Metallabenzene Chemistry

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Ever since Kekulé's[1] intuitive idea on the structure of benzene, "aromaticity" has been one of the most vexing and yet one of the most fascinating topics in chemistry. For over a century, aromatic chemistry has challenged both the theoretician and the synthesist and has provided one of the most fruitful interplays of theory and experiment.[2]

It is, of course, now well-known that cyclic, conjugated, nonbenzenoid organic compounds can exhibit "aromatic" properties, including high thermodynamic stability, low chemical reactivity, delocalization of bonding, and ring currents.[3] Furthermore, formal replacement of a methine (CH) group in benzene with an isoelectronic nitrogen, phosphorus, arsenic, or antimony atom leads to stable heterocyclic compounds in which aromaticity is retained.[4] However, little is known about analogous replacements involving transition metals and their associated ligands. Particularly intriguing is the issue of whether such "metallabenzenes" would exhibit "aromatic" physical and chemical properties.
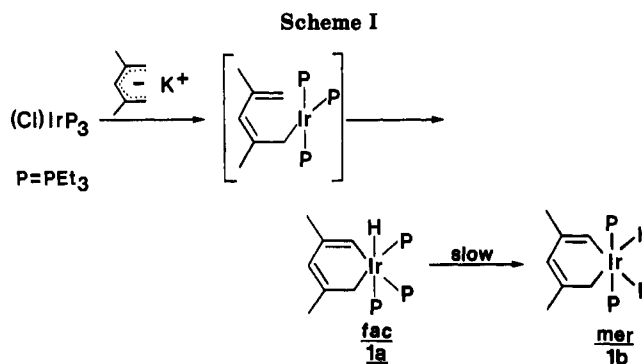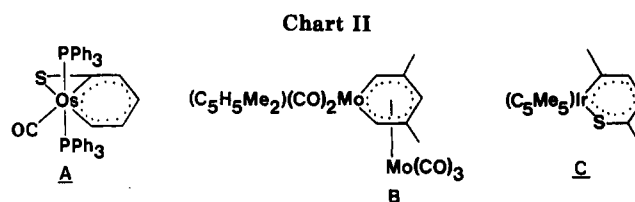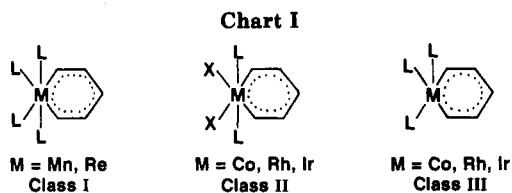
Recently, we have discovered a new high-yield synthetic route to metallabenzenes.[5] This approach involves the "dehydrogenation" of metallacyclohexadiene complexes, which, in turn, are obtained from (pentadienyl)metal precursors. In this Account, we describe the structure, spectroscopy, and chemical reactivity of these fascinating molecules and address the issue of aromaticity in metallabenzenes.

Background

In 1979, Hoffmann and Thorn[6] considered the issue of delocalization in transition-metal metallacycles and predicted on the basis of extended Hückel molecular orbital calculations that the three classes (I–III) of hypothetical metallacycles shown in Chart I should exhibit delocalized bonding and some aromatic character (L = 2e⁻ neutral donor ligand, X = halide). In each of these structures, the metal–ligand fragment is isolobal with CH.[7]

In 1982, Roper and co-workers[8] reported the first (and, prior to our work, only) example of a stable metallabenzene, $(Os\text{-}C(S)\text{-}CH\text{-}CH\text{-}CH\text{-}CH)$-$(CO)(PPh_3)_2$ (see A in Chart II). This complex was prepared via a cyclotrimerization reaction involving acetylene and the osmium–thiocarbonyl complex Os-$(CS)(CO)(PPh_3)_3$. Its X-ray crystal structure revealed a planar six-membered ring with no significant alternation in C–C bond lengths, supporting the idea of

Chart I

M = Mn, Re
Class I

M = Co, Rh, Ir
Class II

M = Co, Rh, Ir
Class III

Chart II

A

$(C_5H_5Me_2)(CO)_2Mo$

$Mo(CO)_3$

B

$(C_5Me_5)Ir$

C

Scheme I

$(Cl)IrP_3$

P = PEt₃

fac
1a

slow

mer
1b

electron delocalization within the ring.

In 1987, Ernst et al.[9] reported the preparation of an (η^6-metallabenzene)metal complex, $[(2,4\text{-}Me_2C_5H_5)\text{-}(CO)_2(Mo\text{-}CH\text{-}C(Me)\text{-}CH\text{-}C(Me)\text{-}CH)]Mo\text{-}(CO)_3$ (see B in Chart II), from the reaction of 2 equiv of $(2,4\text{-}Me_2C_5H_5)Mo(CO)_3^-$ with IC_2H_4I. Very recently, Angelici[10] reported the synthesis of a novel metal-lathiabenzene complex, $(C_5Me_5)(Ir\text{-}S\text{-}C(Me)\text{-}CH\text{-}CH\text{-}C(Me))$ (see C in Chart II), via insertion

John R. Bleeke was born in Port Washington, WI, in 1954. He received his B.A. degree from Carthage College (Kenosha, WI) in 1976 and his Ph.D. degree from Cornell University in 1981 under the direction of the late Earl L. Muetterties. After a short postdoctoral stint with Muetterties at the University of California—Berkeley, he joined the faculty at Washington University in St. Louis, where he is now Associate Professor of Chemistry. His current research focuses on the synthesis, structure, dynamics, and reactivity of transition-metal organometallic complexes, particularly (pentadienyl)metal, (heteropentadienyl)metal, and metallabenzene complexes.

(1) Kekulé, A. *Bull. Soc. Chim. Fr.* 1865, 3, 98.
(2) (a) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge University Press: London, 1969. (b) Garratt, P. J. *Aromaticity*; McGraw-Hill: London, 1971. (c) Bergmann, E. D., Pullman, B., Eds. *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity*; Academic Press: New York, 1971. (d) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons: New York, 1985; pp 37–64.
(3) (a) Ginsburg, D., Ed. *Non-Benzenoid Aromatic Compounds*; Interscience: New York, 1959. (b) Oki, M., Ed. *The Chemistry of Non-Benzenoid Aromatic Compounds*; Butterworths: London, 1971.
(4) (a) Ashe, A. J., III. *Acc. Chem. Res.* 1978, 11, 153. (b) Jutzi, P. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 232.
(5) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* 1989, 111, 4118.
(6) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* 1979, 3, 39.
(7) (a) Hoffmann, R. *Science* 1981, 211, 995. (b) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 711.
(8) (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.
(9) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* 1987, 6, 2612.
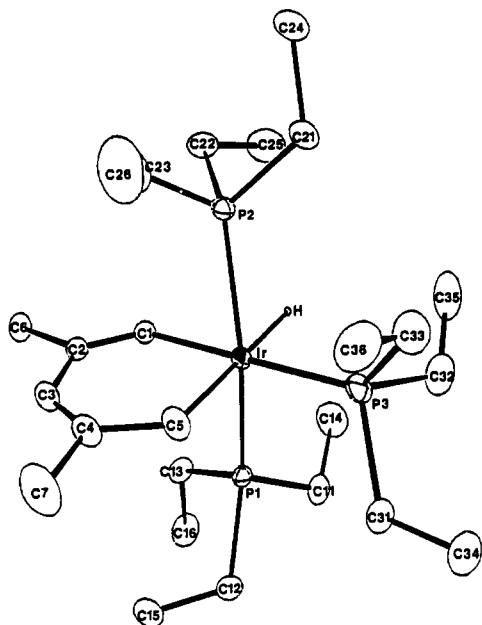(10) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* 1990, 112, 199.

272 *Acc. Chem. Res., Vol. 24, No. 9, 1991*

Bleeke

Figure 1. ORTEP drawing of *mer*-(IrCH=C(Me)CH=C(Me)C-H₂)(PEt₃)₃(H) (1b).
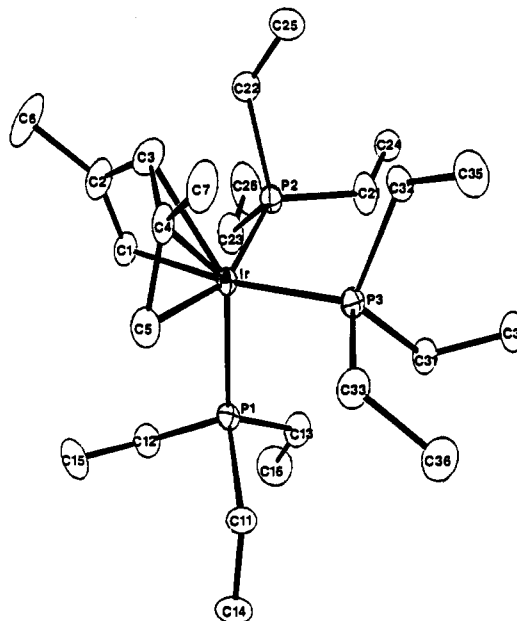
Figure 2. ORTEP drawing of the cation in [((IrCH=C(Me)-CH=C(Me)CH₂)(PEt₃)₃]⁺O₃SCF₃⁻ (2).
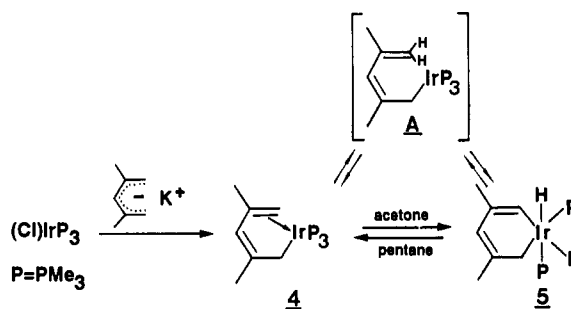
Scheme II

Scheme III
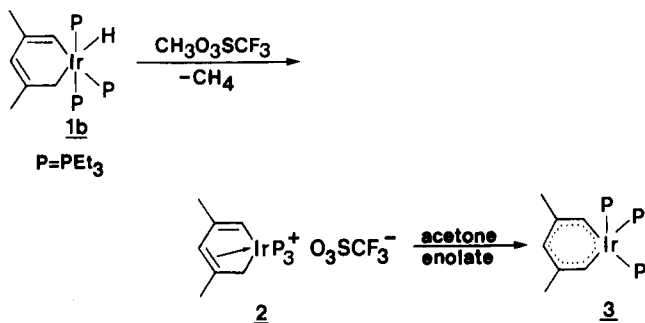
of iridium into a C–S bond of 2,5-dimethylthiophene. Finally, metallabenzenes have been postulated as low-temperature intermediates in the reactions of 1,4-di-lithiobutadiene reagents with transition metal carbonyl halide complexes, which ultimately lead to substituted (cyclopentadienyl)metal complexes,[11] and as possible intermediates in tungsten-based alkyne metathesis reactions.[12]

Synthesis of a Stable Iridabenzene

In the fall of 1986, we[13] discovered serendipitously that (pentadienyl)metal chemistry could provide a convenient synthetic route to unsaturated six-membered metallacycles.[14] In particular, we found that treatment of (Cl)Ir(PEt₃)₃ with potassium 2,4-di-

(11) (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (b) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *4*, 614.
(12) (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (c) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.
(13) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576.
(14) Metallacyclohexadiene complexes are quite rare, although several synthetic approaches have recently been developed. See: (a) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694. (b) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578. (c) Mike, C. A.; Nelson, T.; Graham, J.; Cordes, A. W.; Allison, N. T. *Organometallics* **1988**, *7*, 2573. (d) Alcock, N. W.; Bryars, K. H.; Pringle, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 1433.

methylpentadienide produces the 1-metallacyclohexa-2,4-diene complex *fac*-(IrCH=C(Me)CH=C(Me)C-H₂)(PEt₃)₃(H) (1a), which slowly isomerizes to the thermodynamically more favorable *mer* isomer, 1b (see solid-state structure, Figure 1).[13] The probable mechanism of this metallacycle-forming reaction, shown in Scheme I, involves the intermediacy of 16e⁻ (η¹-2,4-dimethylpentadienyl)Ir(PEt₃)₃, which undergoes intramolecular oxidative addition across a C–H bond on the terminus of the η¹-pentadienyl ligand. In a sense, this reaction is an organometallic actualization of Kekulé's famous dream in which "one of the snakes seizes hold of its own tail", and a ring is formed.[15]

As outlined in Scheme II, the metallacyclohexadiene complex 1b can be readily converted to a stable metallabenzene complex, (Ir⚌CH⚌C(Me)⚌CH⚌C-(Me)⚌CH)(PEt₃)₃ (3), via a two-step "dehydrogenation".[5] In the first step, the hydride ligand is removed from 1b with methyl trifluoromethanesulfonate, producing the cationic complex [(IrCH=C(Me)CH=C(Me)CH₂)(PEt₃)₃]⁺O₃SCF₃⁻ (2), in which one of the ring double bonds is coordinated to the iridium center (see solid-state structure, Figure

(15) Kekulé, A. '*Benzolfest: Rede', Berichte der Deutschen Chemischen Gesellschaft* **1890**, *23*, 1302.

Metallabenzene Chemistry

Acc. Chem. Res., Vol. 24, No. 9, 1991 **273**

Scheme IV
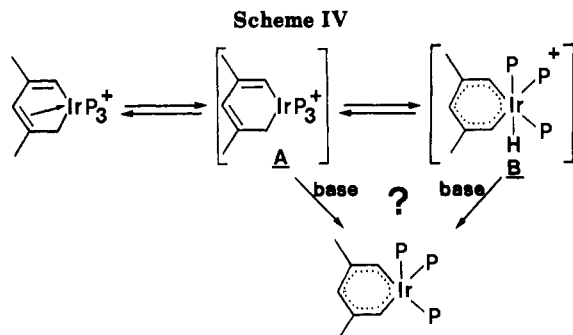
2).[16,17] Treatment of **2** with the enolate of acetone[18] causes deprotonation of the α ring carbon, producing metallabenzene **3** in high yield. This species is the first example of Hoffmann's predicted class III metalla-benzenes (vide supra).

The Tris(trimethylphosphine) Reaction System

Interestingly, the reactions outlined in Schemes I and II are quite sensitive to phosphine ligand sterics; hence, substitution of PMe₃ (cone angle = 118°)[19] for PEt₃ (cone angle = 132°)[19] leads to significantly different (but instructive) chemistry. As shown in Scheme III, treatment of (Cl)Ir(PMe₃)₃ with potassium 2,4-di-methylpentadienide produces an equilibrium mixture of ((1,4,5-η)-2,4-dimethylpentadienyl)Ir(PMe₃)₃ (**4**) and the metallacyclohexadiene complex *fac*-(IrCH=C-(Me)CH=C(Me)CH₂)(PMe₃)₃(H) (**5**).[20,21] Intercon-version between **4** and **5** probably involves the inter-mediacy of (η¹-2,4-dimethylpentadienyl)Ir(PMe₃)₃ (A, Scheme III). The iridium center in this 16e⁻ species can either coordinate the terminal double bond of the pentadienyl (producing **4**) or oxidatively add across a C-H bond on the end of the η¹-pentadienyl (producing **5**). Unlike its PEt₃ analogue, **5** does not isomerize from *fac* to *mer*, apparently because of reduced steric strain in the *fac* isomer.

The position of the equilibrium shown in Scheme III can be pushed far to the right by refluxing the mixture in acetone; pure metallacycle **5** can be obtained from the resulting isomerically enriched solution. Treatment of **5** with methyl trifluoromethanesulfonate cleanly re-moves the hydride ligand, producing the (PMe₃)₃ ana-logue of **2**, [(IrCH=C(Me)CH=C(Me)CH₂)-(PMe₃)₃]⁺O₃SCF₃⁻ (**6**).[22] However, we have not been able to deprotonate this compound to form the (PMe₃)₃ analogue of metallabenzene **3**. Hence, the deprotona-tion step appears to have a steric requirement, but its origin is not yet fully understood.

Figure 3. ORTEP drawing of (Ir⁼CH⁼C(Me)⁼CH⁼C-(Me)⁼CH)(PEt₃)₃ (**3**).

One possibility is that deprotonation requires prior dissociation of the ring double bond from the iridium center; steric crowding would promote this dissociation in the (PEt₃)₃ complex but not in the (PMe₃)₃ system. Ring double bond dissociation would produce 16e⁻ [(IrCH=C(Me)CH=C(Me)CH₂)(PR₃)₃]⁺ (A, Scheme IV). This species might be deprotonated directly or might undergo α-hydride elimination[23] to produce [(Ir⁼CH⁼C(Me)⁼CH⁼C(Me)⁼CH)(PR₃)₃-(H)]⁺ (B, Scheme IV), which could then be deproton-ated.

Structure of Iridabenzene 3

Structural data have historically been an important determinant of "aromatic" character. Planarity, lack of bond length alternation, and multiple-bond character in the ring bonds are all considered to be essential structural features of aromatic systems.[2]

The solid-state structure of (Ir⁼CH⁼C(Me)⁼CH⁼C(Me)⁼CH)(PEt₃)₃ (**3**) has been determined by single-crystal X-ray diffraction[5] (see ORTEP drawing, Figure 3). The coordination geometry is square py-ramidal with C1, C5, P1, and P2 occupying the four basal sites and P3 residing in the axial site. The six-membered ring is nearly planar, with no atom deviating by more than 0.08 Å from the best mean plane. Fur-thermore, there is delocalization of bonding within the ring, and the bond lengths (C1–C2 = 1.37 (1) Å, C2–C3 = 1.40 (1) Å, C3–C4 = 1.37 (1) Å, C4–C5 = 1.39 (1) Å) are comparable to those found in benzene itself (1.398 (9) Å).[24] The iridium–carbon distances (Ir–C1 = 2.024 (8) Å, Ir–C5 = 1.985 (8) Å) are, as expected, interme-diate between normal Ir–C single[25] and double[26] bonds (2.11 and 1.87 Å, respectively). The bond angles within

(16) This species is stable indefinitely in the solid state and in solution at -30 °C but decomposes slowly to [(η⁵-1,3-dimethylcyclopentadienyl)-Ir(PEt₃)₂(H)]⁺O₃SCF₃⁻ in solution at room temperature.

(17) Several closely related compounds have been prepared by Hughes via a different route: (a) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578. (b) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A. *J. Am. Chem. Soc.* **1990**, *112*, 7076.

(18) The enolate was prepared by adding lithium diisopropylamide to acetone.

(19) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(20) Bleeke, J. R.; Boorsma, D.; Chiang, M. Y.; Clayton, T. W., Jr.; Haile, T.; Beatty, A. M.; Xie, Y.-F. *Organometallics* **1991**, *10*, 2391.

(21) The 1,4,5-η-pentadienyl bonding mode is quite rare. For other examples, see: Melendez, E.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 8703.

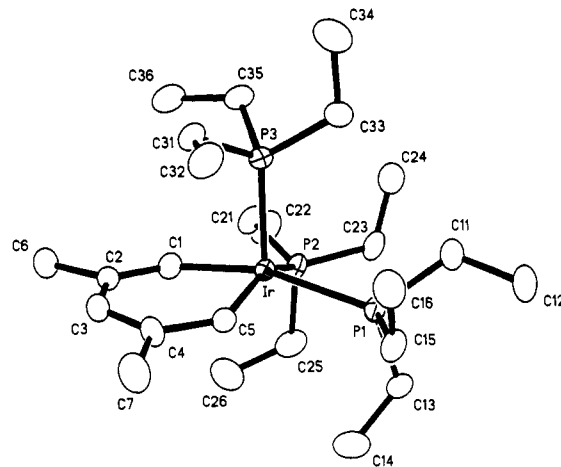(22) Bleeke, J. R.; Boorsma, D.; Xie, Y.-F., details to be published.

(23) While α-hydride eliminations involving late-transition-metal al-kyls are rare, several iridium-based examples have recently been claimed in the literature. (a) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708. (b) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, R. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217. (c) Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620.

(24) Bacon, G. E.; Curry, N. A.; Wilson, S. A. *Proc. R. Soc. London, A* **1964**, *279*, 98.

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

(26) (a) Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1982**, *236*, C7. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708.
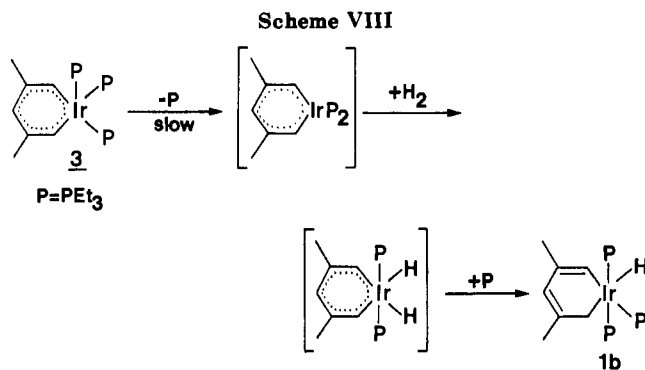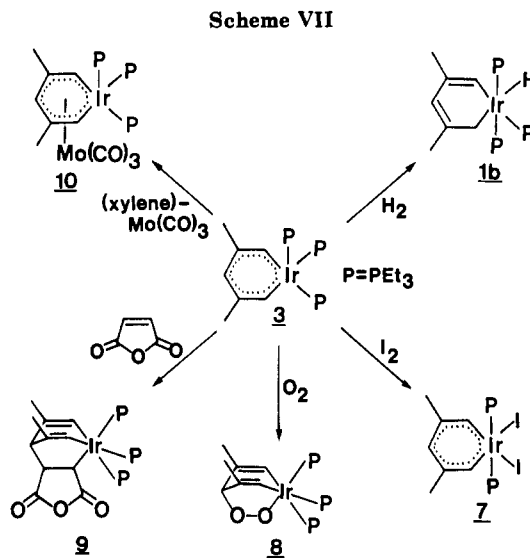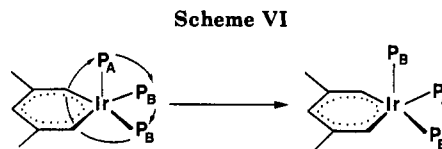
Scheme V

Scheme VI

Scheme VII

Scheme VIII
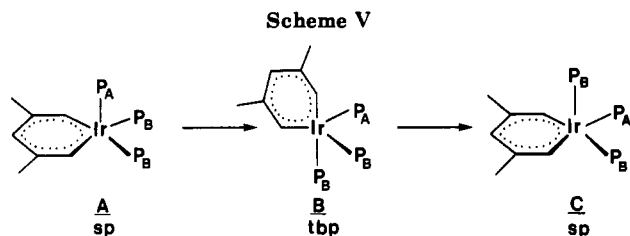
the carbon portion of the ring are 122.6 (7)° (C1–C2–C3), 125.3 (7)° (C2–C3–C4), and 121.8 (7)° (C3–C4–C5), while the Ir–C1–C2 and C4–C5–Ir angles are 131.2 (6)° and 132.9 (6)°, respectively, and the C1–Ir–C5 angle is 84.7 (3)°.[27] All of these structural features are fully consistent with the presence of an aromatic ring system.

Spectroscopy of Iridabenzene 3

The most widely accepted criterion for aromaticity is the ability of a molecule to sustain an induced ring current, a phenomenon which is conveniently measured by NMR spectroscopy. In particular, the peripheral protons of planar aromatic molecules appear at low-field chemical shift values in the ^{1}H NMR spectrum.[2d]

The ^{1}H NMR spectrum of metallabenzene **3** is striking in that the signal for H1/H5 appears far downfield at δ 10.91, while H3 resonates at δ 7.18.[5] In contrast, H1 and H3 of the nonaromatic metallacyclohexadiene precursor, **1b**, resonate at δ 7.00 and 5.93, respectively.[13] The dramatic downfield shift of the H1/H5 protons in **3** is reminiscent of the large shifts observed for the α protons of heavy group 5 heterobenzenes; the chemical shift positions for the α-H's of arsabenzene, stibabenzene, and bismabenzene are δ 9.68, 10.94, and 13.25, respectively.[4] These downfield shifts (beyond what is anticipated for "normal aromatic" protons) have been attributed to magnetic anisotropic influences of the large heteroatom.[4] Such effects are strongly dependent on internuclear separation[28] and are expected to decrease rapidly for protons remote from the heteroatom. This is exactly what we see in the ^{1}H NMR spectrum of **3**, where the remote γ-proton (H3) resonates in the normal aromatic region. The ^{13}C{^{1}H} NMR spectrum of **3** follows the trend seen in the ^{1}H NMR spectrum. Equivalent carbons C1 and C5 resonate quite far downfield at δ 167.3, while C2/C4 and C3 appear in the normal aromatic region, at δ 132.0 and 129.8, respectively.

The ^{31}P{^{1}H} NMR signal for **3** is a sharp singlet, which shows no broadening even upon cooling of the sample to –80 °C. This indicates that **1** is stereochemically nonrigid and that the axial and basal phosphines are exchanging rapidly in solution. The detailed mechanism of this exchange phenomenon is not known, but both a Berry-type process and a turnstile rotation can be envisaged.[29] In the Berry-type process (Scheme V) the square-pyramidal complex **A** isomerizes to a trigonal-bipyramidal intermediate **B** in which one ring carbon atom and one basal phosphine ligand (P_B) assume trans-axial positions. This intermediate then reisom-

(27) The relatively small C–Ir–C angle allows the long Ir–C bonds to be accommodated within a planar ring structure.
(28) McConnell, H. M. *J. Chem. Phys.* **1957**, *27*, 226.
(29) (a) For a discussion of these processes as applied to the trigonal-bipyramidal case, see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed.; John Wiley and Sons: New York, 1980; pp 1218–1221. (b) Phosphine ligand dissociation occurs much too slowly, even at room temperature, to be involved in the fluxional process.
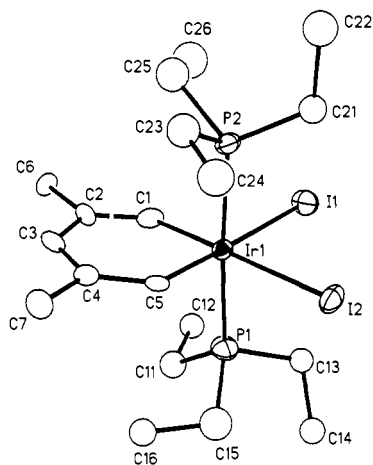
erizes back to square-pyramidal complex **C**, causing P_A/P_B exchange. In the turnstile process (Scheme VI), the three phosphines exchange positions via 120° rotations about an imaginary axis extending from the iridium atom to the centroid of the P_3 triangle. As a result of this fluxional process, the H1/H5 signal in the ^{1}H NMR spectrum of **3** appears as a binomial quartet with $J_{H–P}$ = 7.30 Hz. Likewise the C1/C5 signal in the ^{13}C{^{1}H} NMR spectrum is a binomial quartet with $J_{C–P}$ = 30.2 Hz.

Chemical Reactivity of Iridabenzene 3

Metallabenzenes have been implicated as intermediates in the formation of a variety of (cyclopentadienyl)metal complexes.[11,12c] In fact, it has been suggested that metallabenzenes (or metallacyclohexatrienes) may *in general* be unstable with respect to (cyclopentadienyl)metal formation.[11] However, metallabenzene **3** is quite robust. In the solid state or in solution at room temperature (under an N_2 atmosphere), it is stable indefinitely. Furthermore, heating **3** in refluxing benzene for short periods causes little or no decomposition. However, **3** does undergo a number of interesting chemical reactions, some of which parallel the reactions of conventional benzene derivatives and others of which do not. These reactions are summarized

Metallabenzene Chemistry

Acc. Chem. Res., Vol. 24, No. 9, 1991 **275**

Figure 4. ORTEP drawing of (Ir⬝⬝CH⬝⬝C(Me)⬝⬝CH⬝⬝C-(Me)⬝⬝CH)(PEt$_3$)$_2$(I)$_2$ (**7**).

Figure 5. ORTEP drawing of (OOIrCH=C(Me)CHC(Me)-=CH)(PEt$_3$)$_3$ (**8**).

in Scheme VII and discussed in the sections that follow.

Oxidative Addition Reactions

Unlike organic arenes, **3** reacts slowly with H$_2$ at room temperature and 1 atm of pressure, generating the partially hydrogenated iridacyclohexadiene complex, *mer*-(IrCH=C(Me)CH=C(Me)CH$_2$)(PEt$_3$)$_3$(H) (**1b**).[30,31] As shown in Scheme VIII, this reaction probably proceeds via rate-limiting dissociation of a PEt$_3$ ligand from **3**, producing 16e$^-$ (Ir⬝⬝CH⬝⬝C-(Me)⬝⬝CH⬝⬝C(Me)⬝⬝CH)(PEt$_3$)$_2$. Oxidative addition of H$_2$ followed by hydride migration from the iridium center to the α-carbon of the ring and readdition of PEt$_3$ would yield the observed product. In support of this mechanism, we have found that the rate of the hydrogenation reaction is drastically retarded by addition of excess PEt$_3$ to the reaction mixture.

Treatment of **3** in acetone solution with iodine (I$_2$) leads to very rapid production of (Ir⬝⬝CH⬝⬝C(Me)⬝⬝CH⬝⬝C(Me)⬝⬝CH)(PEt$_3$)$_2$(I)$_2$ (**7**), in which the aromatic ring is retained.[30] Thus, compound **3** undergoes oxidative addition of I$_2$ at the iridium center rather than electrophilic aromatic substitution at carbon.[32] Although the detailed mechanism of this oxidative addition reaction is still unclear, its rapid rate suggests that initial PEt$_3$ ligand dissociation is not required. Compound **7** is the first representative of Hoffmann's predicted class II metallabenzenes (vide supra).

The X-ray crystal structure of **7** (Figure 4) shows the planar ring system and the expected delocalized bonding around the ring. The average C–C and Ir–C bond distances are 1.39 and 1.95 Å, respectively. The ^{1}H NMR signals for ring protons H1/H5 and H3 in **7** are shifted even more dramatically downfield than those in **3**, appearing at δ 13.95 and 7.86, respectively. In addition to the ring current and neighboring group anisotropic effects described earlier, these shifts probably reflect the inductive effect of an oxidized iridium

(30) Bleeke, J. R.; Xie, Y.-F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4703.

(31) This reaction is closely analogous to the reaction of H$_2$ with Bergman's iridium–carbene complex, (C$_5$Me$_5$)Ir(CH$_2$)(PMe$_3$), which yields (C$_5$Me$_5$)Ir(CH$_3$)(H)(PMe$_3$): Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079.

(32) The same product is obtained when the reaction is run in the presence of a Friedel–Crafts catalyst.
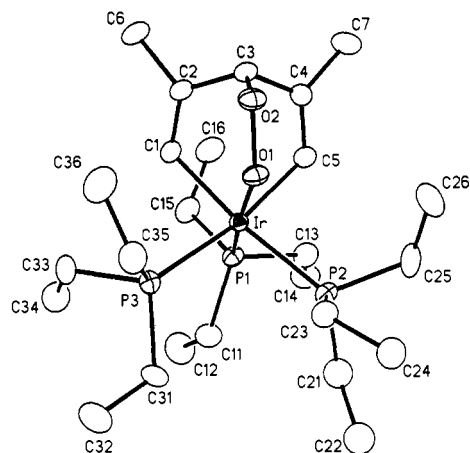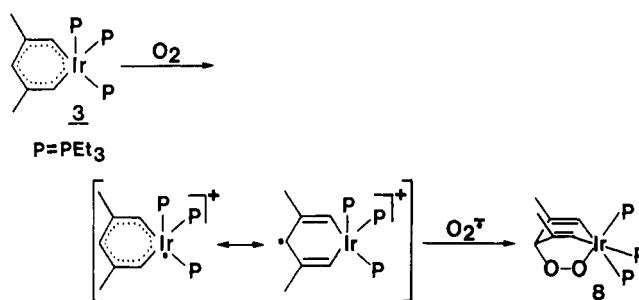
Scheme IX

center and two electronegative iodine atoms in the ring plane.[33] The ^{13}C{^{1}H} NMR spectrum of **7** follows the same chemical shift pattern, with C1/C5, C3, and C2/C4 appearing at δ 215.1, 161.6, and 134.8, respectively.

Cycloaddition Reactions

Compound **3** in pentane solution reacts with atmospheric oxygen to produce the novel dioxygen-bridged species (OOIrCH=C(Me)CHC(Me)=CH)(PEt$_3$)$_3$ (**8**) (see solid-state structure, Figure 5).[30] The dioxygen unit adds to the open face of square-pyramidal **3**; hence, the erstwhile axial phosphine resides trans to an oxygen atom in octahedral **8**, while the formerly basal phosphines are situated trans to ring carbons C1 and C5. The 1-iridacyclohexa-2,5-diene ring in **8** is boat-shaped, and bonding within the metallacyclic ring is localized as expected.

This dioxygen reaction is reminiscent of the reactions of certain polycyclic aromatic compounds (e.g., anthracene) with O$_2$, which lead to internal peroxides.[34] However, unlike these organic reactions, which require singlet oxygen, compound **3** reacts with ground-state (triplet) oxygen. Furthermore, unlike the reaction of **3** with H$_2$ (which requires PEt$_3$ loss and therefore proceeds relatively slowly), the O$_2$ reaction is very rapid and probably involves initial transfer of an electron from **3** to O$_2$, producing (Ir⬝⬝CH⬝⬝C(Me)⬝⬝CH⬝⬝C(Me)⬝⬝CH)(PEt$_3$)$_3^+$ and superoxide (O$_2^-$). As shown in Scheme IX, the radical cation has a resonance

(33) Becker, E. D. *High Resolution NMR*, 2nd ed.; Academic Press: New York, 1980; pp 55–84.

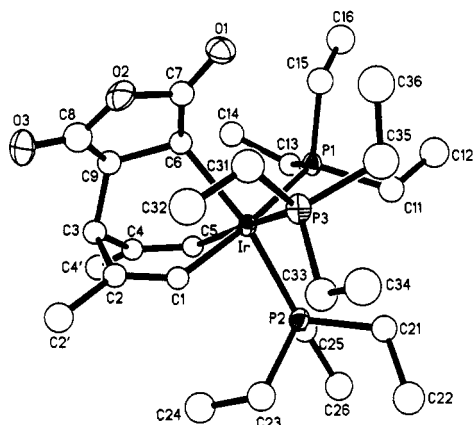(34) Rigaudy, J. *Pure Appl. Chem.* **1968**, *16*, 169.

Figure 6. ORTEP drawing of the Diels–Alder cycloaddition product, **9**, formed in the reaction of (Ir═CH═C(Me)═CH═C(Me)═CH)(PEt₃)₃ (**3**) with maleic anhydride.
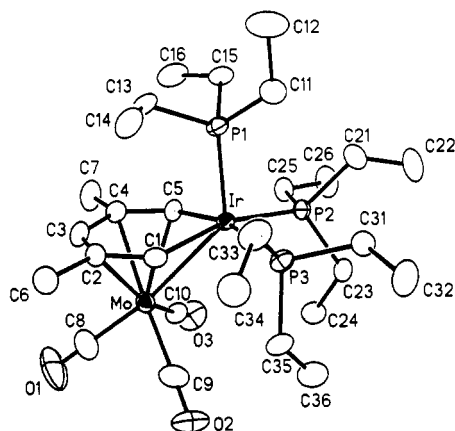
Figure 7. ORTEP drawing of [(Ir═CH═C(Me)═CH═C(Me)═CH)(PEt₃)₃]Mo(CO)₃ (**10**).

form in which the odd electron resides on the γ-carbon (C3) of the ring. Recombination of the iridabenzene radical cation with superoxide would produce the observed product, **8**.

Many arenes, including heterobenzenes such as phosphabenzene, arsabenzene, stibabenzene, and bismabenzene, behave as dienes in the Diels–Alder reaction.[4] Likewise, metallabenzene **3** reacts cleanly with maleic anhydride at −30 °C in acetone solution to produce the Diels–Alder adduct **9** (see solid-state structure, Figure 6).[35] In this reaction, the dienophile approaches compound **3** from its open face and may undergo the 4 + 2 cycloaddition in a concerted fashion. Stepwise mechanisms can also be envisaged.

Coordination to Mo(CO)₃

Metallabenzene **3** cleanly displaces *p*-xylene from (*p*-xylene)Mo(CO)₃ in tetrahydrofuran (THF) solvent, producing the metal-coordinated metallabenzene complex, [(Ir═CH═C(Me)═CH═C(Me)═CH)-(PEt₃)₃]Mo(CO)₃ (**10**)[30] (see solid-state structure, Figure 7). The bonding within the metallabenzene ring in **10** is still fully delocalized, but the average C–C and Ir–C bond distances (1.41 and 2.03 Å, respectively) are slightly longer than those in parent **3**. The molybdenum–iridium bond distance is 2.978 (1) Å. As is normally the case when arenes coordinate to metal frag-

(35) Bleeke, J. R.; Xie, Y.-F.; Chiang, M. Y., details to be published.
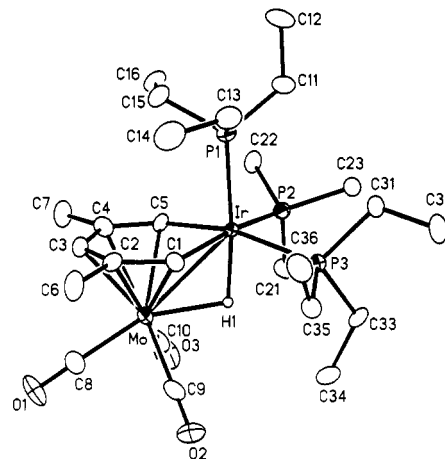
Figure 8. ORTEP drawing of the cation in {[(Ir═CH═C-(Me)═CH═C(Me)═CH)(PEt₃)₂(PMe₃)(μ₂-H)]Mo(CO)₃}⁺BF₄⁻ (**12**).

Scheme X
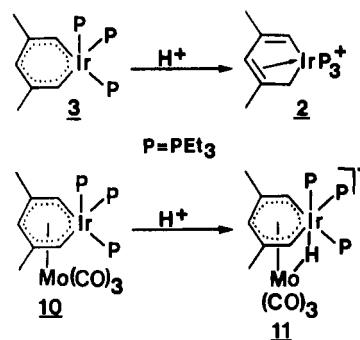
ments, the ¹H NMR signals for ring protons in **10** shift upfield from their positions in the parent metallabenzene, **3**. Protons H1/H5 in **10** appear at δ 8.16 (vs δ 10.91 in **3**), while H3 resonates at δ 6.31 (vs δ 7.18 in **3**). Coordination to Mo(CO)₃ completely shuts down the phosphine exchange process described earlier. Hence the ³¹P{¹H} NMR spectrum of **10** consists of a doublet (due to the equivalent basal phosphines) and a triplet (axial phosphine). However, the metallabenzene moiety in **10** rotates with respect to the Mo(CO)₃ fragment. As a result, the carbonyl carbon atoms in **10** give rise to just one signal in the ¹³C{¹H} NMR spectrum, even at −80 °C.

The infrared CO stretching bands exhibited by **10** in THF solution appear at very low energies (1918 and 1836 cm⁻¹), compared to other (arene)Mo(CO)₃ complexes, reflecting the extremely electron rich nature of **3**.[36] Since the stability of (arene)Mo(CO)₃ complexes increases with increasing arene basicity, it is not surprising that **3** readily displaces organic arenes from (arene)Mo(CO)₃ complexes in THF solvent.[37]

Coordination of metallabenzene **3** to Mo(CO)₃ reduces its reactivity by effectively blocking its open face. Thus, for example, complex **10** is stable to air for several hours,[38] while **3** reacts with oxygen in minutes. Interestingly, both **3** and **10** react with acids, but the site of addition differs (Scheme X). Treatment of **3** with acid

(36) By comparison, the ν(CO) bands for (hexamethylbenzene)Mo-(CO)₃ come at 1958 and 1882 cm⁻¹: Barbeau, C.; Turcotte, J. *Can. J. Chem.* **1976**, *54*, 1612.
(37) Muetterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* **1979**, *178*, 197.
(38) Bleeke, J. R.; Bass, L.; Chiang, M. Y., details to be published.

Figure 9. Key orbital interaction in metallabenzene **3**, involving filled metal d_{xz} orbital and empty $2\pi_s$ orbital of the $C_5H_3Me_2$ organic fragment.

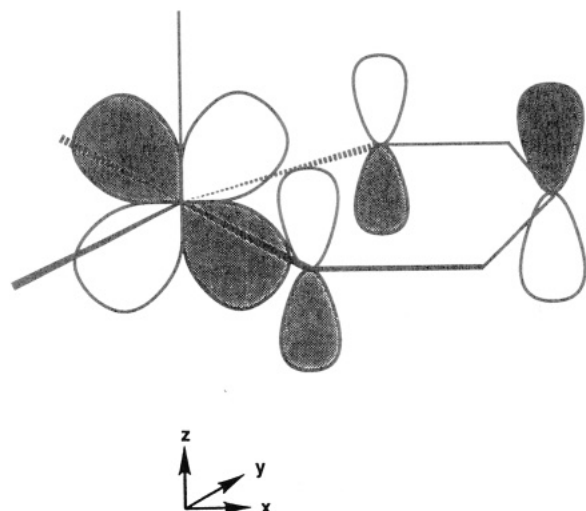leads to protonation of the α-carbon[39] and production of **2**, while compound **10** protonates at the metal centers, producing the novel heterobimetallic μ-hydride complex $\{[(Ir\text{-}\text{-}CH\text{-}\text{-}C(Me)\text{-}\text{-}CH\text{-}\text{-}C(Me)\text{-}\text{-}CH)\text{-}(PEt_3)_3(\mu_2\text{-}H)]Mo(CO)_3\}^+$ (**11**). The solid-state structure of the mono-PMe$_3$ analogue of **11** is shown in Figure 8. The bridging hydride resides 1.771 (64) Å from the iridium atom and 1.972 (67) Å from molybdenum. The P1–Ir–H1 angle is 173.0 (22)°, with the hydride bent in slightly toward the molybdenum atom. In the ^{1}H NMR spectrum, H1 couples relatively weakly to the trans phosphine P1 (J_{H-P} = 42.0 Hz), consistent with the μ_2-bonding mode.

Orbital Considerations

While the π-bonding in aromatic hydrocarbons and in main-group heterobenzenes involves principally p orbital/p orbital overlaps,[40] metallabenzenes require participation of metal d orbitals in the π-bonding of the aromatic ring. This is because the metal p orbitals are, in general, already engaged in σ-bonding the ligands and are not, therefore, available for π-bonding.

The $C_5H_3Me_2$ unit in iridabenzene **3** is perhaps best viewed as a monoanionic ligand. As such, it possesses eight valence electrons, in addition to skeletal electrons which form its σ framework. Four of these valence electrons are used to form σ-bonds to iridium, while the remaining four are π-electrons and occupy the ligand's

$1\pi_s$ and $1\pi_a$ orbitals.[41] The d^8 iridium center contributes two electrons to the π-system via overlap of a filled d_{xz} orbital[42] with the empty $2\pi_s$ orbital of the $C_5H_3Me_2$ unit (see Figure 9). This brings the total π-electron count to six and explains, in a qualitative fashion, the observed aromatic character of **3**. The three highest lying occupied orbitals in **3** are essentially nonbonding metal d orbitals (d_{yz}, $d_{x^2-y^2}$, and d_{z^2}).

The bonding picture in iridabenzene **7**, $(\overline{Ir\text{-}\text{-}CH\text{-}}$ $\overline{\text{-}C(Me)\text{-}\text{-}CH\text{-}\text{-}C(Me)\text{-}\text{-}CH})(PEt_3)_2(I)_2$, is quite similar to that in **3** except that the iridium center is now an octahedral d^6 Ir(III) ion. As before, the filled d_{xz} orbital participates in ring π-bonding, but the d_{z^2} orbital is now fully engaged in σ-bonding the trans-axial PEt$_3$ ligands, leaving only d_{yz} and $d_{x^2-y^2}$ as filled nonbonding orbitals.

Summary

One hundred twenty-five years after Kekulé's celebrated dream,[15] aromatic chemistry continues to be a fascinating and provocative research topic. Metallabenzenes represent a fundamentally new class of aromatic compounds, one in which metal d orbitals participate fully with carbon p orbitals in the formation of ring π-bonds. Many similarities exist between metallabenzenes and conventional arenes, particularly heterobenzenes. Among these similarities are structural features such as ring planarity and the absence of bond length alternation, spectroscopic features such as downfield chemical shifts for ring protons, and chemical reactions such as Diels–Alder cycloadditions and arene displacement from (arene)Mo(CO)$_3$. However, it is also evident that the transition-metal center exerts a powerful influence on the reactivity of metallabenzenes. In fact, the metal center directs much of the reaction chemistry that we have observed by undergoing ligand-dissociation, oxidative-addition, and electron-transfer processes. In the future, we hope to discover new synthetic routes to other members of the metallabenzene family while continuing to explore the chemistry of this remarkable compound class.

(39) It is, of course, quite possible that the proton initially attacks the iridium center and then migrates to C_α.

(40) However, in heterobenzenes containing heavy main-group elements, heteroatom d orbitals may mix with p orbitals to form more directed pd hybrids: see ref 4b.

(41) For drawings of these orbitals, see: Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812.

(42) We define the following coordinate axis system: the axial ligand lies along the z axis, while the four basal ligands, when projected onto the xy plane, lie midway between (at 45° to) the coordinate axes.