

The First Transition Metal Complex of Tetrafluorobenzynes: $\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\eta^2\text{-C}_6\text{F}_4)$

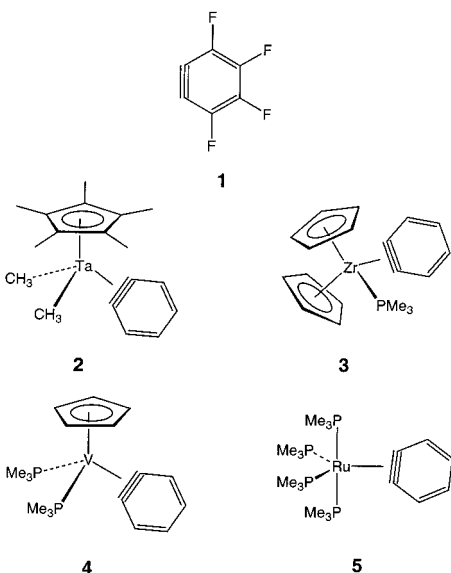
Russell P. Hughes,^{*,§} Alex Williamson,[§]
Roger D. Sommer,^{||} and Arnold L. Rheingold^{||}

Departments of Chemistry, 6128 Burke Laboratory
Dartmouth College, Hanover, New Hampshire 03755
University of Delaware, Newark, Delaware 19716

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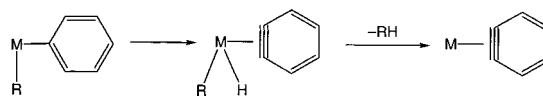
While tetrafluorobenzynes **1** has been proposed as an intermediate in many organometallic transformations, no stable metal complex of this ligand has been prepared, either by in situ generation of the tetrafluorobenzynes ligand^{1–4} or by reaction of exogenous tetrafluorobenzynes with a metal complex.^{5,6} Attempts to prepare transition metal complexes of the hydrocarbon parent, benzyne, have been more successful, and η^2 complexes of both early and late transition metals have been isolated and crystallographically characterized. These compounds (inter alia) have been the subjects of recent reviews.^{7,8} Here we report the synthesis, and the complete structural characterization of, a mononuclear iridium complex of tetrafluorobenzynes that shows a significantly different distribution of intraring bond lengths than do its hydrocarbon analogues.

The principal method for synthesis of metal complexes of benzyne involves an ortho carbon–hydrogen bond activation of a phenyl ligand and elimination of RH (R = CH₃, C₆H₅) as shown in Scheme 1. Representative examples of compounds prepared by this approach include **2**,⁹ **3**,¹⁰ **4**,¹¹ and **5**.¹² An alternative route

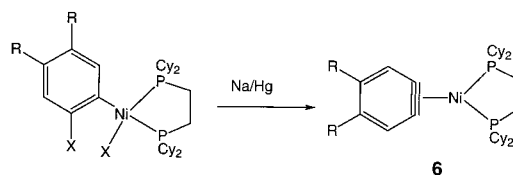


to group 10 complexes of benzyne has been by reduction of ortho-halogenated aryl derivatives, as shown in Scheme 2 for nickel complexes **6**.¹³ Neither route has afforded tetrafluorobenzynes complexes, although the latter has been used to prepare some

Scheme 1

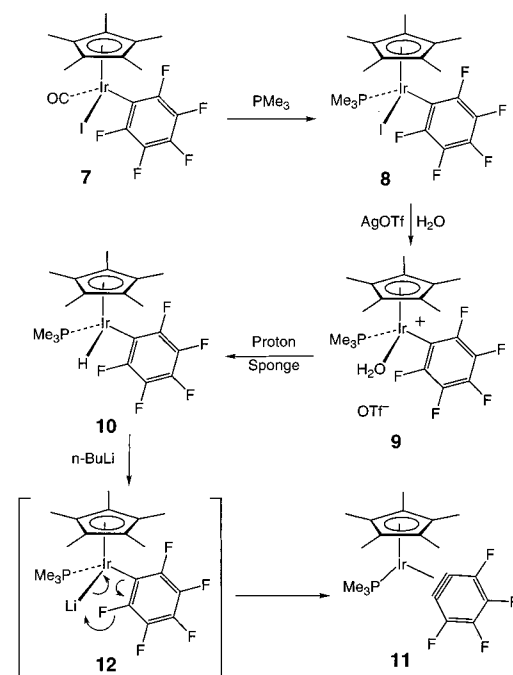


Scheme 2^a



^a R = H, F; X = Cl, Br.

Scheme 3



4,5-difluorobenzynes complexes of nickel, characterized only by their solution spectra and their reactivity patterns.^{7,14}

Our successful approach is shown in Scheme 3. Pentafluorophenyl complex **7** is prepared by oxidative addition of iodo-pentafluorobenzene to $\text{Ir}(\text{C}_5\text{Me}_5)(\text{CO})_2$ in the manner used to prepare perfluoroalkyl-iridium analogues.¹⁵ This reaction requires prolonged refluxing in benzene, while the corresponding perfluoroalkyl iodides react at room temperature.¹⁵ Choice of solvent

[§] Dartmouth College.

^{||} University of Delaware.

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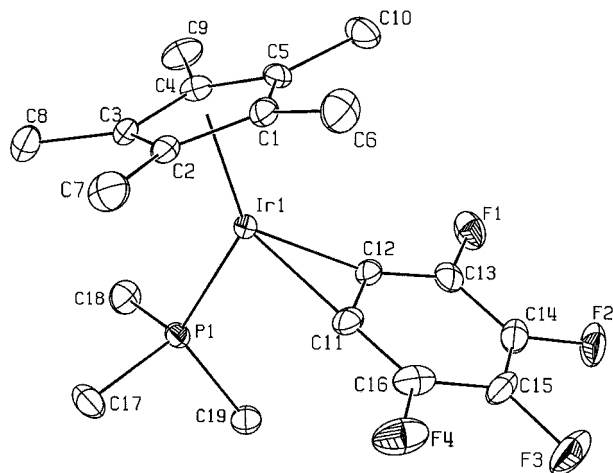
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Table 1. Bond Lengths (Å) for the Benzyne Ligands in Complexes **2–5** and the Tetrafluorobenzyne Ligand in **11**

	C(11)–C(12)	C(12)–C(13)	C(13)–C(14)	C(14)–C(15)	C(15)–C(16)	C(16)–C(11)
2 ⁹	1.346(5)	1.410(5)	1.362(2)	1.403(2)	1.375(6)	1.408(6)
3 ¹⁰	1.364(8)	1.389(8)	1.383(9)	1.380(9)	1.377(9)	1.406(8)
4 ¹¹	1.368(5)	1.384(5)	1.385(5)	1.404(5)	1.382(5)	1.398(5)
5 ¹²	1.355(3)	1.382(3)	1.372(3)	1.411(4)	1.363(4)	1.398(4)
6 ^{a,13}	1.332(6)	1.386(6)	1.383(7)	1.390(8)	1.383(7)	1.389(6)
11	1.374(7)	1.357(7)	1.393(8)	1.355(9)	1.418(9)	1.360(7)

^a R = H.**Figure 1.** ORTEP plot for **11** with ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ir(1)–C(12), 2.046(5); Ir(1)–C(11), 2.058(5); Ir(1)–P(1), 2.2573(13); C(13)–F(1), 1.358(6); C(14)–F(2), 1.355(6); C(15)–F(3), 1.351(6); C(16)–F(4), 1.361(6); C(12)–Ir(1)–C(11), 39.1(2); C(16)–C(11)–C(12), 120.6(5); C(13)–C(12)–C(11), 122.4(5); C(12)–C(13)–C(14), 117.5(5); C(15)–C(14)–C(13), 121.2(5); C(14)–C(15)–C(16), 120.3(5); C(11)–C(16)–C(15), 117.8(5). C–C distances in the benzyne ring are given in Table 1.

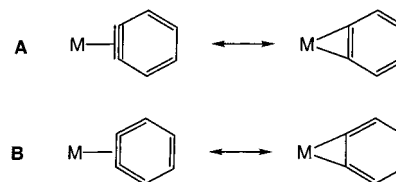
is also important; no reaction is observed in refluxing hexane, and refluxing toluene affords products that do not contain C₆F₅ ligands. Carbonyl displacement with PMe₃ affords **8**, which can be converted to the corresponding aqua cation **9** using AgOTf in moist toluene.^{16,17} As observed with analogous perfluoroalkyl(aqua) complexes, treatment of **9** with 1,8-bis(dimethylamino)naphthalene (Proton Sponge) cleanly affords the hydride **10**.^{16,18} This hydride is obtained less cleanly by direct reaction of **8** with NaBH₄, and has also been prepared recently by Bergman by reaction of the nucleophilic anion [Ir(C₅Me₅)(PMe₃)H][–]Li⁺ with hexafluorobenzene.¹⁹ Finally, treatment of the hydride **10** with an excess of *n*-BuLi affords the benzyne complex **11**, presumably via deprotonation to give **12**, followed by elimination of LiF, as

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**Figure 2.** Resonance structures for an η^2 -benzyne complex.

shown. The ¹⁹F NMR of **11** exhibits a classic AA'XX' pattern for the four fluorines, with an additional ³¹P coupling to the “ortho” set.

An ORTEP diagram of the molecular structure of **11** is shown in Figure 1, along with some representative bond lengths and angles. The fluorinated ligand adopts the expected conformation, with the Ir–P bond bisecting the axis of the coordinated carbon atoms. A comparison of the intraring bond distances of this complex with those in previously characterized benzyne complexes is provided in Table 1. The coordinated C–C bond distance of 1.374(7) Å is significantly longer than the corresponding distances in either the d⁸ analogue **5** or the d¹⁰ analogue **6** (R = H). In addition, the distribution of bond lengths around the tetrafluorobenzyne ring in **11** is significantly different from those of its benzyne relatives. Figure 2 illustrates the resonance structures for an (η^2 -benzyne)metal complex; the pattern of bond distances in **11** appears to be more consistent with the pair of resonance structures shown in Figure 2B, while those in other benzyne complexes either favor those in Figure 2A or a delocalized structure or are not significantly different enough to allow a distinction.^{7,8}

Finally, while compound **11** is air-sensitive, it shows no reactivity toward H₂, CO, C₂H₄, or CH₂=CHCO₂Me after several hours at 70 °C, making it significantly less reactive than many other reported compounds of its hydrocarbon relatives.^{7,8} Further reactivity studies of this compound and its relatives will be reported in due course.

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Supporting Information Available: Synthetic and spectroscopic data for compounds **7–11**; tables of crystal data, atomic coordinates, structure solution and refinement, bond lengths and angles, and anisotropic thermal parameters for **11** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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