Synthesis, Characterization, and Reaction Chemistry of a Family of 1-Iridacyclohexa-2,4-diene Complexes[1]

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The reaction of $(Cl)Ir(PEt_3)_3$ with potassium 2,4-dimethylpentadienide produces the 1-iridacyclohexa-2,4-diene complex $(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3(H)$ (**1**) via an iridium-centered activation of a pentadienyl C—H bond. The kinetic product of this reaction is the *fac* isomer (**1a**), which slowly isomerizes to the thermodynamically preferred *mer* isomer (**1b**). Treatment of **1b** with methyl trifluoromethanesulfonate results in hydride abstraction and production of $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3]^+O_3SCF_3^-$ (**2**), in which one of the ring double bonds coordinates to iridium. Compound **2** can be converted back to **1b** by treating with $K^+BEt_3H^-$ in tetrahydrofuran. In solution at 25 °C, **2** decomposes to $[(\eta^5\text{-}1,3\text{-dimethylcyclopentadienyl})Ir(PEt_3)_2(H)]^+O_3SCF_3^-$ (**3**). However, treatment of **2** at low temperature with a series of ligands (L), including I^-, CO, NCMe, and $CNCMe_3$, produces a family of adducts having the formula $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3(L)]^+O_3SCF_3^-$ (**4-7**, respectively). The iodide and acetonitrile adducts are formed as pure *mer* isomers. In contrast, the carbonyl and *tert*-butyl isocyanide adducts are initially produced as mixtures of *fac* and *mer* isomers but slowly convert to the pure *mer* isomers upon stirring at 25 °C. When **2** is treated with PMe_3, adduct formation is accompanied by exchange of the two axial PEt_3 ligands for smaller PMe_3 ligands. The product of this reaction, $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (**8**), crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a = 14.77 (1) Å, b = 11.588 (9) Å, c = 20.29 (1) Å, β = 109.91 (5)°, V = 3265 (5) Å^3, and Z = 4. Lithium diisopropylamide reacts with **2** at −30 °C in acetone to abstract a proton, producing the metallabenzene complex $(Ir{-}CH{=}C(Me){-}CH{=}C(Me){-}CH)(PEt_3)_3$ (**9**). Compound **9** exhibits the ring current and thermal stability expected for an aromatic species.

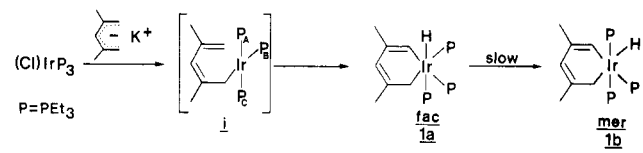
Introduction

While the synthesis and reactivity of metallacyclopentadiene complexes have been extensively studied during the past two decades,[2] the corresponding six-membered ring compounds, the metallacyclohexadienes, have remained largely unexplored. The reason for this inactivity has been a paucity of synthetic routes to the unsaturated six-membered ring systems.

During the past several years, Hughes[3] has developed a synthetic approach to 1-metallacyclohexa-2,4-diene complexes, which involves transition-metal-centered activation of the strained C—C bonds in vinylcyclopropene substrates. For example, Hughes has shown that, by treating 1,2,3-triphenyl-3-vinylcycloprop-1-ene with unsaturated low-valent transition-metal complexes, the 1-metallacyclohexa-2,4-diene complexes $(PtC(Ph){=}C(Ph)C(Ph){=}CHCH_2)(PPh_3)_2$[3a] and $(RhC(Ph){=}C(Ph)C(Ph){=}CHCH_2)(PMe_3)_2(acac)$ (acac = $OC(Me)CHC(Me)O^-$)[3b] can be synthesized.

Very recently, Allison[4] has reported the synthesis of a family of complexes containing the 1-metallacyclohexa-*2,5-diene* ring skeleton. These species are produced by reacting bis(2-lithiophenyl)methane with transition-metal dihalides. Benzannulated six-membered metallacycles where M = cp_2Ti, cp_2Hf, and $cp(PPh_3)Co$ (cp = η^5-cyclopentadienyl) have been produced.

Scheme I



We now report the development of an alternative synthetic approach to 1-metallacyclohexa-2,4-diene complexes that utilizes pentadienide as the source of ring carbon atoms. In the prototypical reaction, $(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3(H)$ (**1**) is produced in high yield upon treatment of $(Cl)Ir(PEt_3)_3$ with potassium 2,4-dimethylpentadienide. Compound **1** can be cleanly converted to the cationic metallacycle $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3]^+O_3SCF_3^-$ (**2**), which serves as the precursor to a large family of new 1-iridacyclohexa-2,4-diene complexes. Furthermore, treatment of **2** with lithium diisopropylamide (LDA) in acetone leads to the production of $(Ir{-}CH{=}C(Me){-}CH{=}C(Me){-}CH)(PEt_3)_3$ (**9**), a rare example of a stable metallabenzene.[5] Two

(1) Metallacyclohexadiene and Metallabenzene Chemistry. 3. For previous papers in this series, see: (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118.

(2) See, for example: (a) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549. (b) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 864-877 and references therein.

(3) (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.

(4) Mike, C. A.; Nelson, T.; Graham, J.; Cordes, A. W.; Allison, N. T. *Organometallics* **1988**, *7*, 2573.

(5) The only other stable metallabenzene was obtained by Roper via a cyclization reaction involving acetylene and an osmium-thiocarbonyl complex. However, the six-membered ring in this compound possessed a sulfido substituent, which coordinated to the metal center and possibly stabilized the structure. See: Elliot, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. More recently, Ernst has synthesized and structurally characterized a molybdenum dimer that contains an apparent molybdabenzene moiety *coordinated* in an η^6 fashion to a second molybdenum center. See: Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612.

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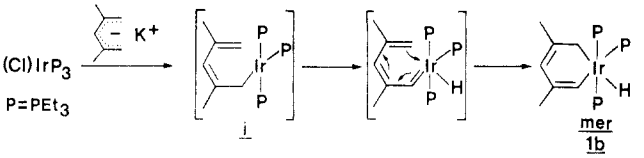
Scheme II



preliminary communications on this work have already appeared.[1]

Results and Discussion

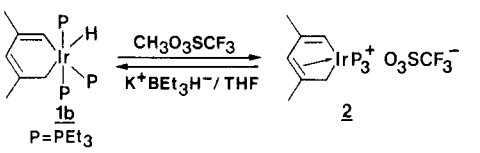
A. Synthesis and Spectroscopy of (IrCH=C(Me)CH=C(Me)CH_2)(PEt_3)$_3$(H) (1). Treatment of (Cl)Ir(PEt_3)$_3$ with potassium 2,4-dimethylpentadienide in tetrahydrofuran at −30 °C produces the 1-iridacyclohexa-2,4-diene complex (IrCH=C(Me)CH=C(Me)CH_2)(PEt_3)$_3$(H) (1) in high yield. The kinetic product of this reaction is the *fac* isomer (**1a**), which slowly isomerizes to the more thermodynamically favorable *mer* isomer (**1b**) over the course of 24 h at 25 °C. The probable mechanism of this reaction, shown in Scheme I, involves the intermediacy of the 16e species (η^1-2,4-dimethylpentadienyl)Ir(PEt_3)$_3$ (i), which undergoes intramolecular oxidative addition across an sp^2 C—H bond on the dangling terminus of the pentadienyl ligand. In order for square-planar intermediate i to undergo the proposed intramolecular oxidative-addition reaction, two cis coordination sites must be made available, requiring a rearrangement of the phosphine ligands. Migration of P_A (see Scheme I) from an "axial" position to an "equatorial" position would generate the required cis coordination sites and would explain the initial production of the *fac* isomer **1a**. (Of course, migration of P_B from one "equatorial" position to the other would also generate the necessary cis coordination sites but would lead directly to the production of the *mer* isomer **1b**.)

An alternative mechanism, shown in Scheme II, involves α-hydride elimination followed by an electrocyclic rearrangement. Although this mechanism cannot be ruled out, it would be expected to yield the *mer* isomer (**1b**) directly, because *it requires no rearrangement* of the phosphine ligands (see Scheme II). Hence, the observation of a phosphine-rearranged isomer (**1a**) as the kinetic product argues against this mechanism.

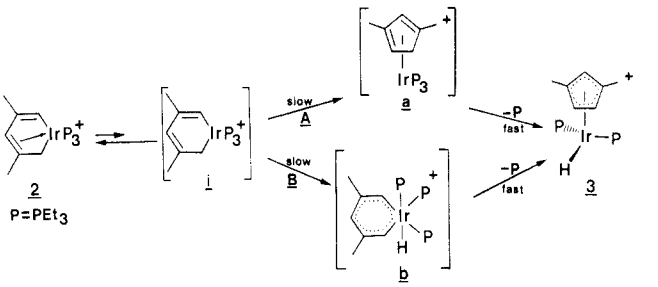
The crystal structure of **1b**, reported in an earlier communication,[1a] shows the metallacyclic ring to be essentially planar. This planarity is also manifested in the solution-phase NMR spectra of **1b**. Hence, the two protons bonded to C5 (the sp^3 ring carbon) are equivalent and give rise to a single peak in the ^{1}H NMR spectrum. Similarly, the two mutually trans phosphines are equivalent by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. In contrast, **1a** possesses no mirror plane, so the two protons on C5 are inequivalent, as are all three phosphorus atoms. Also noteworthy is the fact that in the *fac* compound (**1a**) both ring carbons C1 and C5 are trans to phosphines and couple strongly to phosphorus. In the *mer* isomer (**1b**), only C1 (sp^2 ring carbon) exhibits strong P—C coupling, indicating that it is trans to a phosphine, while C5 (sp^3 ring carbon) is trans to the hydride ligand.

B. Synthesis and Thermal Decomposition of [(IrCH=C(Me)CH=C(Me)CH_2)(PEt_3)$_3$]$^+$$O_3SCF_3^-$ (2). As shown in Scheme III, treatment of **1b** with methyl trifluoromethanesulfonate results in abstraction of the hydride ligand and coordination of ring double bond C3–C4 to the iridium center, generating [(IrCH=C(Me)-CH=C(Me)CH_2)(PEt_3)$_3$]$^+$$O_3SCF_3^-$ (**2**).[6] Compound **2** can be converted back to **1b** by treating with $K^+BEt_3H^-$ in tetrahydrofuran. The crystal structure of **2**, which we reported earlier,[1a] shows a rather weak, strained interaction between the ring double bond and the iridium atom.

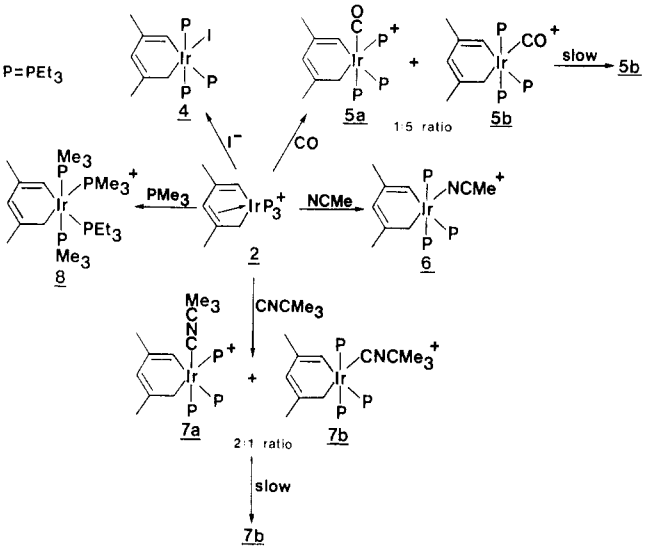
Scheme III



Scheme IV



Scheme V



Compound **2** is stable in the solid state and in solution at −30 °C but slowly (over the course of several hours) decomposes to [(η^5-1,3-Me_2cp)Ir(PEt_3)$_2$(H)]$^+$$O_3SCF_3^-$ (**3**) when warmed to 25 °C in solution. Two reasonable mechanisms for this process are outlined in Scheme IV. Each involves the intermediacy of 16e [(IrCH=C(Me)-CH=C(Me)CH_2)(PEt_3)$_3$]$^+$$O_3SCF_3^-$ (i, Scheme IV), which is believed to be in equilibrium with **2**. The first mechanism (pathway A, Scheme IV) proceeds by coupling of ring carbons C1 and C5 to produce [(η^4-1,3-dimethylcyclopentadiene)Ir(PEt_3)$_3$]$^+$ (a), followed by phosphine loss and transfer of the endo ring hydrogen to the iridium center. The alternative pathway (B, Scheme IV) involves initial α-hydride elimination to produce a transient iridabenzene (b), which then collapses (probably via alkyl to carbene migration) with phosphine loss. While α-hydride eliminations involving late-transition-metal alkyls are rare, several iridium-based examples have recently been claimed

(6) Compounds with similar ring structures have been obtained by Hughes.[3b]

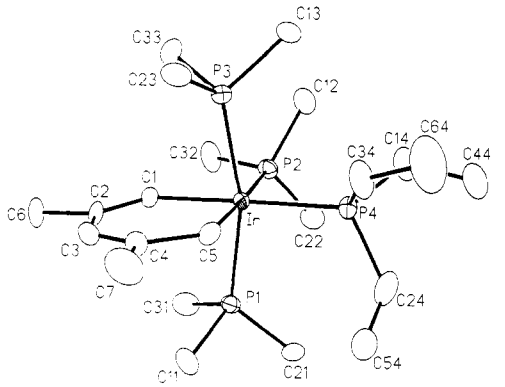


Figure 1. ORTEP drawing of the cation in $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (8).

in the literature.[7] Experiments designed to distinguish between these mechanistic possibilities are underway and will be reported in the future.[8]

C. Reactivity of $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)_3]^+O_3SCF_3^-$ (2). The weakly coordinated double bond in **2** is easily displaced by incoming 2e ligands. Hence, **2** serves as a convenient precursor to a large family of new 1-iridacyclohexa-2,4-diene complexes. As shown in Scheme V, **2** reacts with I^-, CO, MeCN, and $CNCMe_3$ to produce $(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)_3I$ (**4**),[9] $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)_3(CO)]^+O_3SCF_3^-$ (**5**), $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)_3(NCMe)]^+O_3SCF_3^-$ (**6**), and $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)_3(CNCMe_3)]^+O_3SCF_3^-$ (**7**), respectively. The iodide and acetonitrile adducts (**4** and **6**, respectively) are formed as pure *mer* isomers, with the added ligand (L) residing cis to C1 (sp^2 carbon) and trans to C5 (sp^3 carbon) of the ring. In contrast, the carbonyl and *tert*-butyl isocyanide adducts (**5** and **7**, respectively) are initially produced as mixtures of *fac* and *mer* isomers. For **5**, the initial *fac*:*mer* ratio is approximately 1:5, while for **7**, the ratio is 2:1. However, in each case, the isomer mixture slowly (over the course of 30 h) converts to pure *mer* isomer upon stirring at 25 °C.

The ligand orientation in adduct compounds **4**–**7** can be unambiguously determined from their NMR spectra. In the *fac* isomers, all three phosphines are chemically different, giving rise to three equal-intensity doublet-of-doublet patterns in the $^{31}P\{^1H\}$ NMR spectra, while in the *mer* isomers, the mutually trans phosphines are equivalent, so the $^{31}P\{^1H\}$ NMR spectra consist of a doublet (intensity 2) and a triplet (intensity 1). In the $^{13}C\{^1H\}$ NMR spectra of the *mer* isomers, C1 (ring sp^2 carbon) is strongly coupled to phosphorus while C5 (ring sp^3 carbon) is not, indicating that C1 is trans to a phosphine while C5 is trans to the added ligand (L).

When **2** is treated with trimethylphosphine, formation of the adduct is accompanied by exchange of the two axial PEt_3 ligands for PMe_3 ligands, producing $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (**8**). The phosphine exchange process results in a mitigation of unfavorable steric interactions.[10] The solid-state structure

Table I. Positional Parameters and Their Estimated Standard Deviations for Non-Hydrogen Atoms in $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (8)

atom	x	y	z
		Cation	
Ir	0.77402 (3)	0.23971 (3)	0.31664 (2)
P1	0.9372 (2)	0.2467 (2)	0.3214 (2)
P2	0.7798 (2)	0.0332 (2)	0.3250 (2)
P3	0.6311 (2)	0.2479 (3)	0.3441 (2)
P4	0.6941 (2)	0.2515 (3)	0.1909 (2)
C1	0.8392 (7)	0.2543 (8)	0.4249 (5)
C2	0.8670 (8)	0.3500 (9)	0.4646 (6)
C3	0.8478 (8)	0.467 (1)	0.4396 (6)
C4	0.8071 (8)	0.5019 (9)	0.3759 (6)
C5	0.7690 (7)	0.4266 (8)	0.3123 (5)
C6	0.922 (1)	0.340 (1)	0.5418 (6)
C7	0.786 (1)	0.630 (1)	0.3546 (9)
C11	0.9921 (8)	0.389 (1)	0.3400 (7)
C21	0.9782 (8)	0.199 (1)	0.2500 (6)
C31	1.0181 (9)	0.164 (1)	0.3958 (8)
C12	0.6695 (8)	−0.051 (1)	0.2995 (7)
C22	0.848 (1)	−0.043 (1)	0.2775 (7)
C32	0.8342 (9)	−0.030 (1)	0.4136 (7)
C13	0.5154 (8)	0.189 (1)	0.2823 (7)
C23	0.5925 (9)	0.386 (1)	0.3659 (7)
C33	0.6358 (9)	0.172 (1)	0.4241 (6)
C14	0.629 (1)	0.124 (1)	0.1468 (7)
C24	0.763 (1)	0.292 (1)	0.1353 (7)
C34	0.603 (1)	0.370 (1)	0.1618 (7)
C44	0.606 (1)	0.106 (1)	0.0682 (8)
C54	0.813 (1)	0.400 (1)	0.1399 (7)
C64	0.534 (1)	0.378 (1)	0.0944 (9)
		Anion	
S	0.3137 (3)	0.2439 (3)	0.3827 (2)
O1	0.223 (1)	0.204 (1)	0.3394 (7)
O2	0.3603 (9)	0.336 (1)	0.3644 (6)
O3	0.385 (1)	0.150 (1)	0.4088 (9)
C	0.319 (2)	0.274 (2)	0.460 (2)
F1	0.3715 (9)	0.329 (1)	0.5096 (7)
F2	0.230 (1)	0.363 (2)	0.4450 (8)
F3	0.265 (1)	0.202 (2)	0.489 (1)

Table II. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (8)

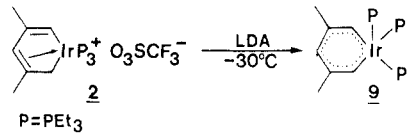
	Bond Distances		
Ir-P1	2.379 (2)	C1-C2	1.35 (1)
Ir-P2	2.399 (2)	C2-C3	1.45 (1)
Ir-P3	2.360 (2)	C2-C6	1.51 (1)
Ir-P4	2.423 (2)	C3-C4	1.29 (1)
Ir-C1	2.084 (8)	C4-C5	1.50 (1)
Ir-C5	2.167 (7)	C4-C7	1.54 (1)
	Bond Angles		
P1-Ir-P2	91.16 (8)	P4-Ir-C1	172.0 (2)
P1-Ir-P3	164.37 (8)	P4-Ir-C5	84.5 (2)
P1-Ir-P4	99.48 (8)	C1-Ir-C5	87.6 (3)
P1-Ir-C1	81.8 (2)	Ir-C1-C2	129.3 (6)
P1-Ir-C5	89.3 (2)	C1-C2-C3	125.4 (9)
P2-Ir-P3	92.09 (8)	C1-C2-C6	120.1 (8)
P2-Ir-P4	97.10 (8)	C3-C2-C6	114.4 (8)
P2-Ir-C1	90.8 (2)	C2-C3-C4	127.8 (8)
P2-Ir-C5	178.3 (2)	C3-C4-C5	126.2 (8)
P3-Ir-P4	95.28 (8)	C3-C4-C7	124.0 (9)
P3-Ir-C1	82.9 (2)	C5-C4-C7	109.7 (9)
P3-Ir-C5	87.0 (2)	Ir-C5-C4	123.3 (6)

(7) (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.

(8) Assuming that the first step (C–C bond formation for pathway A and α-H elimination for pathway B) is rate-determining, these two mechanisms can be distinguished by measuring deuterium isotope effects. Pathway B should show a pronounced primary deuterium isotope effect since the rate-determining step involves C–H bond breaking. Pathway A, on the other hand, involves no C–H bond breaking in the rate-determining step and should exhibit only a small secondary isotope effect (at most).

(9) The iodide adduct, **4**, can also be generated directly from the reaction of **1b** with methyl iodide. This reaction probably proceeds through the intermediacy of cation **2**.

Scheme VI



of **8** is shown in Figure 1; positional parameters of nonhydrogen atoms are listed in Table I, while significant bond distances and angles are given in Table II. As in the *mer* isomers of compounds **4–7**, the added ligand (PMe_3 in this case) resides trans to C5. The two axial PMe_3 ligands bend substantially away from the bulky equatorial phosphines and toward the ring; the P1–Ir–P3 angle equals 164.37 (8)°. The metallacyclic ring is essentially planar, the C–C bond lengths exhibit a clear alternation around the ring, and the ring angles, except C1–Ir–C5, are all greater than 120°.

D. Synthesis of the Stable Iridabenzene (Ir⎓CH⎓C(Me)⎓CH⎓C(Me)⎓CH)$(PEt_3)_3$ (9). Treatment of **2** with lithium diisopropylamide (LDA) in acetone at −30 °C results in proton abstraction, producing (Ir⎓CH⎓C(Me)⎓CH⎓C(Me)⎓CH)$(PEt_3)_3$ (**9**), a rare example of a stable metallabenzene[5] (see Scheme VI). Since this reaction is carried out in acetone solvent, the active deprotonation reagent is probably acetone enolate, not LDA.[11] It is not known whether the proton is removed directly from **2** or whether it is removed from 16e $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)_3]^+O_3SCF_3^-$ (i, Scheme IV) or even $[(Ir⎓CH⎓C(Me)⎓CH⎓C(Me)⎓CH)(PEt_3)_3(H)]^+O_3SCF_3^-$ (b, Scheme IV). The solid-state structure of **9**, reported earlier,[1b] shows the coordination geometry around iridium to be square pyramidal, with C1 and C5 of the ring and two phosphorus atoms occupying basal positions and the remaining phosphorus atom occupying the axial site. In addition, the structure supports the assertion that **9** is an aromatic species; the six-membered ring is nearly planar and there is delocalization of ring bonding. Furthermore, the ^1H NMR spectrum clearly shows the presence of a ring current; protons H1 and H5 resonate at δ 10.91, while H3 resonates at δ 7.18. The $^{31}P\{^1H\}$ NMR signal of **9** is a sharp singlet, which shows no broadening even upon cooling to −60 °C. This indicates that the phosphines are exchanging rapidly in solution. The most likely mechanism for this exchange is a Berry-type process in which the ground-state square-pyramidal complex isomerizes to a trigonal-bipyramidal intermediate and then back to the ground state, exchanging axial and basal phosphines.[12] Compound **9** is remarkably robust, surviving for several hours in refluxing benzene with little or no decomposition.

Experimental Section

General Comments. All manipulations were carried out under an inert atmosphere, with use of either drybox or Schlenk techniques. Diethyl ether and tetrahydrofuran were dried over sodium/benzophenone and distilled before use. Pentane was dried over calcium hydride and distilled. Acetone, acetonitrile, and ethanol were dried over magnesium sulfate and distilled. 2,4-Dimethylpentadiene (Wiley), cyclooctene (Aldrich), methyl trifluoromethanesulfonate (Aldrich), methyl iodide (Aldrich), tetramethylammonium iodide (Aldrich), *tert*-butyl isocyanide (Aldrich), 1.0 M potassium triethylborohydride in tetrahydrofuran (Aldrich), trimethylphosphine (Strem), triethylphosphine (Pressure), carbon monoxide (Air Products), and $IrCl_3{\cdot}3H_2O$ (Johnson Matthey) were used without further purification. Potassium 2,4-dimethylpentadienide–tetrahydrofuran was prepared by the method of Yasuda and Nakamura.[13] (Cl)$Ir(PEt_3)_3$ was synthesized from the reaction of $[(cyclooctene)_2IrCl]_2$[14] with 6 equiv of PEt_3 in tetrahydrofuran.

NMR experiments were performed on a Varian XL-300 or Gemini 300 (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz) NMR spectrometer. ^1H and ^{13}C spectra were referenced to tetramethylsilane. ^{31}P spectra were referenced to external H_3PO_4. Probe temperatures were calibrated by using the temperature dependence of the frequency separation of the ^1H resonances of the methyl and hydroxyl groups of neat methanol below room temperature and the ^1H resonances of the methylene and hydroxyl groups of neat ethylene glycol above room temperature. In general, ^1H connectivities were determined from ^1H–^1H shift-correlated (COSY) 2D spectra; ^1H and ^{13}C peak assignments were made with use of the ^{13}C gated-decoupled spectra and ^{13}C–^1H shift-correlated (HETCOR) 2D spectra. Some reported ^1H–^1H and ^1H–^{31}P coupling constants were determined with use of ^1H *J*-resolved (HOM2DJ) spectra.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of *fac*-(IrCH=C(Me)CH=C(Me)CH_2)$(PEt_3)_3H$ (1a). A cold (−30 °C) solution of potassium 2,4-dimethylpentadienide–tetrahydrofuran (0.20 g, 1.0×10^{-3} mol) in 20 mL of tetrahydrofuran was added dropwise to a cold (−30 °C) stirred solution of (Cl)$Ir(PEt_3)_3$ (0.58 g, 1.0×10^{-3} mol) in 20 mL of tetrahydrofuran. The reaction solution was stirred for 5 min, and then the solvent was removed under vacuum. The residue was extracted with cold (−30 °C) pentane and the extract filtered, followed by immediate removal of pentane under vacuum. The oily product was dissolved in acetone and cooled to −30 °C, yielding 0.48 g (75%) of crystalline **1a**. Anal. Calcd for $C_{25}H_{56}IrP_3$: C, 46.77; H, 8.81. Found: C, 46.26; H, 8.69. ^1H NMR (CD_2Cl_2, −65 °C): δ 6.52 (br m, 1 H1), 5.14 (s, 1, H3), 2.35 (br s, 1, one of the two H5's), 1.81–0.90 (complex multiplets, containing PEt_3 H's, pentadienyl CH_3's, and one H5), −12.87 (d of t, J_{H-P} = 145.2 and 16.8 Hz, Ir–H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −65 °C): δ 141.9, 128.3 (s's, C2 and C4), 126.9 (br s, C3), 121.7 (br d, J_{C-P} = 84.4 Hz, C1), 28.0 (d, J_{C-P} = 10.4 Hz, C6 or C7), 27.1 (d, J_{C-P} = 7.6 Hz, C7 or C6), 19.2–18.3 (complex m, PEt_3 CH_2's), 9.0–8.0 (complex m, PEt_3 CH_3's), −6.2 (br d, J_{C-P} = 72.5 Hz, C5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −65 °C): δ −32.2 (br s), −32.9 (br s), −39.8 (br d, J_{P-H} = 133 Hz, with normal decoupler offset (at 46 Hz); br s, with decoupler offset shifted toward the resonance of the hydride (at −4000 Hz)).

Synthesis of *mer*-(IrCH=C(Me)CH=C(Me)CH_2)-$(PEt_3)_3H$ (1b). Method A: Synthesis from 1a. Compound **1a** (0.64 g, 1.0×10^{-3} mol) was stirred in diethyl ether at room temperature for 24 h. The solvent was then removed under vacuum, and the residue was treated with pentane. After filtration, the pentane solution was cooled to −30 °C, producing 0.51 g (80%) of crystalline **1b**.

Method B: Synthesis from (Cl)$Ir(PEt_3)_3$ and Potassium 2,4-Dimethylpentadienide–Tetrahydrofuran. Potassium 2,4-dimethylpentadienide–tetrahydrofuran (0.41 g, 2.0×10^{-3} mol) in 50 mL of tetrahydrofuran was added dropwise to a cold (0 °C) stirred solution of (Cl)$Ir(PEt_3)_3$ (1.16 g, 2.0×10^{-3} mol) in 40 mL of tetrahydrofuran. The reaction solution was warmed to room temperature and stirred for 24 h. The solvent was removed under vacuum, and the residue was treated with pentane. After filtration, the saturated pentane solution was cooled to −30 °C, producing 1.0 g (78%) of crystalline **1b**. Anal. Calcd for $C_{25}H_{56}IrP_3$: C, 46.77; H, 8.81. Found: C, 46.27; H, 9.08. ^1H NMR

(10) PEt_3 has a cone angle of 132°, while PMe_3's cone angle is 118°: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(11) Compound **9** is also produced when **2** is treated with MeLi or $K^+BEt_3H^-$ in acetone. As in the reaction involving LDA, the active deprotonation agent in these systems is probably acetone enolate.

(12) Jesson, J. P.; Muetterties, E. L. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M. Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 253–316.

(13) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakumura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

(14) Herde, J. L.; Lambert, J. C.; Senoff, C. V. In *Inorganic Syntheses*; Parshall, G. W., Ed.; McGraw-Hill: New York, 1974; Vol. 15, pp 18–20.

(C_6D_6, 22 °C): δ 7.00 (s, 1 H1), 5.93 (s, 1, H3), 2.68 (br t, J_{H-P} = 10.9 Hz, 2, H5's), 2.24 (s, 3, pentadienyl CH_3), 2.12 (s, 3, pentadienyl CH_3), 1.85–1.45 (m, 18, PEt_3 CH_2's), 1.05–0.85 (m, 27, PEt_3 CH_3's), −13.10 (t of d, J_{H-P} = 19.3 and 12.0 Hz, 1, Ir–H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 138.5, 129.0 (s's, C2 and C4), 128.0 (s, C3), 120.0 (d of t, J_{C-P} = 76.5 and 16.5 Hz, C1), 31.2 (s, C7), 30.5 (d, J_{C-P} = 9.1 Hz, C6), 21.1 (d, J_{C-P} = 21.0 Hz, CH_2's of PEt_3 trans to C1), 18.2 (virtual t, J_{C-P} = 30.0 Hz, CH_2's of mutually trans PEt_3's), 9.0, 8.5 (s's, PEt_3 CH_3's), −13.1 (q, J_{C-P} = 3.8 Hz, C5). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C): δ −21.6 (d, J_{P-P} = 20 Hz, 2, mutually trans PEt_3's), −33.1 (t, J_{P-P} = 20 Hz, 1, PEt_3 trans to C1).

Synthesis of [(IrCH=C(Me)CH=C(Me)CH$_2$)(PEt$_3$)$_3$]$^+$O$_3$SCF$_3^-$ (2). $CH_3O_3SCF_3$ (0.16 g, 1.0 × 10^{-3} mol) was cooled to −30 °C and added dropwise to a cold (−30 °C) stirred solution of **1b** (0.64 g, 1.0 × 10^{-3} mol) in 25 mL of diethyl ether. The resulting light yellow solution was stirred for a few minutes, during which time it warmed to about −10 °C, and then the solution was stored in a −30 °C freezer for 12 h. The solvent was then evaporated, the resulting residue dissolved in a minimal amount of ethanol, and the solution cooled to −30 °C, causing **2** to crystallize as yellow blocks, yield 0.50 g (63%). Anal. Calcd for $C_{26}H_{55}IrP_3SO_3F_3$: C, 39.53; H, 7.03. Found: C, 39.37; H, 7.07. Solution NMR experiments of **2** were done at −50 °C, because signals were broad at higher temperature. ^1H NMR ($(CD_3)_2CO$, −50 °C): δ 5.65 (br t, J_{H-P} = 22 Hz, 1, H1), 5.05 (br s, 1, H3), 2.68, 2.55 (s's, 2, H5's), 2.35, 1.37 (s's, 2 × 3, pentadienyl CH_3's), 2.05 (br m, 18, PEt_3 CH_2's), 1.10 (br m, 27, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, −50 °C): δ 136.7 (s, C2), 120.0 (s, C4), 115.0 (d, J_{C-P} = 74 Hz, C1), 74.5 (br s, C3), 22.8–7.1 (complex m's, C5/pentadienyl CH_3's/PEt_3 CH_2's and CH_3's). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −50 °C): δ −19.9 (t, J_{P-P} = 14 Hz, 1), −29.7 (t, J_{P-P} = 14 Hz, 1), −36.8 (t, J_{P-P} = 14 Hz, 1).

Reaction of 2 with K$^+$BEt$_3$H$^-$. To a cold (−78 °C) solution of compound **2** (0.43 g, 5.5 × 10^{-4} mol) in 20 mL of tetrahydrofuran was added $K^+BEt_3H^-$ (1.0 M in THF, 0.55 mL, 5.5 × 10^{-4} mol). After the solution was warmed to room temperature and stirred for 30 min, the solvent was removed under vacuum. The residue was dissolved in pentane and the solution filtered through Celite and cooled to −30 °C overnight, producing 0.28 g (80%) of **1b**.

Synthesis of [(η^5-1,3-Me$_2$Cp)Ir(PEt$_3$)$_2$(H)]$^+$O$_3$SCF$_3^-$ (3). Compound **2** (0.50 g, 6.3 × 10^{-4} mol) was dissolved in 25 mL of acetone and the solution stirred for several hours at room temperature, during which time the red color of the solution faded to almost colorless. The amount of solvent was reduced under vacuum, and the solution was cooled to −30 °C, causing **3** to crystallize as a colorless solid, yield 0.38 g (90%). Anal. Calcd for $C_{20}H_{40}IrP_2SO_3F_3$: C, 35.75; H, 6.01. Found: C, 36.13; H, 5.91. ^1H NMR ($(CD_3)_2CO$, 22 °C): δ 5.35 (s, 2, H4/H5), 5.30 (s, 1, H2), 2.32 (s, 6, cp CH_3's), 2.05–1.85 (complex m, 12, PEt_3 CH_2's), 1.08–0.95 (m, 18, PEt_3 CH_3's), −17.36 (t, J_{H-P} = 30 Hz, 1, Ir–H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 22 °C): δ 104.8 (s, C1/C3), 86.9 (s, C2), 83.1 (s, C4/C5), 22.2 (t, J_{H-P} = 19 Hz, PEt_3 CH_2's), 14.3 (s, cp CH_3's), 8.4 (s, PEt_3 CH_3's). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 22 °C): δ −1.7 (s).

Synthesis of [IrCH=C(Me)CH=C(Me)CH$_2$](PEt$_3$)$_3$I (4). Method A: Reaction of 1b with Methyl Iodide. CH_3I (0.70 g, 5.0 × 10^{-3} mol) was added to a cold stirred solution of **1b** (0.64 g, 1.0 × 10^{-3} mol) in 10 mL of tetrahydrofuran. The solution was stirred for 15 min, during which time it warmed to about 0 °C. The solution was then cooled to −30 °C and kept at this temperature for 5 h before the volatile components were removed under vacuum to yield a solid residue. The solid residue was extracted with diethyl ether and the extract filtered to remove a small amount of $PEt_3Me^+I^-$, which was formed in the reaction. The volume of diethyl ether was reduced, and the solution was cooled to −30 °C, causing the product to crystallize as white needles, yield 0.61 g (79%).

Method B: Reaction of 2 with NMe$_4$I. NMe_4I (0.10 g, 5.0 × 10^{-4} mol) and **2** (0.40 g, 5.0 × 10^{-4} mol) were added together with stirring to a flask containing 30 mL of cold (−30 °C) acetone. The solution was then stirred while being warmed slowly to room temperature, during which time the color of the solution faded. The solvent was removed, and the product was extracted with diethyl ether and crystallized at −30 °C as white needles, yield 0.30 g (77%). Anal. Calcd for $C_{25}H_{55}IrP_3I$: C, 39.10; H, 7.23. Found: C, 39.15; H, 7.44. ^1H NMR (1:2 $(CD_3)_2CO$–$DCCl_3$, 22 °C): δ 7.98 (s, 1, H1), 5.35 (s, 1, H3), 2.79 (t of d, J_{H-P} = 12.2 and 7.3 Hz, 2, H5's), 2.20–1.80 (m, 18, PEt_3 CH_2's), 1.72 (s, 3, pentadienyl CH_3's), 1.57 (s, 3, pentadienyl CH_3's), 1.22–0.93 (m, 27, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR (1:2 $(CD_3)_2CO$–$DCCl_3$, 22 °C): δ 134.4 (s, C2 or C4), 130.0 (d of t, J_{C-P} = 82.5 and 14.9 Hz, C1), 129.5 (s, C3), 127.9 (s, C2 or C4), 29.6 (d, J_{C-P} = 7.0 Hz, C6), 28.9 (s, C7), 21.0 (d, J_{C-P} = 24.0 Hz, CH_2's of PEt_3 trans to C1), 17.7 (virtual t, J_{C-P} = 30.0 Hz, CH_2's of mutually trans PEt_3's), 10.1, 9.7 (s's, PEt_3 CH_3's), −3.8 (s, C5). $^{31}P\{^1H\}$ NMR (1:2 $(CD_3)_2CO$–$DCCl_3$, 22 °C): δ −35.0 (d, J_{P-P} = 19 Hz, 2, mutually trans PEt_3's), −42.3 (t, J_{P-P} = 19 Hz, 1, PEt_3 trans to C1).

Synthesis of [(IrCH=C(Me)CH=C(Me)CH$_2$)(PEt$_3$)$_3$(CO)]$^+$O$_3$SCF$_3^-$ (5). Compound **2** (0.40 g, 5.1 × 10^{-4} mol) was dissolved in 20 mL of acetone and the solution cooled to −78 °C in a dry ice–acetone bath. The solution was then gradually warmed to room temperature while CO gas was bubbled through it. The solvent was then removed under vacuum. The residue was dissolved in an ethanol–diethyl ether mixture (1:10 by volume) and the solution cooled to −30 °C, causing **5** to precipitate in a *fac*:*mer* isomer ratio of approximately 1:5. Stirring the isomer mixture in acetone at room temperature for 30 h caused the *fac* isomer to be converted to the thermodynamically preferred *mer* isomer; yield 0.35 g (80%). Anal. Calcd for $C_{27}H_{55}IrP_3O_4SF_3$: C, 39.64; H, 6.79. Found: C, 39.47; H, 6.78.

The small quantity of *fac* isomer (**5a**) could best be detected in the $^{31}P\{^1H\}$ NMR spectrum, where it gave rise to multiplets at approximately δ −33.5, −35.2, and −36.4.

***mer* Isomer (5b).** ^1H NMR ($(CD_3)_2CO$, 22 °C): δ 6.63 (br s, 1, H1), 5.53 (s, 1, H3), 2.29 (t of d, 2, J_{H-P} = 15 and 9 Hz, H5's), 2.22–2.00 (complex m's, 18, PEt_3 CH_2's), 1.86, 1.77 (s's, 2 × 3, pentadienyl CH_3's), 1.27–1.05 (complex m's, 27, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 22 °C): δ 172.0 (s, CO), 137.2, 130.9 (s's, C2 and C4), 129.1 (s, C3), 106.7 (d of t, J_{C-P} = 68 and 12 Hz, C1), 28.5 (d, J_{C-P} = 15 Hz, C6), 28.6 (s, C7), 19.2 (d, J_{C-P} = 25 Hz, CH_2's of PEt_3 trans to C1), 16.9 (virtual t, J_{C-P} = 34 Hz, CH_2's of mutually trans PEt_3's), 9.1 (d, J_{C-P} = 10 Hz, CH_3's of PEt_3 trans to C1), 8.3 (s, CH_3's of mutually trans PEt_3's), 2.2 (q, J_{C-P} = 11 Hz, C5). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 22 °C): δ −22.4 (d, J_{P-P} = 14.4 Hz, 2, mutually trans PEt_3's), −41.4 (t, J_{P-P} = 14.4 Hz, PEt_3 trans to C1).

Synthesis of [(IrCH=C(Me)CH=C(Me)CH$_2$)(PEt$_3$)$_3$(NCMe)]$^+$O$_3$SCF$_3^-$ (6). To a cold (−30 °C) solution of **2** (0.64 g, 8.1 × 10^{-4} mol) in 10 mL of acetone was added $NCCH_3$ (0.034 g, 8.1 × 10^{-4} mol). The resulting solution was shaken by hand for several minutes and then stored at −30 °C for $^1/_2$ h. After removal of the solvent under vacuum, the light yellow residue was dissolved in a minimal quantity of an ethanol–diethyl ether mixture (1:10 by volume) and the solution cooled to −30 °C. Light yellow crystals of **6** (0.52 g, 77% yield) were obtained overnight. Anal. Calcd for $C_{28}H_{58}IrNP_3O_3SF_3$: C, 40.46; H, 7.05. Found: C, 40.84; H, 7.10. ^1H NMR ($(CD_3)_2CO$, 17 °C): δ 7.02 (s, 1, H1), 5.49 (s, 1, H3), 2.73 (s, 3, acetonitrile CH_3), 2.54 (t of d, J_{H-P} = 12 and 6.1 Hz, 2, H5's), 2.25–1.75 (m, 18, PEt_3 CH_2's), 1.66 (s, 6, pentadienyl CH_3's), 1.4–0.9 (complex m, 27, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ 135.3, 129.7 (s's, C2 and C4), 128.5 (s, C3), 124.5 (d of t, J_{C-P} = 77.3 and 13.0 Hz, C1), 121.3 (s, nitrile C), 28.3 (d, J_{C-P} = 9.3 Hz, C6), 27.4 (s, C7), 18.6 (d, J_{C-P} = 22.4 Hz, CH_2's of PEt_3 trans to C1), 15.1 (virtual t, J_{C-P} = 33.0 Hz, CH_2's of mutually trans PEt_3's), 9.0 (d, J_{C-P} = 4.7 Hz, CH_3's of PEt_3 trans to C1), 8.1 (d, CH_3's of mutually trans PEt_3's), 3.44 (s, acetonitrile CH_3), −8.3 (s, C5). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ −26.1 (d, J_{P-P} = 17.6 Hz, 2, mutually trans PEt_3's), −38.2 (t, J_{P-P} = 17.6 Hz, PEt_3 trans to C1).

Synthesis of [(IrCH=C(Me)CH=C(Me)CH$_2$)(PEt$_3$)$_3$(CNCMe$_3$)]$^+$O$_3$SCF$_3^-$ (7). To a cold (−30 °C) solution of **2** (0.63 g, 8.0 × 10^{-4} mol) in 10 mL of acetone was added $CNCMe_3$ (0.066 g, 8.0 × 10^{-4} mol). The resulting solution was shaken by hand for several minutes and then stored at −30 °C for $^1/_2$ h. After removal of the solvent under vacuum, the residue was dissolved in a minimal quantity of an ethanol–diethyl ether mixture (1:10 by volume) and cooled to −30 °C. A mixture of light yellow powder

(*fac* isomer, **7a**) and light yellow needles (*mer* isomer, **7b**) in an approximate 2:1 ratio was obtained overnight (0.53 g, 76% yield). When the mixture was redissolved in acetone and the solution stirred at room temperature for 30 h, the *fac* isomer was gradually converted to the thermodynamically preferred *mer* isomer. Anal. Calcd for $C_{31}H_{64}IrNP_3O_3SF_3$: C, 42.64; H, 7.40. Found: C, 42.74; H, 7.45.

***fac* Isomer (7a).** ^1H NMR ($(CD_3)_2CO$, 17 °C): δ 6.30 (br s, 1, H1), 5.46 (s, 1, H3), 3.0 (m, 1 or 2, one or two H5's), 2.3–1.9 (complex m, 18, PEt_3 CH_2's), 1.83, 1.79 (s's, 2 × 3, pentadienyl CH_3's), 1.47 (s, 9, isocyanide CH_3's), 1.5–1.0 (complex m, 27, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ 137.5, 132.5 (s's, C2 and C4), 129.2 (s, C3), 109.4 (d of t, J_{C-P} = 76.7 and 15.0 Hz, C1), 58.6 (s, quaternary C of isocyanide), 28.3 (d, J_{C-P} = 7.6 Hz, C6), 28.1 (s, C7), 18.9 (d, J_{C-P} = 27.7 Hz, CH_2's of PEt_3 trans to C1), 18.1, 17.6 (s's, PEt_3 CH_2's), 9.8 (s, isocyanide CH_3's), 9.0 (d, J_{C-P} = 6.2 Hz, CH_3's of PEt_3 trans to C1), 8.5 (s, PEt_3 CH_3's), –5.5 (v br s, C5). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ –35.1 (d of d, 1, J_{P-P} = 21.3 and 18.0 Hz), –36.7 (d of d, 1, J_{P-P} = 21.3 and 10.8 Hz), –38.3 (d of d, 1, J_{P-P} = 18.0 and 10.8 Hz).

***mer* Isomer (7b).** ^1H NMR ($(CD_3)_2CO$, 17 °C): δ 6.74 (br s, 1, H1), 5.48 (s, 1, H3), 2.48 (br t, 2, J_{H-P} = 17.9 Hz, H5's), 2.20–1.94 (complex m, 18, PEt_3 CH_2's), 1.84, 1.75 (s's, 2 × 3, pentadienyl CH_3's), 1.64 (s, 9, isocyanide CH_3's), 1.32–1.06 (complex m, 27, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ 137.8, 132.6 (s's, C2 and C4), 129.4 (s, C3), 113.2 (d of t, J_{C-P} = 77.4 and 15.3 Hz, C1), 59.2 (s, quaternary C of isocyanide), 28.9 (d, J_{C-P} = 10.5 Hz, C6), 28.6 (s, C7), 19.3 (d, J_{C-P} = 23.8 Hz, CH_2's of PEt_3 trans to C1), 16.4 (virtual t, J_{C-P} = 34.4 Hz, CH_2's of mutually trans PEt_3's), 9.9 (s, isocyanide CH_3's), 9.29 (d, J_{C-P} = 4.7 Hz, CH_3's of PEt_3 trans to C1), 8.5 (s, CH_3's of mutually trans PEt_3's), –3.0 (br s, C5). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ –26.3 (d, J_{P-P} = 16.6 Hz, 2, mutually trans PEt_3's), –43.0 (t, J_{P-P} = 16.6 Hz, 1, PEt_3 trans to C1).

Synthesis of $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (8). To a cold (–30 °C) solution of compound **2** (0.45 g, 6.0 × 10^{-4} mol) in 10 mL of acetone was added PMe_3 (0.18 g, 2.4 × 10^{-3} mol). After the mixture was stirred for 20 min at –30 °C, the solvent was removed under vacuum and the residue was dissolved in a minimal quantity of ethanol. Cooling of this solution to –30 °C overnight resulted in the formation of 0.31 g (72%) of light yellow crystals of **8**. Anal. Calcd for $C_{23}H_{52}IrP_4O_3SF_3$: C, 35.33; H, 6.70. Found: C, 35.68; H, 6.90. ^1H NMR ($(CD_3)_2CO$, 17 °C): δ 6.50 (br d, J_{H-P} = 18 Hz, 1, H1), 5.51 (s, 1, H3), 2.57 (t of t, J_{H-P} = 17 and 5 Hz, 2, H5's), 2.2–2.0 (m, 6, PEt_3 CH_2's), 1.75 (s, 3, pentadienyl CH_3's), 1.65 (s, 3, pentadienyl CH_3's), 1.52 (m, 27, PMe_3 CH_3's), 1.28–1.18 (m, 9, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ 136.7 (s, C2), 130.2 (br s, C4), 128.1 (s, C3), 117.8 (d of t of d, J_{C-P} = 71, 14, and 3 Hz, C1), 29.0 (s, C6 or C7), 27.6 (d, J_{C-P} = 10 Hz, C6 or C7), 19.5–18.9 (m, PEt_3 CH_2's and PMe_3 CH_3's), 16.7 (t, J_{C-P} = 19 Hz, PMe_3 CH_3's), 9.64 (d, J_{C-P} = 5 Hz, PEt_3 CH_3's), 2.0 (d of t of d, J_{C-P} = 66, 6, and 3 Hz, C5). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ –44.1 (t of d, J_{P-P} = 16 and 12 Hz, 1, PEt_3), –50.2 (d of d, J = 20 and 16 Hz, 2, mutually trans PMe_3's), –62.9 (t of d, J_{P-P} = 20 and 12 Hz, 1, PMe_3).

Synthesis of $(\overline{Ir{-}CH{-}C(Me){-}CH{-}C(Me){-}CH})(PEt_3)_3$ (9). Compound **2** (0.50 g, 6.3 × 10^{-4} mol) was mixed with lithium diisopropylamide (0.068 g, 6.3 × 10^{-4} mol) and dissolved in 10 mL of cold (–30 °C) acetone. The resulting solution was shaken by hand for 1 min and then stored at –30 °C for 1 h. After removal of the solvent under vacuum, the red residue was redissolved in a minimal quantity of acetone and the solution cooled to –30 °C. Red crystals (0.30 g, 75% yield) were obtained overnight. Anal. Calcd for $C_{25}H_{54}IrP_3$: C, 46.92; H, 8.52. Found: C, 46.38; H, 8.72. ^1H NMR ($(CD_3)_2CO$, 17 °C): δ 10.91 (quartet, J_{H-P} = 7.30 Hz, 2, H1/H5), 7.18 (s, 1, H3), 2.49 (s, 6, ring CH_3's), 1.85–1.74 (m, 18, PEt_3 CH_2's), 0.94–0.81 (m, 27, PEt_3 CH_3's). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ 167.3 (quartet, J_{C-P} = 30.2 Hz, C1/C5), 132.0 (s, C2/C4), 129.8 (s, C3), 28.4 (s, ring CH_3's), 22.4 (d, J_{C-P} = 15.9 Hz, PEt_3 CH_2's), 9.2 (d, J_{C-P} = 9.2 Hz, PEt_3 CH_3's). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 17 °C): δ –4.8 (s).

X-ray Diffraction Studies. Single crystals of **8** were sealed in glass capillaries under an inert atmosphere. Data were collected at room temperature, with use of graphite-monochromated Mo Kα radiation. Three standard reflections were measured every 100 events as check reflections for crystal deterioration and/or misalignment. Data reduction and refinement were done by using the Enraf-Nonius SDPVAX structure determination package (modified by B. A. Frenz and Associates, Inc., College Station, TX) on a VAX 11/780 computer. Crystal data and details of data collection and structure analysis are summarized in Table III.[15]

Table III. X-ray Diffraction Structure Summary for $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (8)

Crystal Parameters and Data Collection Summary	
formula	$C_{23}H_{52}IrP_4SO_3F_3$
fw	781.82
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	14.77 (1)
b, Å	11.588 (9)
c, Å	20.29 (1)
α, deg	90
β, deg	109.91 (5)
γ, deg	90
V, Å^3	3265 (5)
Z	4
cryst dimens, mm	0.5 × 0.5 × 0.3
cryst color	light yellow
calcd density, g/cm^3	1.590
diffractometer model	Nicolet P3
radiation, Å	Mo Kα, λ = 0.71069
scan type	$\theta/2\theta$
scan rate, deg/min	variable; 4.88–29.3
scan range, deg	2.4 (2θ)
2θ range, deg	4.0–50.0
data collected	$h,k,\pm l$
total decay, %	1
Treatment of Intensity Data and Refinement Summary	
no. of unique data collected	6107
no. of data with $I > 3\sigma(I)$	4027
Mo Kα linear abs coeff, cm^{-1}	43.661
abs cor applied	ψ scans/empirical
data:param ratio	14.5
R^a	0.050
$R_w{}^b$	0.067

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

The iridium atom position in **8** was calculated from a Patterson map; the remaining non-hydrogen atoms were found by successive full-matrix least-squares refinement and difference Fourier map calculations. Non-hydrogen atoms in the cation were refined anisotropically, while those in the anion exhibited relatively large thermal parameters and were refined isotropically. Hydrogen atoms were placed at idealized positions with use of the program HYDRO and included in the structure factor calculations but not refined.

Summary

A new synthetic approach to 1-metallacyclohexa-2,4-diene complexes has been developed. This method utilizes pentadienide as the source of the ring carbon atoms and involves a metal-centered C–H bond activation step. In the prototypical reaction, $(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)_3(H)$ (**1**) is produced in high yield from the reaction of $(Cl)Ir(PEt_3)_3$ with potassium 2,4-dimethylpentadienide.

The hydride ligand in **1** is readily removed upon treatment with methyl trifluoromethanesulfonate, producing $[(\overline{IrCH{=}C(Me)CH{=}C(Me)CH_2})(PEt_3)_3{}^+O_3SCF_3^-$ (**2**). In solution at 25 °C, **2** is unstable with respect to decomposition to $[(\eta^5\text{-}1,3\text{-}Me_2cp)Ir(PEt_3)_2(H)]^+O_3SCF_3^-$ (**3**). This

(15) Atomic scattering factors were obtained from: *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

process *may* involve an α-hydride elimination step.

Compound **2** reacts with a series of 2e ligands (L) at low temperature to produce a family of adducts having the formula $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)](PEt_3)_3L]^+O_3SCF_3^-$ (L = I^-, CO, NCMe, and $CNCMe_3$; compounds **4**–**7**, respectively). Reaction of **2** with PMe_3 also leads to adduct formation but is accompanied by phosphine exchange. The product in this case is $[(IrCH{=}C(Me)CH{=}C(Me)CH_2)(PEt_3)(PMe_3)_3]^+O_3SCF_3^-$ (**8**). Treatment of **2** with lithium diisopropylamide (LDA) in acetone results in proton abstraction and production of the stable metallabenzene complex $(Ir{-}CH{-}C(Me){-}CH{-}C(Me){-}CH)(PEt_3)_3$ (**9**).

The chemistry of metallacyclohexadienes and metallabenzenes continues to be investigated in our laboratories and will be described in future reports.

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Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compound **8** (7 pages); a listing of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

Thermal and Photolytic Substitution of Dimanganese Decacarbonyl with Trifluorophosphine

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Under thermal conditions, the PF_3 substitution of $Mn_2(CO)_{10}$ produces five different compounds: 1-$Mn_2(CO)_9(PF_3)$, 1,1′-$Mn_2(CO)_8(PF_3)_2$, 1,2-$Mn_2(CO)_8(PF_3)_2$, 1,1′,2-$Mn_2(CO)_7(PF_3)_3$, and 1,1′,2,2′-$Mn_2(CO)_6(PF_3)_4$. Photolytic excitation results in the formation of four additional compounds. Substitution is rigorously limited to the replacement of four carbon monoxides, but that replacement is fairly readily achieved. Compounds are identified by using a combination of GC-MS, ^{19}F NMR, and IR. Back reaction of 1,1′,2,2′-$Mn_2(CO)_6(PF_3)_4$ with ^{13}CO produces only the previously observed PF_3-substituted compounds having extensive label. Side products produced include the monometallic hydride series $HMn(CO)_{5-x}(PF_3)_x$ (x = 1–5), the hydrogen-bridged series $Mn_2(\mu\text{-}H)(\mu\text{-}PF_2)(CO)_{8-x}(PF_3)_x$ (x = 2–5), and the bisphosphido-bridged series $Mn_2(\mu\text{-}PF_2)_2(CO)_{8-x}(PF_3)_x$ (x = 2–7).

Introduction

With monometallic carbonyl complexes such as $Mo(CO)_6$ and $Fe(CO)_5$, PF_3 can sequentially replace CO and ultimately yield the compounds $Mo(PF_3)_6$ and $Fe(PF_3)_5$.[1,2] Trifluorophosphine has been shown to form σ and π bonds to metals with bonding characteristics similar to those of CO.[3] Numerous PF_3 analogues of mononuclear metal carbonyls have been prepared, and their intermediate species have been extensively studied.[4] However, little is known about the substitution reactions of PF_3 with simple polynuclear complexes such as $Mn_2(CO)_{10}$[5] $Fe_2(CO)_9$, and $Co_2(CO)_8$. The substitution chemistry of dimanganese decacarbonyl has been studied under both thermal and photolytic conditions by using various ligands.[5-10] With bulkier ligands, substitution stops with the replacement of two carbonyls, while with smaller ligands up to four ligands may be replaced. The mechanism of substitution was controversial for many years. It is now generally assumed that under thermal conditions, the substitution occurs through the dissociative loss of a CO to form an unsaturated enneacarbonyl complex with the metal–metal bond intact.[11] Under photolytic conditions, dissociative loss of a CO is observed, as well as a second mechanism involving the homolytic cleavage of the metal/metal bond.[9,12,13] The relative rates of the two mechanisms have been shown to be wavelength dependent with the ratio of the homolytic cleavage route to the dissociative CO loss increasing with increasing wavelengths.

The clear separation of a potentially large number of physically similar compounds and their definitive characterization are among the problems that stand in the way of an extensive study of PF_3 substitution into polynuclear

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