

# Communications

## Synthesis, Structure, and Spectroscopy of Iridacyclohexadiene Complexes<sup>1</sup>

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**Summary:** Reaction of  $\text{ClIr}(\text{PEt}_3)_3$  with potassium 2,4-dimethylpentadienide yields the iridacyclohexadiene complex,  $[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PEt}_3)_3(\text{H})$  (**1**), by iridium-centered activation of a pentadienyl C-H bond.

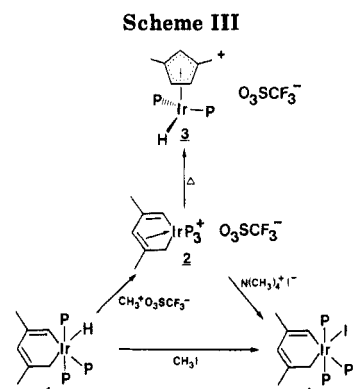
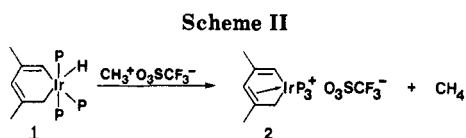
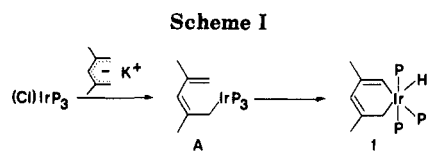
Treatment of **1** with  $\text{CH}_3\text{O}_3\text{SCF}_3$  produces methane and  $\{[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PEt}_3)_3\}^+ \text{O}_3\text{SCF}_3^-$  (**2**), in

which one of the ring double bonds coordinates to Ir. Both **1** and **2** have been structurally characterized. Above 0 °C, **2** decomposes in solution to  $[(\eta^5\text{-}1,3\text{-dimethylcyclopentadienyl})\text{Ir}(\text{PEt}_3)_2(\text{H})]^+ \text{O}_3\text{SCF}_3^-$  (**3**).

Treatment of **1** with  $\text{CH}_3\text{I}$  or **2** with  $\text{NMe}_4\text{I}$  yields  $[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PEt}_3)_3(\text{I})$  (**4**).

While the synthesis and reactivity of metallacyclopentadiene<sup>2</sup> complexes have been extensively studied during the past two decades, the corresponding six-membered ring compounds, the metallacyclohexadienes, have remained unexplored. In fact, the first example of a metallacyclohexadiene complex,  $[\text{PtC}(\text{Ph})=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{CHCH}_2](\text{PPh}_3)_2$ , was only recently obtained by Hughes<sup>3</sup> from the reaction of a highly strained vinylcyclopropene with  $\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2$ . We now report a new synthetic approach to metallacyclohexadienes which utilizes pentadienide as the source of ring carbon atoms.

Treatment of  $\text{ClIr}(\text{PEt}_3)_3$  with potassium 2,4-dimethylpentadienide produces in high yield the iridacyclohexadiene complex,  $[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PEt}_3)_3(\text{H})$  (**1**).<sup>4</sup> This reaction probably proceeds through the intermediacy of  $(\eta^1\text{-}2,4\text{-dimethylpentadienyl})\text{Ir}(\text{PEt}_3)_3$  (**A**, Scheme I), which undergoes intramolecular oxidative



addition across an  $\text{sp}^2$  C-H bond on the dangling terminus of the pentadienyl ligand.

Compound **1** has been characterized by a single-crystal X-ray diffraction study,<sup>5</sup> and an ORTEP drawing of the molecular structure is shown in Figure 1. Unlike the platinacyclohexadiene reported by Hughes, the metallacycline in **1** is almost planar; none of the atoms deviates by more than 0.015 Å from the plane. The nonplanarity of

(5) Crystals of **1** were triclinic of space group  $\text{P}\bar{1}$  with  $a = 9.993$  (2) Å,  $b = 18.558$  (7) Å,  $c = 8.529$  (2) Å,  $\alpha = 92.59$  (3)°,  $\beta = 101.11$  (2)°,  $\gamma = 104.47$  (2)°,  $V = 1495.6$  (8) Å<sup>3</sup>,  $Z = 2$ , and  $d_{\text{calcd}} = 1.43$  g/cm<sup>3</sup>.

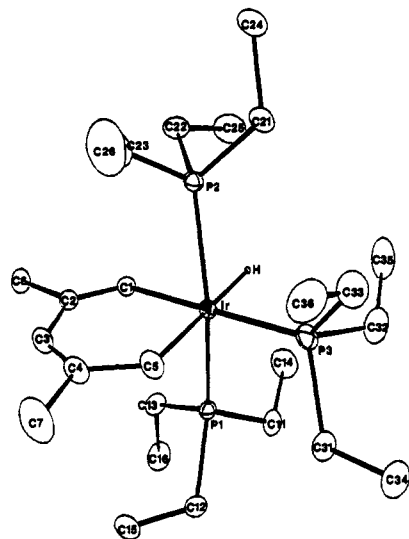
A single crystal (orange block) of dimensions 0.5 mm × 0.5 mm × 0.4 mm was grown from a saturated diethyl ether solution and sealed in a glass capillary under an inert atmosphere. Data were collected at 22 °C on a Nicolet P3 diffractometer using graphite-monochromated Mo K $\alpha$  radiation. A total of 8614 independent reflections with  $3^\circ < 2\theta < 60^\circ$  were collected by using the  $\theta/2\theta$  scanning technique and a variable scan rate of 4.0–30.0°/min. All of the data reduction and structure refinement were done with a modified Enraf-Nonius Structure Determination Package (modified by B.A. Frenz and Assoc. Inc., College Station, TX) on a VAX 11/780 computer. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction ( $\mu = 46.145$  cm<sup>-1</sup>) was applied by using the azimuthal scans of three near-axial reflections. Only the 6638 independent reflections with intensities greater than 3 times their estimated standard deviations were used in the least-squares refinements. The structure was solved by standard Fourier techniques following the location of the Ir atom from a Patterson map. All non-hydrogen atoms were refined anisotropically. The metal-bound hydrogen atom was located from a difference Fourier map but not refined. All other hydrogens were calculated by using program HYDR0 and included in the structure factor calculations, but not refined. The convergence values of the agreement indices were  $R_F = 0.047$  and  $R_{wF} = 0.063$ . Note: Three of the C-C bonds in the  $\text{PEt}_3$  ligands, C(23)–C(26), C(32)–C(35), and C(33)–C(36), were abnormally short (1.34–1.36 Å). These short distances may be due to an irresolvable disorder involving slightly different rotameric conformations of the ethyl groups or to an incompletely resolved false minimum problem. Similar problems have been encountered in other structural studies involving ethylated phosphine ligands. See, for example: Askham, F. R.; Stanley, G. G.; Marques, E. C. *J. Am. Chem. Soc.* **1985**, *107*, 7423.

(1) Pentadienyl-Metal-Phosphine Chemistry. 12. For the previous paper in this series, see: Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 1367.

(2) See, for example: (a) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298. (b) Mosely, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169. (c) Wakatsuki, Y.; Kiramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, *51/52*, 4549. (d) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666.

(3) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694.

(4) In a typical reaction, potassium 2,4-dimethylpentadienide-tetrahydrofuran<sup>4a</sup> (0.41 g,  $2.0 \times 10^{-3}$  mol) in 50 mL of tetrahydrofuran (THF) was added dropwise with stirring to a 0 °C solution of  $\text{ClIr}(\text{PEt}_3)_3$ <sup>4b</sup> (1.16 g,  $2.0 \times 10^{-3}$  mol) in 50 mL of THF. The mixture was stirred for 0.5 h at 0 °C, warmed slowly to 25 °C, and stirred for an additional 2 h at 25 °C, before removal of the THF solvent under vacuum. **1** was extracted from the resulting residue with pentane and crystallized from diethyl ether. Yield (crystalline): 0.9 g (70%). Anal. Calcd for  $\text{C}_{25}\text{H}_{56}\text{IrP}_3$ : C, 46.77; H, 8.81. Found: C, 46.27; H, 9.08. (a) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036. (b) Synthesized from the reaction of [(cyclooctene)<sub>2</sub>IrCl]<sub>2</sub> with 6 equiv of  $\text{PEt}_3$  in tetrahydrofuran and recrystallized from diethyl ether.



**Figure 1.** ORTEP drawing of  $[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PET}_3)_3(\text{H})$  (1). Bond distances (Å): Ir-P(1), 2.313 (2); Ir-P(2), 2.321 (2); Ir-P(3), 2.349 (2); Ir-C(1), 2.085 (6); Ir-C(5), 2.189 (6); Ir-H, 1.75; C(1)-C(2), 1.332 (9); C(2)-C(3), 1.46 (1); C(3)-C(4), 1.33 (1); C(4)-C(5), 1.49 (1). Bond angles (deg): P(1)-Ir-P(2), 160.23 (6); P(1)-Ir-P(3), 95.93 (7); P(2)-Ir-P(3), 99.75 (7); C(1)-Ir-P(3), 178.7 (2); C(5)-Ir-H, 179.3; Ir-C(1)-C(2), 129.5 (5); C(1)-C(2)-C(3), 125.2 (7); C(2)-C(3)-C(4), 127.9 (7); C(3)-C(4)-C(5), 126.7 (6); C(4)-C(5)-Ir, 121.7 (5); C(5)-Ir-C(1), 89.0 (3).

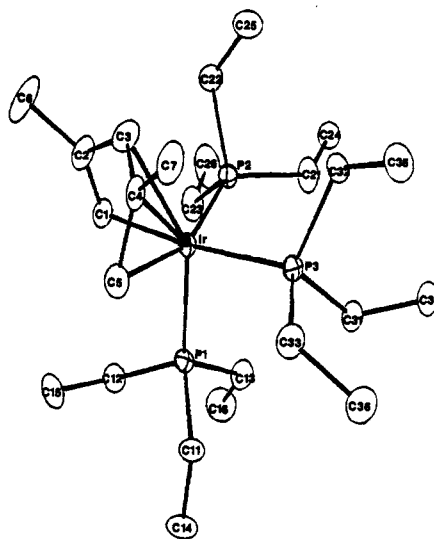
the ring in Hughes' complex may result from a minimization of steric contacts between the phenyl substituents on ring carbon atoms C(1), C(2), and C(3). As expected, there is a clear alternation in the C-C bond lengths around the six-membered ring; C(1)-C(2) and C(3)-C(4) are each 1.33 Å long, while C(2)-C(3) and C(4)-C(5) are 1.46 and 1.49 Å long, respectively. The hydride ligand resides cis to C(1), the ring carbon to which it was originally bonded, and trans to the other end of the metallacycle, C(5).

The planarity of the metallacycle is also manifested in the solution-phase NMR spectra of 1.<sup>6</sup> Hence, the two protons bonded to C(5) give rise to a single peak in the <sup>1</sup>H NMR spectrum, while the two mutually trans phosphines [P(1) and P(2)] are equivalent by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy. One other noteworthy feature of the <sup>13</sup>C spectrum is the strong coupling of C(1) to P(3) ( $J_{\text{C-P}} = 76.5$  Hz).

As shown in Scheme II, the reaction of 1 with methyl trifluoromethanesulfonate results in abstraction of the hydride ligand and coordination of the ring double bond C(3)-C(4) to the iridium center, generating  $[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PET}_3)_3^+ \text{O}_3\text{SCF}_3^-$  (2).<sup>7,8</sup> The X-

(6) Spectroscopic Data for 1. <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 22 °C, 300 MHz):  $\delta$  7.00 (s, 1, H(1)), 5.93 (s, 1, H(3)), 2.68 (br t,  $J_{\text{H-P}} = 10.9$  Hz, 2, H(5)'s), 2.24 (s, 3, CH<sub>3</sub>), 2.12 (s, 3, CH<sub>3</sub>), 1.85-1.45 (m, 18, CH<sub>2</sub>'s on  $\text{PET}_3$ 's), 1.05-0.85 (m, 27, CH<sub>3</sub>'s on  $\text{PET}_3$ 's), -13.10 (t of d,  $J_{\text{H-P}} = 19.3$  Hz,  $J_{\text{H-P}} = 12.0$  Hz, 1, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 22 °C, 75 MHz):  $\delta$  138.5, 129.0 (s, C(2)/C(4)), 128.0 (s, C(3)), 120.0 (d of t,  $J_{\text{C-P}} = 76.5$  Hz,  $J_{\text{C-P}} = 16.5$  Hz, C(1)), 31.2 (s, C(7)), 30.5 (d,  $J_{\text{C-P}} = 9.1$  Hz, C(6)), 21.1 (d,  $J_{\text{C-P}} = 21.0$  Hz, CH<sub>3</sub>'s of  $\text{PET}_3$ ), 18.2 (virtual t,  $J_{\text{C-P}} = 30.0$  Hz, CH<sub>2</sub>'s of trans  $\text{PET}_3$ 's), 9.0, 8.5 (s, CH<sub>3</sub>'s of  $\text{PET}_3$ 's), -13.1 (q,  $J_{\text{C-P}} = 3.8$  Hz, C(5)). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 22 °C, 121 MHz, referenced to  $\text{H}_3\text{PO}_4$ ):  $\delta$  -21.6 (d,  $J_{\text{P-P}} = 20$  Hz, 2), -33.1 (t,  $J_{\text{P-P}} = 20$  Hz, 1). IR ( $\text{C}_6\text{H}_6$ , selected peaks): 1929 (s, Ir-H stretch), 1634, 1559 (w, C=C stretch), 1023 (s, P-C stretch)  $\text{cm}^{-1}$ .

(7)  $\text{CH}_3\text{SO}_3\text{CF}_3$  (0.16 g,  $1.0 \times 10^{-3}$  mol) was cooled to -30 °C and added dropwise with stirring to a cold (-30 °C) solution of 1 (0.64 g,  $1.0 \times 10^{-3}$  mol) in 25 mL of acetone. The resulting light yellow solution was warmed to -10 °C, stirred for several minutes, and evaporated to dryness. The residue was redissolved in a minimal quantity of acetone and cooled to -30 °C, causing 2 to crystallize as yellow blocks. Yield: 0.65 g (82%). Anal. Calcd for  $\text{C}_{28}\text{H}_{55}\text{IrP}_3\text{SO}_3\text{F}_3$ : C, 39.53; H, 7.03. Found: C, 39.37; H, 7.07.



**Figure 2.** ORTEP drawing of  $[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PET}_3)_3^+ \text{O}_3\text{SCF}_3^-$  (2). Bond distances (Å): Ir-P(1), 2.297 (2); Ir-P(2), 2.369 (2); Ir-P(3), 2.395 (2); Ir-C(1), 2.088 (8); Ir-C(3), 2.390 (7); Ir-C(4), 2.307 (6); Ir-C(5), 2.174 (7); C(1)-C(2), 1.33 (1); C(2)-C(3), 1.47 (1); C(3)-C(4), 1.35 (1); C(4)-C(5), 1.45 (1). Bond angles (deg): P(1)-Ir-P(2), 100.66 (6); P(1)-Ir-P(3), 94.57 (6); P(2)-Ir-P(3), 97.06 (7); C(1)-Ir-P(3), 171.8 (2); C(3)-Ir-P(1), 147.3 (2); C(5)-Ir-P(2), 159.1 (2); Ir-C(1)-C(2), 103.4 (6); C(1)-C(2)-C(3), 109.1 (7); C(2)-C(3)-C(4), 123.4 (8); C(3)-C(4)-C(5), 119.8 (7); C(4)-C(5)-Ir, 76.1 (4); C(5)-Ir-C(1), 81.0 (3).

ray crystal structure of 2<sup>9</sup> shows an alternation in C-C bond lengths around the metallacyclic ring similar to those observed for 1 (see Figure 2). However, bond C(3)-C(4), which is now coordinated to iridium, is lengthened slightly (to 1.35 Å from 1.33 Å), while C(4)-C(5) is shortened slightly (to 1.45 Å from 1.49 Å). The distances from Ir to C(3) and C(4) are quite long (2.390 and 2.307 Å, respectively), indicating a rather weak, strained interaction between the double bond and the iridium center.<sup>10</sup> Although 2 is stable at 25 °C in the solid state, it slowly decomposes to  $[(\eta^5-1,3-\text{Me}_2\text{Cp})\text{Ir}(\text{PET}_3)_2(\text{H})]^+ \text{O}_3\text{SCF}_3^-$  (3)<sup>11,12</sup> when

(8) Spectroscopic Data for 2. <sup>1</sup>H NMR ( $(\text{CD}_3)_2\text{CO}$ , -50 °C, 300 MHz):  $\delta$  5.65 (br t,  $J_{\text{H-P}} = 22$  Hz, 1, H(1)), 5.05 (br s, 1, H(3)), 2.68, 2.55 (s's, 2, H(5)'s), 2.35, 1.37 (s's, 6, pentadienyl CH<sub>3</sub>'s), 2.05 (br m, 18 H's,  $\text{PET}_3$  CH<sub>2</sub>'s), 1.10 (br m, 27 H's,  $\text{PET}_3$  CH<sub>3</sub>'s). <sup>13</sup>C{<sup>1</sup>H} NMR ( $(\text{CD}_3)_2\text{CO}$ , -50 °C, 75 MHz):  $\delta$  136.7 (s, C(2)), 120.0 (s, C(4)), 115.0 (d,  $J_{\text{C-P}} = 74$  Hz, C(1)), 74.5 (br s, C(3)), 22.8-7.1 (complex m's, C(5)/pentadienyl CH<sub>3</sub>'s/ $\text{PET}_3$  CH<sub>2</sub>'s and CH<sub>3</sub>'s). <sup>31</sup>P{<sup>1</sup>H} NMR ( $(\text{CD}_3)_2\text{CO}$ , -50 °C, 121 MHz, referenced to  $\text{H}_3\text{PO}_4$ ):  $\delta$  -19.9 (t,  $J_{\text{P-P}} = 14$  Hz, 1), -29.7 (t,  $J_{\text{P-P}} = 14$  Hz, 1), -36.8 (t,  $J_{\text{P-P}} = 14$  Hz, 1).

(9) Crystals of 2 were monoclinic, space group  $P2_1/c$ , with  $a = 10.425$  (1) Å,  $b = 17.531$  (3) Å,  $c = 18.488$  (2) Å,  $\beta = 93.16$  (1)°,  $V = 3346.2$  (8) Å<sup>3</sup>,  $Z = 4$ , and  $d_{\text{calc}} = 1.57$  g/cm<sup>3</sup>. Data were obtained at 22 °C on a single crystal (yellow prism) of dimensions 0.5 mm × 0.5 mm × 0.5 mm × 0.4 mm by using the diffractometer described in footnote 5. A total of 7287 independent reflections with  $3^\circ < 2\theta < 60^\circ$  were collected by using the  $\omega$  scanning technique and a variable scan rate of 2-30°/min. Data reduction was carried out as described in footnote 5 ( $\mu = 41.952$  cm<sup>-1</sup>). Only the 4717 reflections with  $I > 3\sigma(I)$  were used in the least-squares refinements. The structure was solved by standard Fourier techniques following the location of the iridium atom from a Patterson map. All non-hydrogen atoms of the cation were refined anisotropically, while hydrogens were calculated by using program HYDRO and included in the structure factor calculations, but not refined. One of the phosphine methyl carbon atoms, C(24), exhibited a 2-fold disorder, which we were able to model successfully by using a multiplicity of 0.5 for each site. In the anion, the S and C atoms were refined anisotropically. The oxygen and fluorine atoms exhibited a 2-fold rotational disorder which we modeled by using multiplicities of 0.6 and 0.4 for the two sites. Both sets of O and F atoms were refined isotropically. The convergence values of the agreement indices were  $R_F = 0.033$  and  $R_{wF} = 0.049$ .

(10) A "normal" Ir-C<sub>olefin</sub> distance is 2.1-2.2 Å. See, for example: Restivo, R. J.; Ferguson, G.; Kelly, T. L.; Senoff, C. V. *J. Organomet. Chem.* 1975, 90, 101.

warmed above 0 °C in acetone solution. The formation of **3** probably proceeds by coupling of C(1) and C(5) to produce  $[(\eta^4\text{-}1,3\text{-dimethylcyclopentadiene})\text{Ir}(\text{PEt}_3)_3]^+\text{O}_3\text{SCF}_3^-$ , followed by phosphine loss and transfer of the endo ring hydrogen to the iridium center.<sup>13</sup>

As shown in Scheme III, the reaction of **2** with  $\text{NMe}_4\text{I}$  or the reaction of **1** with methyl iodide produces  $[\text{IrCH}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{CH}_2](\text{PEt}_3)_3(\text{I})$  (**4**),<sup>14</sup> a compound which is identical with **1**, except that an iodo ligand has replaced the hydride ligand. The methyl iodide reaction probably proceeds through the intermediacy of cation **2**.

The NMR spectra of **4**<sup>15</sup> are very similar to those of **1** except for the absence of the hydride resonance at  $\delta -13.1$  in the <sup>1</sup>H NMR spectrum. The position of the iodo ligand trans to C(5) is clear from the fact that C(5) does not exhibit phosphorus coupling in the <sup>13</sup>C NMR spectrum. In contrast, C(1) is strongly coupled to phosphorus ( $J_{\text{C-P}} = 82.5$  Hz) and must reside trans to a phosphine ligand. Compound **4**, like **1**, exhibits mirror plane symmetry in solution. Hence, the two protons bonded to C(5) are equivalent and the two mutually trans phosphine ligands are equivalent by NMR spectroscopy.

We are continuing to study the reactivity of these unusual iridacycles. Particularly intriguing is the possibility that they may be convertible to the corresponding iridabenzene.<sup>16,17</sup>

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**Registry No.** 1, 108296-94-2; 2, 108296-96-4; 3, 108296-98-6; 4, 108296-99-7;  $\text{ClIr}(\text{PEt}_3)_3$ , 91513-65-4; potassium 2,4-dimethylpentadienide-tetrahydrofuran, 72013-05-9; methyl trifluoromethanesulfonate, 333-27-7; methane, 74-82-8.

**Supplementary Material Available:** Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and significant least-squares planes for **1** and **2** (16 pages); listings of observed and calculated structure factor amplitudes for **1** and **2** (45 pages). Ordering information is given on any current masthead page.

### Transition-Metal-Promoted Ring-Opening Reactions of Vinylcyclopropenes. 1,2,3,5- $\eta$ -Penta-2,4-dienediyl and 1,5- $\eta$ -Penta-2,4-dienediyl (1-Metallacyclohexa-2,4-diene) Complexes of Rhodium(III) and Iridium(III) and Their Conversion to ( $\eta^5$ -Cyclopentadienyl)hydridometal Compounds

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**Summary:** 1,2,3-Triphenyl-3-vinyl-1-cyclopropene (**2**) reacts with " $\text{MCl}(\text{PMe}_3)_2$ " ( $\text{M} = \text{Rh}, \text{Ir}$ ) to give novel complexes **3a,b** containing the 1,2,3,5- $\eta$ -penta-2,4-dienediyl ligand, one of which, the iridium species **3b**, has been crystallographically characterized. In contrast, reaction of **2** with the bulkier reagent " $\text{RhCl}(\text{P-}i\text{-Pr}_3)_2$ " yields directly the (cyclopentadienyl)hydridorhodium complex **6**. Reaction of **3a** with (acetylacetonato)thallium affords the (1,5- $\eta$ -penta-2,4-dienediyl)rhodium (1-rhodacyclohexa-2,4-diene) complex **8** which has also been crystallographically characterized.

Recently we reported the isolation and structural characterization of a 1,5- $\eta$ -penta-2,4-dienediyl (1-metallacyclohexa-2,4-diene) complex of platinum(II) (**1**), from the oxidative addition reaction of triphenylvinylcyclopropene **2** with the labile Pt(0) complex  $[\text{Pt}(\eta\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ .<sup>2a</sup> The crystallographically characterized compound **1** contained the first reported example of this unsaturated metallacyclic skeleton. The ring is severely puckered in the solid state, and this structure is maintained in solution with a substantial activation barrier for inversion of the ring, as shown by the NMR inequivalence of the  $\text{CH}_2$  protons. Thermolysis of **1** resulted in reductive elimination to give free 1,2,3-triphenylcyclopentadiene, and the intermediacy of analogous metallacycles in the stepwise formation of ( $\eta^4$ -cyclopentadiene)rhodium and ( $\eta^4$ -cyclohexadienone)-

(11) Compound **2** (0.50 g,  $6.3 \times 10^{-4}$  mol) was dissolved in 25 mL of acetone and stirred at 20 °C for several hours, during which the color of the solution lightened. After removal of the volatiles under vacuum, the residue was redissolved in a minimal quantity of acetone and cooled to -30 °C, producing colorless crystals of **3**. Yield: 0.38 g (90%). Anal. Calcd for  $\text{C}_{20}\text{H}_{16}\text{IrP}_2\text{SO}_3$ : C, 35.75; H, 6.01. Found: C, 36.13; H, 5.91.

(12) Spectroscopic Data for **3**. <sup>1</sup>H NMR ( $(\text{CD}_3)_2\text{CO}$ , 22 °C, 300 MHz):  $\delta$  5.35 (s, 2, H(4)/H(5)), 5.30 (s, 1, H(2)), 2.32 (s, 6,  $\text{CH}_3$ 's of Cp), 2.05-1.85 (complex m, 12,  $\text{CH}_2$ 's of  $\text{PEt}_3$ 's), 1.08-0.95 (m, 18,  $\text{CH}_3$ 's of  $\text{PEt}_3$ 's), -17.36 (t,  $J_{\text{H-P}} = 30$  Hz, 1, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $(\text{CD}_3)_2\text{CO}$ , 22 °C, 75 MHz):  $\delta$  104.8 (s, C(1)/C(3)), 86.9 (s, C(2)), 83.1 (s, C(4)/C(5)), 22.2 (t,  $J_{\text{C-P}} = 19$  Hz,  $\text{CH}_2$ 's of  $\text{PEt}_3$ 's), 14.3 (s,  $\text{CH}_3$ 's of Cp), 8.4 (s,  $\text{CH}_3$ 's of  $\text{PEt}_3$ 's). <sup>31</sup>P{<sup>1</sup>H} NMR ( $(\text{CD}_3)_2\text{CO}$ , 22 °C, 121 MHz, referenced to  $\text{H}_3\text{PO}_4$ ):  $\delta$  -1.7 (d,  $J_{\text{P-H}} = 22$  Hz).

(13) Alternatively, the sequence of steps may involve dissociation of double bond C3-C4 and abstraction of a hydrogen from C5 by Ir to produce a transient iridabenzene (or iridacyclohexatriene) species, which then collapses to **3** with phosphine loss.

(14) Method A.  $\text{NMe}_4\text{I}$  ( $0.20$  g,  $1.0 \times 10^{-3}$  mol) was added to a cold (-30 °C) solution of **2** ( $0.79$  g,  $1.0 \times 10^{-3}$  mol) in tetrahydrofuran. After the solution was warmed to room temperature, stirred for 0.5 h, and filtered, the volume of solvent was reduced and the resulting saturated solution was cooled to -30 °C, causing **4** to crystallize as light yellow needles. Yield (crystalline): 0.46 g (60%).

Method B.  $\text{CH}_3\text{I}$  ( $0.14$  g,  $1.0 \times 10^{-3}$  mol) was added dropwise with stirring to a solution of **1** ( $0.64$  g,  $1.0 \times 10^{-3}$  mol) in 10 mL of tetrahydrofuran. The pale yellow reaction solution was cooled to -30 °C, causing **4** to crystallize from it as light yellow needles. Yield (crystalline): 0.38 g (50%). Anal. Calcd for  $\text{C}_{25}\text{H}_{18}\text{IrP}_3\text{I}$ : C, 39.10; H, 7.23. Found: C, 39.15; H, 7.44.

(15) Spectroscopic Data for **4**. <sup>1</sup>H NMR (1:2  $(\text{CD}_3)_2\text{CO}/\text{DCCl}_3$ , 22 °C, 300 MHz):  $\delta$  7.98 (s, 1, H(1)), 5.35 (s, 1, H(3)), 2.79 (t of d,  $J_{\text{H-P}} = 12.16$  Hz,  $J_{\text{H-P}} = 7.30$  Hz, 2, H(5)'s), 2.20-1.80 (m, 18,  $\text{CH}_2$ 's of  $\text{PEt}_3$ 's), 1.72 (s, 3,  $\text{CH}_3$ ), 1.57 (s, 3,  $\text{CH}_3$ ), 1.22-0.93 (m, 27,  $\text{CH}_3$ 's of  $\text{PEt}_3$ 's). <sup>13</sup>C{<sup>1</sup>H} NMR (1:2  $(\text{CD}_3)_2\text{CO}/\text{DCCl}_3$ , 22 °C, 75 MHz):  $\delta$  134.4 (s, C(2) or C(4)), 130.0 (d of t,  $J_{\text{C-P}} = 82.5$  Hz,  $J_{\text{C-P}} = 14.9$  Hz, C(1)), 129.5 (s, C(3)), 127.9 (s, C(2) or C(4)), 29.6 (d,  $J_{\text{C-P}} = 7$  Hz, C(6)), 28.9 (s, C(7)), 21.0 (d,  $J_{\text{C-P}} = 24.0$  Hz,  $\text{CH}_2$ 's of  $\text{PEt}_3$ 's), 17.7 (virtual t,  $J_{\text{C-P}} = 30.0$  Hz,  $\text{CH}_2$ 's of trans  $\text{PEt}_3$ 's), 10.1, 9.7 (s,  $\text{CH}_3$ 's of  $\text{PEt}_3$ 's), -3.8 (s, C(5)). <sup>31</sup>P{<sup>1</sup>H} NMR (1:2  $(\text{CD}_3)_2\text{CO}/\text{DCCl}_3$ , 22 °C, 121 MHz, referenced to  $\text{H}_3\text{PO}_4$ ):  $\delta$  -35.0 (d,  $J_{\text{P-P}} = 19$  Hz, 2), -42-3 (t,  $J_{\text{P-P}} = 19$  Hz, 1).

(16) Only one metallabenzene, an osmium derivative, has been reported to date: Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* 1982, 811.

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