Communications to the Editor

Direct Synthesis of an Iridabenzene from a Nucleophilic 3-Vinyl-1-cyclopropene

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The reactions of cyclopropenes with transition-metal complexes often generate interesting organometallic products,[1] mainly due to the large amount of strain energy (>50 kcal/mol) contained within the three-membered ring.[2] For example, 3,3-disubstituted cyclopropenes form metal alkylidenes[3] and metallacyclobutenes,[4] while ring-opening reactions of 3-vinyl-1-cyclopropenes produce metallacyclohexadienes and η^5-cyclopentadienyl complexes as well as metallacyclobutenes.[5] One particularly attractive aspect of this chemistry is that a metallacyclohexadiene has been transformed into a metallabenzene,[6] a transition-metal analogue which is isolobal with benzene and retains aromatic physical and chemical properties.[6,7] We sought a method that would allow direct entry into the metallabenzene manifold using a cyclopropene precursor. Reported herein is the preparation of iridabenzene **1**[8] directly from the reaction of a nucleophilic 3-vinyl-1-cyclopropene with Vaska's complex and characterization of the metallacycle by X-ray crystallography.

Considering the aforementioned chemistry, this approach should favor the formation of both a metal−carbon single bond

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(2) For a comprehensive review of cyclopropenes, see: (a) *Methods of Organic Chemistry (Houben-Weyl)*; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17d. (b) Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; pp 1223−1339.

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(6) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606−623 and references therein.

(7) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39−45.

(8) **1** (72% from toluene/hexanes 1:1): mp 196−198 °C. ¹H NMR (benzene-d_6) δ 10.79 (ddt, H(5), J_{H-P} = 11.3 Hz, J_{5-4} = 10.1 Hz, J_{5-3} = 1.3 Hz, 1H), 8.44 (ddt, H(3), J_{H-P} = 7.0 Hz, J_{3-4} = 7.5 Hz, J_{3-5} = 1.3 Hz, 1H), 7.79 (dd, H(4), J_{4-5} = 10.1 Hz, J_{4-3} = 7.5 Hz, 1H), 7.45 (dd, J = 8.1, 1.2 Hz, 2H), 7.25−7.13 (m, 16H), 7.03−6.92 (m, 21H), 6.75 (t, J = 7.5 Hz, 1H). ¹³C NMR (benzene-d_6) δ 203.26 (t, C(6), J_{C-P} = 51 Hz), 187.74 (t, C(1), J_{C-P} = 6.1 Hz), 187.49 (s, C(5)), 169.46 (t, C(4), J_{C-P} = 4.0 Hz), 147.93 (t, J_{C-P} = 4.0 Hz), 142.83 (t, J_{C-P} = 6.0 Hz), 141.16 (t, C(3), J_{C-P} = 8.1 Hz), 136.86 (m, PPh₃), 134.83 (t, PPh₃, J_{C-P} = 4.5 Hz), 132.02 (s), 130.02 (s, PPh₃), 127.64 (s), 126.50 (s), 125.28 (s), 125.21 (t, J_{C-P} = 5.0 Hz), 123.49 (s) (two carbon signals are obscured by the benzene solvent). ³¹P NMR (benzene-d_6, chemical shift reported relative to external H₃PO₄) δ 17.88 (s). IR (KBr) 1989 cm⁻¹ (CO). Anal. Calcd for C₅₄H₄₃IrOP₂: C, 67.41; H, 4.50. Found: C, 66.89; H, 4.43.
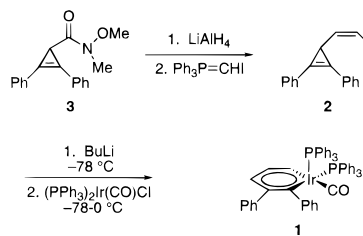
and a metal−carbon double bond. The use of a vinyl lithiate would provide the former, whereas rearrangement of a cyclopropene unit to a vinyl carbene should afford the latter. Our approach would be a one-step route to metallabenzenes since both of the essential metal−carbon bonds can be formed from separate ends of a C_5 ligand. Combining these features into a single molecule suggested the use of a functionalized 3-vinyl-1-cyclopropene, such as **2,** as the appropriate precursor. The *Z*-geometry about the vinyl group should ensure that both the nucleophilic addition and the cyclopropene rearrangement occur with the same organometallic fragment.

Synthesis of **2** was achieved as shown in Scheme 1. Reduction of Weinreb amide **3**[9] at low temperature with LiAlH₄ gave the corresponding aldehyde in 93% yield. Wittig reaction of the aldehyde with iodomethyltriphenylphosphorane[10] furnished cyclopropene **2** in 81% yield with high stereoselectivity (>95% *Z* as determined by ¹H NMR integration). Lithium−iodine exchange of **2** with 1 equiv of butyllithium at −78 °C, followed by trapping of the intermediate vinyl lithiate with (PPh₃)₂Ir(CO)Cl directly resulted in formation of iridabenzene **1**. When the initial suspension was slowly warmed to 0 °C, a color change from yellow to red was observed. Excess lithiate was quenched with ethanol, and the insoluble salts were removed by filtration through a glass frit. After removal of solvent, the crude reaction mixture was dissolved in a mixture of toluene and hexanes (1:1) at room temperature and then cooled to −35 °C, giving **1** as X-ray quality red prisms in 72% yield.

Unambiguous confirmation of the structure of **1** was provided by single-crystal X-ray diffraction (Figure 1). Selected bond lengths and bond angles are given in Table 1. The structure is similar in many respects to that reported for Bleeke's iridabenzene (**4**),[6] which has been thoroughly studied. Iridabenzene **1** has a
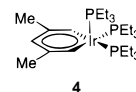
slightly distorted square pyramidal coordination geometry with P1 occupying the axial site and C1, C5, C6, and P2 filling the basal sites. The metallabenzene ring is essentially planar (mean deviation 0.024 Å) and delocalization of the π system is evident in bond lengths throughout the ring. The Ir−C1 (2.021(8) Å) and Ir−C5 (2.025(8) Å) bonds are nearly identical in length, and the carbon−carbon bonds of the metallacycle are typical of a benzene derivative. Although the structure of **1** is quite similar to **4**, iridabenzene **1** is air stable in both the solid state and in solution, whereas **4** reacts with atmospheric oxygen to produce a unique

Scheme 1

(9) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015−1019.
(10) (a) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 2173-2174. (b) Bestmann, H. J.; Rippel, H. C.; Dostalek, R. *Tetrahedron Lett.* **1989**, *30*, 5261−5262.
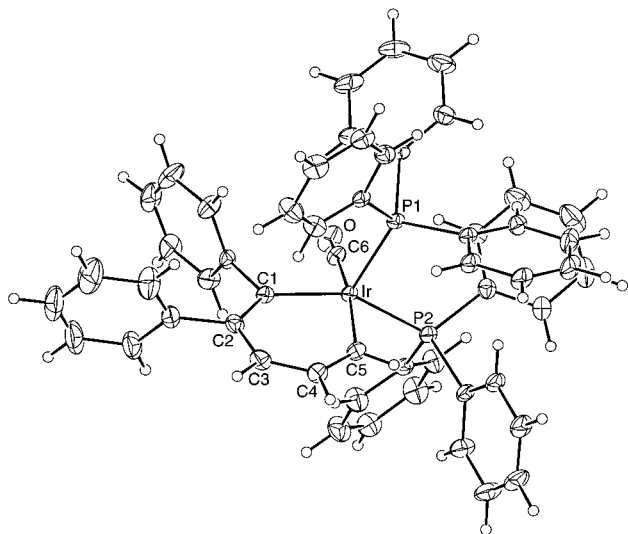
Figure 1. Molecular structure of iridabenzene **1**; ellipsoids drawn at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Iridabenzene **1**

Ir–P1	2.317(2)	P1–Ir–P2	99.2(2)
Ir–P2	2.373(2)	P1–Ir–C1	112.6(2)
Ir–C1	2.021(8)	P1–Ir–C5	95.4(3)
Ir–C5	2.025(8)	P1–Ir–C6	99.3(3)
Ir–C6	1.925(9)	P2–Ir–C1	148.2(2)
C1–C2	1.41(1)	C5–Ir–C6	165.0(4)
C2–C3	1.41(1)	C1–Ir–C5	86.9(3)
C3–C4	1.38(1)	Ir–C1–C2	128.8(6)
C4–C5	1.33(1)	C1–C2–C3	123.6(8)
C6–O	1.14(1)	C2–C3–C4	124.2(8)
		C3–C4–C5	125.5(8)
		C4–C5–Ir	130.7(7)

dioxygen-bridged species.[6] Iridabenzene **1** does, however, react with maleic anhydride in a [4 + 2] fashion to give an octahedral adduct.[11]

A likely reaction pathway is shown in Scheme 2. Initial substitution of the chloride ligand by the vinyl lithiate should give **5**.[12] Bicyclic, Dewar-type metallabenzene **6** could then be formed by direct insertion of the Ir atom of **5** into one of the cyclopropene σ-bonds. An intermediate such as **6** could rapidly valence isomerize to **1**.[13] Alternatively, the free cyclopropene in complex **5** could coordinate to the iridium through the cyclopropene π electrons to give an intermediate similar to **7**. Rearrange-

(11) Cycloaddition reactions involving iridabenzene **4** are described in ref 6.

(12) Schwartz, J.; Hart, D. W.; McGiffert, B. *J. Am. Chem. Soc.* **1974**, *96*, 5613–5614.

(13) For a discussion concerning the interconversion of metallacyclobutenes and vinylcarbene complexes see: Doxsee, K. M.; Juliette, J. J. J.; Mouser, J. K. M.; Zientara, K. *Organometallics* **1993**, *12*, 4742–4744.

Scheme 2
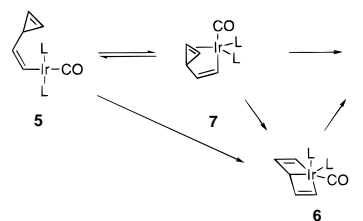
ment of the η^2-cyclopropene in **7** could give **1** directly,[14] or indirectly by first rearranging to **6**.[15] However, the equilibrium between **5** and **7** likely favors uncoordinated cyclopropene **5** to a large degree because of the steric interaction that would result between the PPh$_3$ ligands and the cyclopropene phenyl groups when forming **7**.[16] Direct formation of **6** by insertion of Ir into a cyclopropene σ-bond would conceivably be a sterically less demanding process and, therefore, appears more likely than formation and rearrangement of **7** in our view. Cyclopropenes frequently undergo rearrangement to vinyl carbenes,[2] a reaction that would allow formation of **1** without involving either **6** or **7**. However, this process typically occurs only at elevated temperatures or photochemically and is, therefore, an unlikely event in the transformation of **5** to **1**. Coordination of the cyclopropene to Ir prior to nucleophilic attack of the vinyl lithiate on the Ir atom is also unlikely in the present case due to the large cone angle of the triphenylphosphine ligands.[16]

In summary, we have prepared iridabenzene **1** by a novel, direct method. The reaction involves an intramolecular Ir-mediated rearrangement of a cyclopropene. The individual reactions involved in our preparation of iridabenzene **1** (i.e., addition of carbon nucleophiles to low-valent metals and metal–cyclopropene rearrangements) are commonly used in conjunction with numerous transition metals.[1,3–5,9,12] For this reason, we are currently attempting to extend the methodology described to prepare metallabenzenes incorporating different transition metals.

Supporting Information Available: General experimental procedures and spectral data for **1** and **2**, X-ray crystal structure of **1**, tables of atomic coordinates, thermal parameters, bond lengths and bond angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Direct conversion of transition metal η^2-cyclopropenes to metal carbenes has been observed. See ref 3d and: Fischer, H.; Hofmann, J.; Mauz, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 998–999.

(15) Direct rearrangement of η^2-cyclopropene complexes to metallacyclobutenes has been observed. See ref 4c.

(16) Coordination complexes of 3,3-diphenylcyclopropene to Vaska-type complexes are in equilibrium with the uncoordinated starting materials. With small cone angle phosphines the equilibrium lies far to the side of the metal η^2-cyclopropene complex. However, with larger cone angle phosphines, such as PPh$_3$, the equilibrium lies exclusively to the side of the free cyclopropene.[3f] Additionally, NMR experiments in our lab have shown that (PPh$_3$)$_2$Ir(CO)Cl does not coordinate with **2** in benzene at ambient temperature.