition reactions are concerted, their facility and their specificity strongly suggest that they are.⁵

Treatment of **1** with maleic anhydride, nitrosobenzene, or carbon disulfide leads to clean $4\pi + 2\pi$ cycloaddition reactions in which the substrate adds across iridium and C3 of the iridabenzene ring, producing compounds **2**, **3**, and **4**, respectively. Similarly, **1** undergoes a cheletropic ($4\pi + 2\omega$) reaction with sulfur dioxide to produce adduct **5**. In contrast, treatment of **1** with carbon dioxide leads exclusively to the formation of the $2\pi + 2\pi$ cycloaddition product, **6** (see ORTEP drawing, Figure 2).⁶

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(1) Metallacyclohexadiene and Metallabenzene Chemistry. 10. Part 9: Bleeke, J. R.; Rohde, A. M.; Boorsma, D. W. *Organometallics* 1993, 12, 970.

(2) (a) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* 1982, 811. (b) Elliott, G. P.; McAuley, N. M.; Roper, W. R. *Inorg. Synth.* 1989, 26, 184.

(3) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* 1989, 111, 4118. See also: (a) Bleeke, J. R.; Xie, Y.-F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* 1991, 113, 4703. (b) Bleeke, J. R. *Acc. Chem. Res.* 1991, 24, 271.

(4) (a) This orbital picture is derived from Fenske–Hall molecular orbital calculations (full details to be published). (b) We use the term "effective HOMO" because there are actually three filled, essentially nonbonding d orbitals ($d_{x^2-y^2}$, d_{yz} , and d_{xz}/d_{z^2} hybrid) that lie slightly higher in energy than the orbital of interest. However, these d orbitals do not appear to participate in the cycloaddition reactions.

(5) Typical reaction conditions: Under nitrogen, substrate was added to a cold (0 °C), stirred solution of **1** in tetrahydrofuran. The solution was warmed to room temperature, stirred for 30 min, filtered, and evacuated to dryness. The precipitate was dissolved in a minimal quantity of acetone and cooled to –30 °C overnight, producing crystals. Typical yield: 70%.

Scheme 1

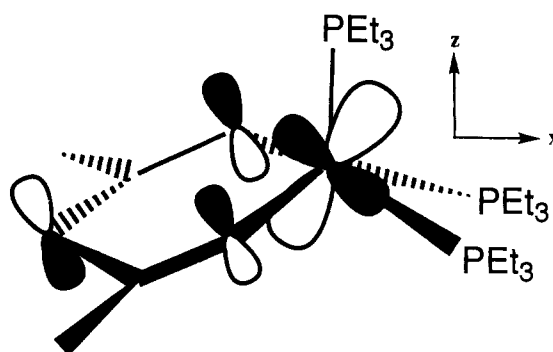
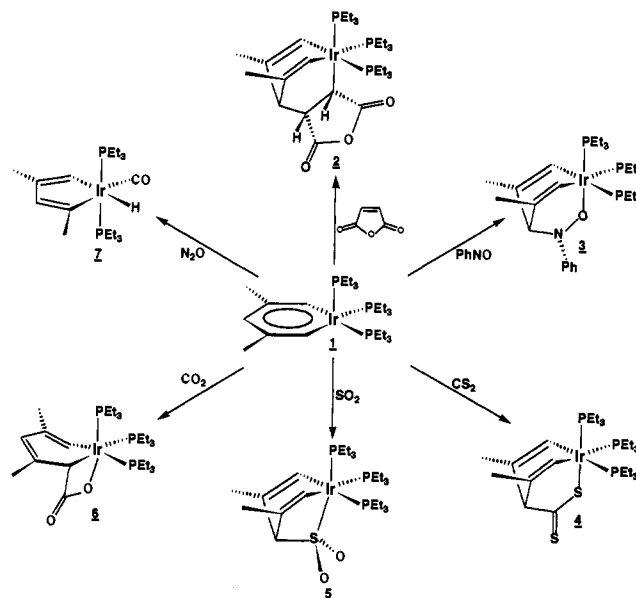


Figure 1. The effective highest occupied molecular orbital for iridabenzene **1**.

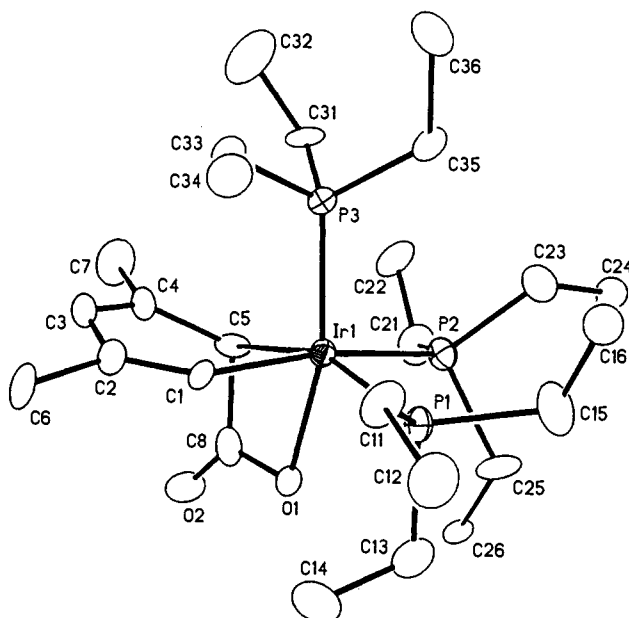
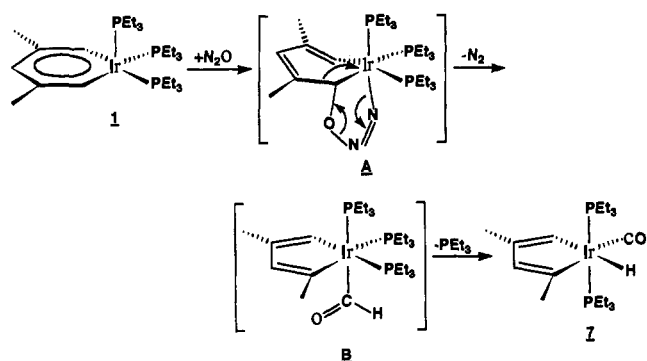


Figure 2. ORTEP drawing of **6**, the cycloaddition product of carbon dioxide and iridabenzene **1**.

The iridacyclohexadiene ring in this compound is perhaps best described as a half-boat with Ir lying 0.649 Å out of the C1/

Scheme 2



C2/C3/C4/C5 plane. While at first glance this reaction appears to violate the pericyclic selection rules, it may in fact be an allowed $2\pi_s + 2\pi_a$ cycloaddition, analogous to the concerted cycloadditions of ketenes to olefins.⁷ The minimal steric demands of CO_2 and the presence of a second set of π orbitals may provide stabilization of the perpendicular approach required for a $2\pi_s + 2\pi_a$ cycloaddition.⁸ Finally, treatment of **1** with nitrous oxide, a 1,3-dipolar reagent, leads to ring contraction and formation of the

(6) For a related reaction, see: Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079.

(7) Bartlett, P. D. *Pure Appl. Chem.* **1971**, *27*, 599 and references therein.

(8) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970; p 163.

iridacyclopentadiene complex **7**. Although we have not been able to isolate intermediates in this reaction, we postulate an initial 2π (iridabenzene) + 4π (N_2O) cycloaddition to produce **A**, Scheme 2. Rearrangement with loss of N_2 would lead to formyl species **B**, and migration of the formyl hydrogen ("retroinsertion") would generate the carbonyl-hydride product, **7**.

In conclusion, we have demonstrated that iridabenzene **1** undergoes cycloaddition reactions with a wide variety of substrates. In each case, the reactions appear to obey the pericyclic selection rules with the key orbital interaction involving the effective HOMO of iridabenzene and the LUMO of the substrate. Strategies for extruding the metal-ligand moiety from these novel structures are currently under investigation.

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Supplementary Material Available: Detailed synthetic procedures and full spectroscopic data for compounds **2-7** and structure determination summary and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compound **6** (16 pages); observed and calculated structure factors for compound **6** (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.