Iridium and Rhodium Complexes Containing Fluorinated Phenyl Ligands and Their Transformation to η^2-Benzyne Complexes, Including the Parent Benzyne Complex IrCp*(PMe$_3$)(C$_6$H$_4$)

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Treatment of IrCp*(CO)$_2$ (**1**) with C$_6$F$_5$I in benzene under reflux gives the oxidative addition product IrCp*(C$_6$F$_5$)(CO)I (**2**). Treatment of **2** with PMe$_3$ gives IrCp*(C$_6$F$_5$)(PMe$_3$)I (**3**), which, on treatment with AgO$_3$SCF$_3$ in the presence of traces of water, affords the cationic complex [IrCp*(C$_6$F$_5$)(PMe$_3$)(OH$_2$)]O$_3$SCF$_3$ (**4**). Treatment of **4** with 1,8-bis(dimethylamino)naphthalene (Proton Sponge) affords the hydride complex IrCp*(C$_6$F$_5$)(PMe$_3$)H (**5**), which reacts with *n*-BuLi to give the tetrafluorobenzyne complex IrCp*(η^2-C$_6$F$_4$)(PMe$_3$) (**6**) in high yield. Similarly, treatment of RhCp*(CO)$_2$ (**7**) with C$_6$F$_5$I in toluene at 80 °C affords a pentafluorophenyl complex of rhodium, RhCp*(C$_6$F$_5$)(CO)I (**8**). Treatment of **8** with PMe$_3$ at room temperature affords RhCp*(C$_6$F$_5$)(PMe$_3$)I (**9**), which reacts with NaBH$_4$ to give RhCp*(C$_6$F$_5$)(PMe$_3$)H (**10**). Treatment of **10** with *n*-BuLi gives the rhodium tetrafluorobenzyne complex RhCp*(η^2-C$_6$F$_4$)(PMe$_3$) (**11**) in high yield. Treatment of IrCp*(CO)$_2$ with 1-fluoro-2-iodobenzene in toluene under reflux gives the oxidative addition product IrCp*(2-C$_6$FH$_4$)(CO)I (**12**), which is converted to IrCp*(2-C$_6$FH$_4$)(PMe$_3$)I (**13**) by treatment with PMe$_3$. Treatment of **13** with NaBH$_4$ gives IrCp*(2-C$_6$FH$_4$)(PMe$_3$)H (**14**), which, on treatment with *n*-BuLi, is converted to a mixture of the nonfluorinated benzyne complex IrCp*(η^2-C$_6$H$_4$)(PMe$_3$) (**15**) and the phenyl butyl complex IrCp*(C$_6$H$_5$)(*n*-Bu)(PMe$_3$) (**16**). Treatment of Ir(C$_5$Me$_4$Et)(CO)$_2$ with 2,3,4,5-tetrafluorobenzoyl chloride at 110 °C under reflux gives the oxidative addition product Ir(C$_5$Me$_4$Et)(2,3,4,5-C$_6$F$_4$H)(CO)Cl (**17**), which on treatment with PMe$_3$ gives Ir(C$_5$Me$_4$Et)(C$_6$F$_4$H)(PMe$_3$)Cl (**18**). Using analogous methodology this was converted to the unsymmetrical trifluorobenzyne complex Ir(C$_5$Me$_4$Et)(η^2-3,4,5-C$_6$F$_3$H)(PMe$_3$) (**21**), in which the benzyne ligand is shown to be stereochemically rigid on the NMR time scale, allowing a minimum value for the rotational barrier about the iridium−benzyne bond to be estimated at 20.3 kcal mol^{-1}. The crystal structures of complexes **2**, **3**, **9**, **11**−**15**, **17**, and **18** are reported and discussed, and the "through-space" nature of some coupling constants between ^{31}P, ^{1}H, and ^{19}F is confirmed using heteronuclear Overhauser enhancement (HOESY) NMR spectroscopy.

Introduction

There are many examples of oxidative addition reactions involving aryl halides and low-valent metal complexes.[1−7] However, to the best of our knowledge, there is only one example involving oxidative addition of an aryl halide to a metal complex with a cyclopentadienyl ligand.[8] Examples of oxidative addition reactions of perfluorinated aryl halides to transition metals seem to be restricted to reactions with transition-metal powders or atoms[9−11] and to examples of oxidative addition of hexafluorobenzene to metal complexes, in which C$_6$F$_6$ undergoes cleavage of a C−F bond to produce pentafluorophenyl fluoride complexes.[8,12,13]

Many examples of η^2-benzyne complexes have been reported in the literature[14−16] and include examples

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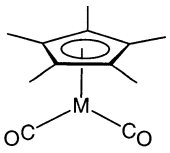
from early[17−20] and late[15,21−23] transition metals. While benzyne complexes of early transition metals,[17,18,20] and of ruthenium,[23] can be synthesized using thermally induced β-elimination of methane or benzene from aryl methyl and diaryl complexes, respectively, this method is not useful for group 10 complexes, due to competing reductive elimination of the σ-bound carbon ligands. Instead, benzyne complexes of nickel and platinum have been synthesized by reduction of preformed (2-haloaryl)-metal(II) halide complexes.[15,21,22] Benzyne complexes of both ruthenium and nickel have been shown to undergo a variety of insertion reactions with unsaturated molecules and addition reactions with electrophiles.[15,21−23]

In a preliminary communication, we described the synthesis of the first example of an η^2-tetrafluorobenzyne transition metal complex using a route different from those previously described.[24] Here we provide a detailed account of this work, with a full examination of the preparations and properties of the precursor compounds and the fluorinated benzyne product. Extensions to the syntheses and properties of an analogous rhodium tetrafluorobenzyne complex and to an iridium complex of the parent hydrocarbon benzyne ligand are also presented.

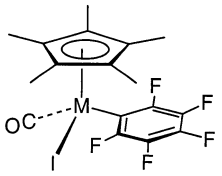
Results and Discussion

The iridium(I) complex $IrCp^*(CO)_2$ (**1**) readily undergoes oxidative addition reactions with a variety of fluorinated alkyl iodides at room temperature.[25−27] In



1 M = Ir
7 M = Rh

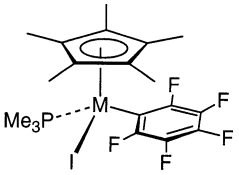
contrast, more vigorous conditions are required for the analogous oxidative addition reaction with C_6F_5I to form $IrCp^*(C_6F_5)(CO)I$ (**2**). Careful attention must be paid to the reaction conditions to ensure good yields of **2**. When hexane is used as the reaction solvent, reflux conditions



2 M = Ir
8 M = Rh

provide negligible conversion to the desired product. Refluxing toluene leads to formation of a large amount of $IrCp^*I_2(CO)$, together with other unidentified decomposition products. Best results are achieved when a benzene solution is heated under gentle reflux for 40 h. The product, after recrystallization, contains about 10% $IrCp^*I_2(CO)$ together with a small amount of unidentified decomposition product, but complex **2** is easily purified by column chromatography. The ^{19}F NMR spectrum of this compound shows broad signals for the ortho and meta fluorine atoms on the pentafluorophenyl ring. We attribute this to restricted rotation about the Ir−C bond on the NMR time scale, a phenomenon that has been observed previously in transition metal pentafluorophenyl complexes[8,13,28−34] and has been attributed to combinations of steric hindrance from other ligands and high electron density on the metal, resulting in stronger dπ−pπ interactions.

Treatment of complex **2** with PMe_3 in refluxing toluene gives the trimethylphosphine complex $IrCp^*(C_6F_5)(PMe_3)I$ (**3**). The ^{19}F NMR spectrum of **3** comprises



3 M = Ir
9 M = Rh

five distinct resonances, indicating that rotation about the Ir−C_6F_5 bond is slow on the NMR time scale. It is interesting to note that, in this complex, the protons of the PMe_3 ligand couple with only one of the ortho fluorine atoms of the pentafluorophenyl ligand ($^6J_{HF}$ = 1.5 Hz). This is a "six-bond" coupling constant and is likely to contain a strong component of through-space, as opposed to through-bond, coupling. Remote H−F coupling of ortho fluorines with protons has been seen in other C_6F_5 complexes and has also been attributed

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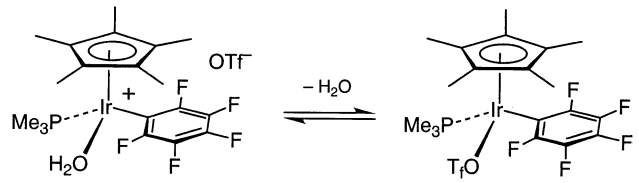
to through-space coupling.[28,33] Clearly, the favored conformation for the C_6F_5 ligand orients one of the ortho fluorine atoms closer to the PMe_3 ligand than the other ortho fluorine atom, as borne out by the solid-state structure (see below). The $^{31}P\{^1H\}$ NMR spectrum of **3** appears as a doublet ($^4J_{PF}$ = 19 Hz) arising from coupling of the phosphorus atom with the same ortho fluorine atom. But which fluorine atom is responsible for this coupling: the proximal ortho fluorine, or its distal analogue? Each is a candidate for six-bond coupling. $^1H/^{19}F$ HOESY experiments have been shown to be very useful indicators of ion-pair proximity between protons and fluorine atoms in organometallic salts.[35] An analogous experiment for **3** shows a significant cross-peak between the hydrogen atoms of the PMe_3 ligand and the same ortho fluorine atom that exhibits the F−P coupling, but no cross-peak to the other ortho fluorine atom. The HOESY experiment also shows significant cross-peaks between both ortho fluorine atoms and the Cp* ligand protons. These data are consistent with a pentafluorophenyl ring conformation similar to that observed in the solid state (see below), and as shown in the drawing. Since the HOESY cross-peaks are dependent only on distance, this provides confirmation that the *J* coupling between ^{31}P and ^{19}F in this compound, and presumably in other analogues, occurs selectively to the proximal ortho fluorine.

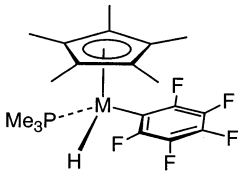
Treatment of complex **3** with AgO_3SCF_3 in toluene and subsequent exposure to moist air affords [IrCp*-(C_6F_5)(PMe_3)(OH_2)]O_3SCF_3 (**4a**). The ^{19}F, ^1H, and ^{31}P



4a **4b**

NMR spectra of **4a** in CD_2Cl_2 are broad at room temperature. When the temperature is lowered to −40 °C, the ^{19}F NMR spectrum decoalesces into two sets of resonances, which we attribute to [IrCp*(C_6F_5)(PMe_3)-(OH_2)]O_3SCF_3 (**4a**) and IrCp*(C_6F_5)(PMe_3)O_3SCF_3 (**4b**). The ratio of **4a** and **4b** is variable and depends on the moisture content of the CD_2Cl_2 (the relative concentration of **4b** being higher when air is excluded from the NMR tube). At −40 °C, the ^{19}F resonances of **4a** are sharp and exist as five individual resonances, showing that the Ir−C_6F_5 rotation is slow at this temperature. However, the resonances due to the ortho and meta fluorines of **4b** are broad at this temperature, but on further cooling to −75 °C, the spectrum sharpens into five individual resonances. These observations can be explained either by slowing of Ir−C_6F_5 rotation as the temperature is lowered, as observed in other C_6F_5 complexes,[8,13,29] or to a situation in which the C_6F_5 ring is conformationally rigid, with rapid dissociation of water, inversion at the metal, and reassociation of water being the process resulting in exchange of fluorine resonances. A similar phenomenon has already been described for analogous fluoroalkyl complexes containing water ligands.[27,36] A combination of both pathways may be more likely, given the precedent for each, and we have not attempted to distinguish between them.

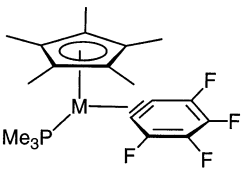
We have shown previously that 1,8-bis(dimethylamino)naphthalene (Proton Sponge) can behave as a hydride donor, and we have used this extensively in the preparation of Group 9 metal (fluoroalkyl)hydride complexes from cationic precursors.[37] In the same way, complex **4a** reacts with proton sponge in toluene at room temperature to give the hydride complex IrCp*(C_6F_5)-(PMe_3)H (**5**). A slightly less pure sample of **5** can be



5 M = Ir
10 M = Rh

obtained by direct reaction of **3** and $NaBH_4$ in refluxing 2-propanol, but in this case it is difficult to remove the last traces of solvent from the product, and the alcohol interferes with subsequent chemistry. This complex has been reported previously by Bergman[38] from the reaction of [IrCp*(PMe_3)H]$^-Li^+$ with C_6F_6. The ^{19}F NMR spectrum of **5** also contains five separate fluorine resonances, indicating slow rotation about the Ir−C_6F_5 bond. While the $^{31}P\{^1H\}$ NMR spectrum of this compound was initially reported as a singlet,[38] we observe it as a doublet of doublets ($^4J_{PF}$ = 6.8 Hz, $^4J_{PF}$ = 2.9 Hz), due to inequivalent coupling to each ortho fluorine atom of the pentafluorophenyl ligand. It is interesting that the molecular structure of a related aryl hydrido complex (see below) shows a conformation of the aryl ligand different from that observed when the adjacent ligand is more bulky than H, in which the two ortho positions are closer to phosphorus, perhaps explaining the less selective *J* values compared to those of other complexes.

Treatment of complex **5** with 10 equiv of a solution of *n*-BuLi in hexanes effects slow conversion to the tetrafluorobenzyne complex IrCp*(η^2-C_6F_4)(PMe_3) (**6**). The



6 M = Ir
11 M = Rh

excess of lithiation reagent is used to give a convenient reaction time. We have proposed[24] that the mechanism of the reaction involves deprotonation of the Ir−H

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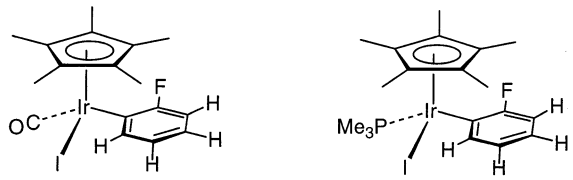
bond,[38,39] followed by elimination of an ortho fluorine atom and formation of LiF. The $^{13}C\{^1H\}$ NMR spectrum of **6** shows a multiplet at δ 84.2 ppm corresponding to the coordinated carbon atoms of the benzyne ligand. This is a very high field chemical shift relative to those of previously reported benzyne complexes, which fall in the range 141.8−230.5 ppm.[16] The ortho and meta carbon atoms on the benzyne ligand resonate as doublets at δ 135.3 and 142.8 ppm ($^1J_{CF}$ = 253 Hz).

To confirm the generality of this synthetic approach to tetrafluorobenzyne complexes, we explored the chemistry of analogous pentafluorophenyl complexes of rhodium. Treatment of $RhCp^*(CO)_2$ (**7**) with C_6F_5I in toluene in an oil bath at 80 °C affords the oxidative addition product $RhCp^*(C_6F_5)(CO)I$ (**8**), which is generally contaminated with a small amount of $RhCp^*I_2(CO)$. Purification is easily achieved by column chromatography. Like the iridium analogue, the ^{19}F NMR spectrum exhibits broad peaks corresponding to the ortho and meta fluorines of the pentafluorophenyl ring. Treatment of **7** with PMe_3 in toluene at room temperature cleanly produces the trimethylphosphine complex $RhCp^*(C_6F_5)(PMe_3)I$ (**9**). The ^{19}F NMR spectrum of this complex, like its iridium analogue, shows five individual resonances corresponding to each of the fluorine atoms of the pentafluorophenyl ring. The $^{31}P\{^1H\}$ NMR spectrum exists as a doublet of doublets with a phosphorus−rhodium coupling constant of 144.3 Hz and a single phosphorus−fluorine coupling constant of 25.3 Hz, due to coupling with the proximal ortho fluorine.

Treatment of **9** with $NaBH_4$ in THF at 50 °C for 16 h affords the highly air-sensitive compound $RhCp^*(C_6F_5)(PMe_3)H$ (**10**). This compound was previously reported by Jones,[40] who obtained it by heating a mixture of $RhCp^*(PMe_3)H_2$ and C_6F_6 at 85 °C in d_5-pyridine. As observed in the ^1H NMR spectrum of the iridium analogue, the hydride ligand of **10** couples with both of the inequivalent ortho fluorine atoms. However, in this case the coupling constants are equivalent, forming a triplet pattern ($^4J_{PF}$ = 9.3 Hz), so it not possible to distinguish between a static structure, in which both coupling constants are fortuitously equal, and a structure containing a rapidly rotating aryl ring, in which they are averaged. To obtain a pure sample of the required rhodium−benzyne complex, it is necessary to treat a freshly synthesized sample of **10** with 1.3 equiv of *n*-BuLi at −78 °C. After this mixture is stirred for 1 h at room temperature, conversion to $RhCp^*(\eta^2\text{-}C_6F_4)(PMe_3)$ (**11**) is complete and clean. This reaction rate is in contrast to the much slower reaction of the Ir analogue (vide supra), which requires a large excess of BuLi to proceed at a convenient rate. Complex **11** is air-sensitive in solution and decomposes in air in the solid state over a few days. The ^{19}F NMR spectrum shows the expected AA′XX′ coupling pattern with extra rhodium coupling observed for the two ortho fluorines ($^4J_{FRh}$ = 4.5 Hz). The structure was confirmed by X-ray diffraction (see below).

To explore the generality of the synthetic method for formation of nonfluorinated η^2-benzyne complexes, we approached the synthesis of a nonfluorinated benzyne complex of iridium using the same method. Treatment of **1** with 1-fluoro-2-iodobenzene in toluene under reflux affords the monofluorophenyl complex $IrCp^*(2\text{-}C_6FH_4)(CO)I$ (**12**). Treatment of this complex with PMe_3 leads to formation of $IrCp^*(2\text{-}C_6FH_4)(PMe_3)I$ (**13**). Complex **13**



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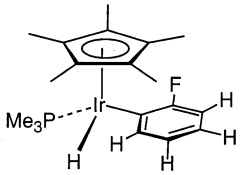

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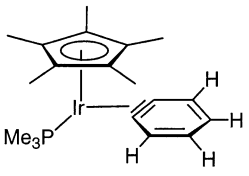
is converted to $IrCp^*(2\text{-}C_6FH_4)(PMe_3)H$ (**14**) by reaction with $NaBH_4$ in EtOH at 70 °C. It is not possible to deduce from the room-temperature NMR spectra of **13** whether there is facile or restricted rotation about the Ir−C_6FH_4 bond on the NMR time scale, as only a single fluorine resonance is observed, showing a coupling ($^4J_{FP}$ = 10.5 Hz) to phosphorus. However, in complex **14** at room temperature, the ^1H, ^{19}F, and ^{31}P NMR spectra are broad and decoalesce at −60 °C into two sets of resonances in a ratio of 2.8:1, which leads us to deduce that the Ir−C_6FH_4 rotation is relatively fast on the NMR time scale at room temperature. The major rotamer shows a coupling ($^4J_{FP}$ = 4.4 Hz) between the single F and P, indicating it to be the proximal isomer; the minor (distal) rotamer shows no such coupling. Therefore, in a sterically more hindered complex such as **13**, we conclude that rotation about the Ir−C_6FH_4 bond is slow on the NMR time scale at room temperature. Treatment of **14** with 10 equiv of *n*-BuLi and stirring for 4 h at room temperature leads, after workup, to formation of the benzyne complex $IrCp^*(\eta^2\text{-}C_6H_4)(PMe_3)$ (**15**) together with small amounts of starting material and the phenyl *n*-butyl complex $IrCp^*(C_6H_5)(n\text{-}Bu)(PMe_3)$ (**16**). The



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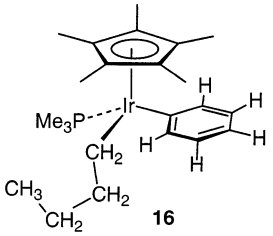

16

relative amount of **16** increases if the reaction is allowed to proceed for longer periods or is conducted at a higher temperature. The benzyne complex **15** is separated by slow evaporation of a hexane solution to produce large transparent crystals. The butyl complex **16** can be separated by column chromatography (silica, hexanes) and exists as a transparent oil. For complex **15**, the aromatic region of the phosphorus-decoupled proton NMR spectrum shows the expected AA′XX′ coupling pattern. The ^{13}C NMR spectrum shows a doublet at

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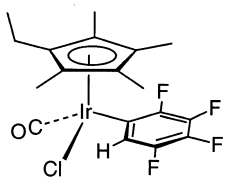
107.9 ppm ($^2J_{CP}$ = 9.2 Hz) which corresponds to the ipso carbon atoms of the benzyne ligand. This is downfield from the corresponding value for the tetrafluorobenzyne analogue (**6**) by 23.7 ppm but still significantly upfield from those of other reported benzyne complexes. The ortho and meta carbon atoms of the benzyne ligand resonate as singlets at 116.3 and 126.9 ppm, both significantly upfield from those in the tetrafluorobenzyne analogue (**6**).

The rotational barrier about a metal−benzyne bond in mononuclear η^2-benzyne complexes has previously been addressed. The first report, by Schrock, of a structurally characterized mononuclear benzyne complex, Cp*Ta(Me)$_2$(C_6H_4),[17] states that the benzyne ligand is rapidly rotating in solution. A later report by Wilkinson[41] indicates that, for the complex [Re(η^2-C_6H_3Me)(C_6H_4Me)$_2$(PMe_3)$_2$]O_3SCF_3, rotation about the Re−benzyne bond is slow on the NMR time scale up to 100 °C. Also, Bennett[21] has shown that, for the complex Ni(η^2-C_6H_4)($Cy_2PCH_2CH_2PCy_2$), rotation about the Ni−benzyne bond is slow on the NMR time scale at room temperature.

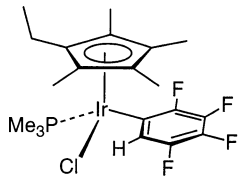
The IrCp*(PMe_3) fragment is isolobal with CH_2,[42] and a relatively high barrier to rotation of the coordinated alkene or alkyne is expected.[43] However, to examine the rotational barrier about the Ir−benzyne bond in an iridium benzyne complex of the type IrCp*(PMe_3)(η^2-benzyne) in which each side of the benzyne ligand is related by a symmetry plane, it is necessary to introduce some asymmetry into the molecule to provide inequivalent sites that are exchanged by benzyne ligand rotation. Replacing one of the fluorine substituents on the benzyne ligand by a different atom breaks the symmetry, and restricted rotation about the Ir−benzyne bond makes the metal a stereocenter whose configuration is inverted by benzyne rotation. An indirect reporter group is incorporated using an ethyltetramethylcyclopentadienyl ligand; the stereocenter at Ir generates four C−Me environments and diastereotopic protons of the CH_2 group, and rapid inversion by virtue of benzyne rotation would cause pairwise exchange of C−Me groups and remove the diastereotopic inequivalence of the CH_2 protons. We chose as our target molecule Ir(C_5Me_4Et)(η^2-3,4,5-C_6F_3H)(PMe_3).

Synthesis of Ir(C_5Me_4Et)(CO)$_2$ was achieved from [Ir(C_5Me_4Et)Cl$_2$]$_2$ and $Fe_3(CO)_{12}$, using the method developed by Maitlis for the Cp* analogue.[44] Due to the commercial unavailability of any isomers of iodotetrafluorobenzene, we opted to attempt oxidative addition of 2,3,4,5-tetrafluorobenzoyl chloride to this dicarbonyl precursor to give a benzoyl complex that could be decarbonylated to give the required aryl group. To our delight, heating a mixture of 2,3,4,5-tetrafluorobenzoyl chloride and Ir(C_5Me_4Et)(CO)$_2$ at 110 °C for 48 h produces Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(CO)Cl (**17**), which was purified by column chromatography and characterized crystallographically (see below). Formation of **17** presumably proceeds via the benzoyl complex Ir(C_5Me_4Et)(CO-2,3,4,5-C_6F_4H)(CO)Cl, which slowly decarbonylates on heating. Indeed, NMR examinations of aliquots



17

during the reaction show initial formation of a transient C_6F_4H-containing complex, which slowly converts to the desired compound **17**, but no attempts were made to isolate this intermediate. Treatment of **17** with PMe_3 produces Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(PMe_3)Cl (**18**), also



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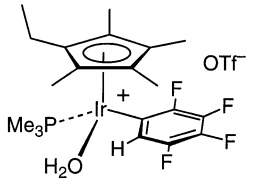

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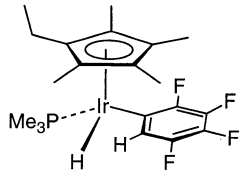

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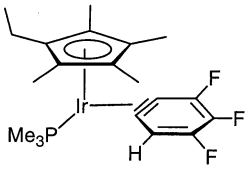

21

crystallographically characterized, which was then converted to [Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(PMe_3)(OH_2)]O_3SCF_3 (**19**) by treatment with AgO_3SCF_3. Treatment of **19** with Proton Sponge affords Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(PMe_3)H (**20**), which was converted to the desired benzyne complex Ir(C_5Me_4Et)(η^2-3,4,5-C_6F_3H)(PMe_3) (**21**) by treatment with 10 equiv of *n*-BuLi. At room temperature, the ^{1}H NMR spectrum of **21** shows that one of the sets of ring-bound methyl substituents on the C_5Me_4Et ligand is split into two signals, indicating the presence of a stereocenter at the metal. Consequently, at room temperature the rotation about the Ir−benzyne bond is slow on the NMR time scale. Heating to 100 °C in d_{10}-xylene does not produce any sign of coalescence, and therefore, a minimum barrier to rotation of 20.3 kcal mol^{-1} can be calculated.

Crystal Structures. (a) Fluorinated Phenyl Complexes. ORTEP diagrams of the molecular structures of the fluorinated phenyl complexes **2**, **3**, **9**, **12**−**14**, **17**, and **18** are presented in Figures 1−8, respectively, and details of the crystallographic determinations are compiled in Table 1. The atom-numbering scheme for each complex is self-consistent, and selected bond distances and angles are assembled in Table 2. The hydride complex **14** contains two molecules in the asymmetric unit, but the hydride ligand was not found. In addition, the fluorine atom in **14** is disordered between C(2) and C(6), with the major occupancy site (F(21)) at C(2); this is the structure illustrated for each molecule. Each of the eight structures shows the expected three-legged

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(42) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *10*, 711−724.
(43) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801−3812.
(44) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970−5977.

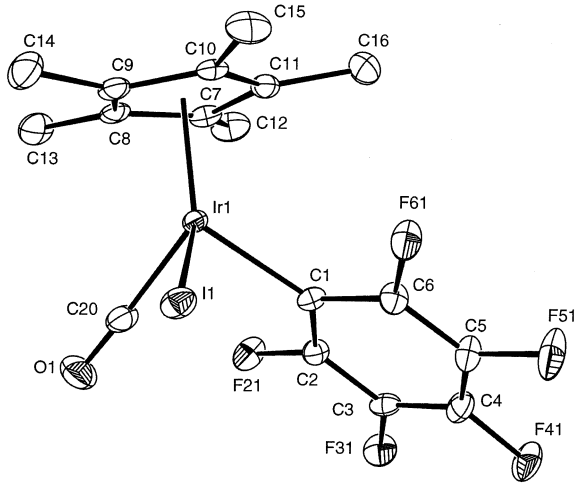

Figure 1. ORTEP diagram of the non-hydrogen atoms of compound **2**, with thermal ellipsoids shown at the 30% level.

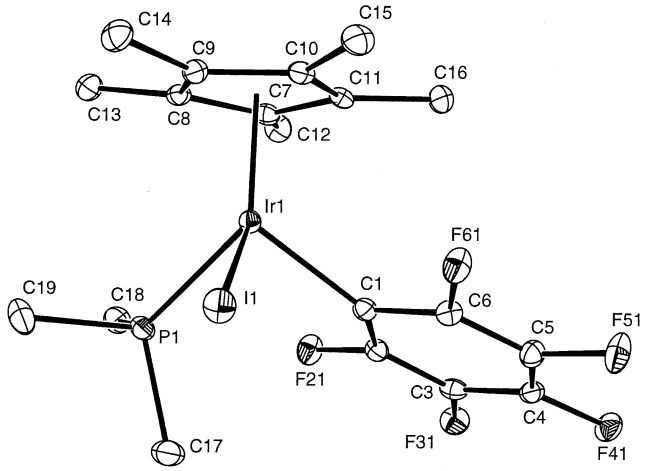

Figure 2. ORTEP diagram of the non-hydrogen atoms of compound **3**, with thermal ellipsoids shown at the 30% level.

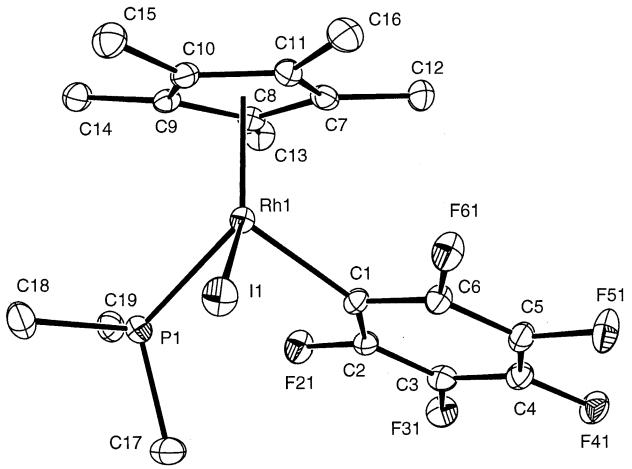

Figure 3. ORTEP diagram of the non-hydrogen atoms of compound **9**, with thermal ellipsoids shown at the 30% level.

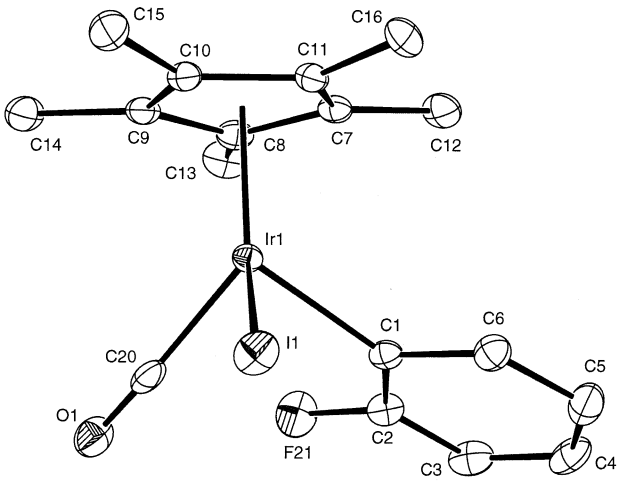

Figure 4. ORTEP diagram of the non-hydrogen atoms of compound **12**, with thermal ellipsoids shown at the 30% level.

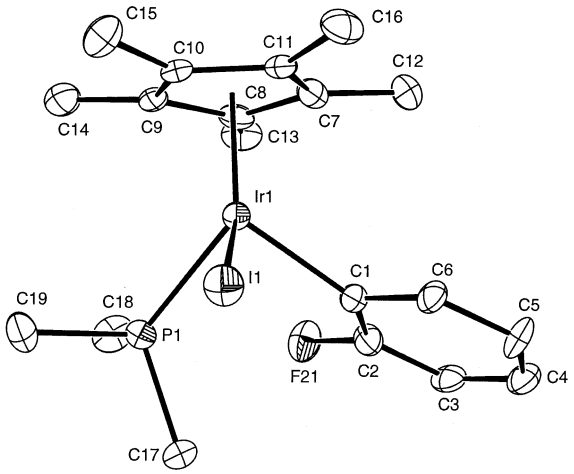

Figure 5. ORTEP diagram of the non-hydrogen atoms of compound **13**, with thermal ellipsoids shown at the 30% level.

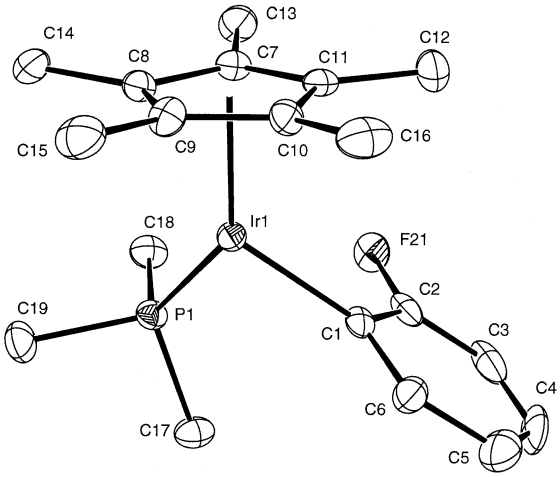

Figure 6. ORTEP diagram of the non-hydrogen atoms of one of the crystallographically independent molecules of compound **14**, with thermal ellipsoids shown at the 30% level.

piano-stool geometry. Figure 9 contains projections of these structures, with only the ring centroid included; each projection is viewed down the Ir−C(1) bond, with the M−Ct(01) vector perpendicular. The angles between the ligands comprising the legs of the piano stool are all close to 90°, while those between Ct(01) and the other ligands are much more obtuse and lie in the 120−130° range. The M−C(1) distances are not significantly

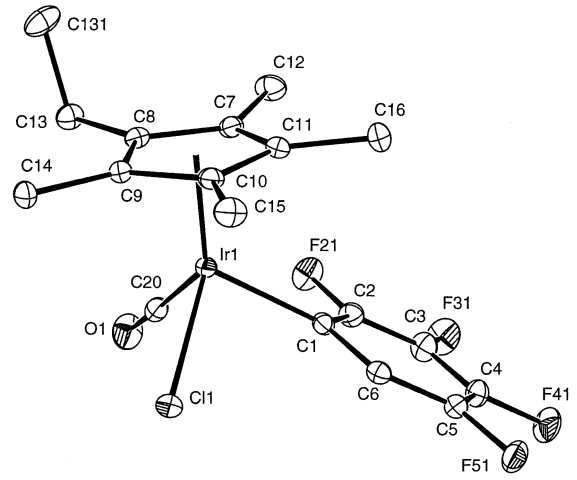

Figure 7. ORTEP diagram of the non-hydrogen atoms of compound **17**, with thermal ellipsoids shown at the 30% level.

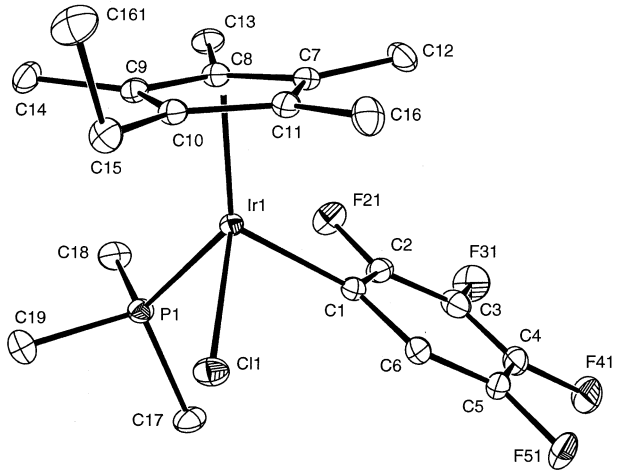

Figure 8. ORTEP diagram of the non-hydrogen atoms of compound **18**, with thermal ellipsoids shown at the 30% level.

different in any of the compounds, except for hydride complex **14**, in which they are slightly smaller (Table 2). The effect of replacing Ir by Rh is insignificant, as judged by metric parameters for compounds **3** and **9**. The effect of replacing a CO ligand with a PMe_3 ligand is a general increase in the bond angles between the monodentate ligands, as judged by data for **2** and **3**.

Although the M−C(1) distances to the phenyl rings are statistically identical, there are significant differences in the orientation of the phenyl ring with respect to the rest of the molecule, as shown in Figure 9. These structural differences are quantified as the torsion angles Ct(01)−M−C(1)−C(2) and Ct(01)−M−C(1)−C(6) and the angle M−C(1)−C(4), as presented in Table 2. In the carbonyl iodo complexes **2** and **12** the aryl rings are canted toward the CO ligand and away from the iodide. In **12** this canting is less, probably due in part to the absence of a fluorine on C(6), with consequently less steric interaction with I(1). When the iodide is replaced by the smaller chloride ligand, and without a fluorine on C(6) as in **17**, the aryl ring lies almost perpendicular to the M−Ct(01) vector. Comparison of **2** and **3** illustrates the effect of replacing CO with PMe_3; the additional repulsion between PMe_3 and F(21) results

Table 1. Crystal Data and Summary of X-ray Data Collection

	2	**3**	**9**	**11**	**12**	**13**	**14**	**15**	**18**	**19**
formula	$C_{17}H_{15}F_5$-IIrO	$C_{19}H_{24}F_5$-IIrP	$C_{19}H_{24}F_5$-IPRh	$C_{19}H_{24}F_4$-PRh	$C_{17}H_{19}F$-IIrO	$C_{19}H_{28}F$-IIrP	$C_{19}H_{29}F$-IrP	$C_{19}H_{28}$IrP	$C_{20}H_{27}Cl$-F_4IrP	$C_{18}H_{18}Cl$-F_4IrO
fw	649.39	697.45	608.16	462.26	577.42	625.48	499.59	479.58	602.04	553.97
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	*Pbca*	$P2_1/n$	$P\bar{1}$	$P2_1/m$	*I*2/*a*	$P\bar{1}$
a, Å	7.3285(6)	8.4610(8)	8.4528(6)	17.4322(10)	13.8360(8)	8.4486(5)	9.0591(7)	8.5423(5)	16.1351(13)	7.2340(11)
b, Å	27.103(2)	8.6375(8)	8.6270(6)	12.9851(8)	14.7440(9)	15.3854(10)	13.0694(10)	12.3320(8)	8.8168(7)	10.1244(16)
c, Å	9.2769(7)	15.9703(15)	15.9691(11)	18.0272(11)	16.7244(10)	15.7401(10)	16.4288(13)	9.1542(6)	30.683(2)	12.3876(19)
α, deg	90	90.694(2)	90.6580(10)	90	90	90	90.5250(10)	90	90	81.743(2)
β, deg	90.989(2)	102.1630(10)	102.1160(10)	102.1890(10)	90	93.6900(10)	97.139(2)	105.3520(10)	99.9310(10)	88.259(2)
γ, deg	90	111.3790(10)	111.2710(10)	90	90	90	90.8740(10)	90	90	86.093(2)
V, Å^3	1842.3(3)	1057.35(17)	1056.08(13)	3988.6(4)	3411.7(4)	2041.7(2)	1929.7(3)	929.93(10)	4299.5(6)	895.6(2)
Z	4	2	2	8	8	4	4	2	8	2
D(calcd), g/cm^3	2.341	2.191	1.913	1.540	2.248	2.035	1.720	1.713	1.860	2.054
abs coeff, mm^{-1}	8.972	7.894	2.390	0.971	9.642	8.136	7.006	7.258	6.446	7.645
$R(F)$, %[a]	2.89	1.93	3.24	4.36	2.11	3.90	3.73	2.03	1.91	1.56
$R_w(F^2)$, %[a]	6.43	4.87	9.58	11.30	5.33	15.49	7.69	4.76	4.93	4.94
temp, K	173(2)	153(2)	173(2)	173(2)	173(2)	193(2)	293(2)	173(2)	173(2)	173(2)
diffractometer	Siemens P4									
radiation	Mo Kα (λ = 0.710 73 Å)									

[a] Quantity minimized: $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

Table 2. Selected Distances (Å) and Angles (deg) in Fluorophenyl Complexes

	2	**12**	**17**	**3**	**9**	**18**	**13**	**14**[b]
M−C(1)	2.093(5)	2.086(3)	2.085(3)	2.086(3)	2.079(3)	2.075(2)	2.088(6)	2.055(8), 2.068(8)
M−P(1)				2.2899(8)	2.2962(10)	2.2839(7)	2.2783(19)	2.234(2), 2.231(2)
M−C(20)	1.880(6)	1.916(5)	1.878(3)					
M−X	2.7010(4)	2.6876(3)	2.4000(7)	2.7320(3)	2.7234(4)	2.4120(6)	2.7257(6)	
M−Ct(01)[a]	1.864(5)	1.882(5)	1.858(5)	1.856(5)	1.850(5)	1.845(5)	1.853(5)	1.893(5), 1.890(5)
Ct(01)−M−C(1)	125.59(5)	121.61(5)	124.13(5)	121.26(5)	120.81(5)	124.84(5)	123.02(5)	126.09(5), 125.17(5)
Ct(01)−M−P(1)				129.53(5)	128.81(5)	131.70(5)	130.56(5)	133.26(5), 133.00(5)
Ct(01)−M−C(20)	129.58(6)	130.40(5)	129.37(5)					
Ct(01)−M−X	122.27(4)	122.90(5)	121.51(5)	122.36(5)	122.31(5)	123.42(5)	121.65(5)	
C(1)−M−P(1)				93.90(8)	94.21(10)	90.69(7)	92.02(18)	90.0(2), 90.9(2)
C(1)−M−C(20)	90.03(6)	91.22(14)	90.08(12)					
C(1)−M−X	91.10(5)	89.65(9)	88.65(8)	92.87(8)	94.10(10)	88.63(7)	90.48(18)	
P(1)−M−X				86.74(2)	87.05(3)	84.14(2)	87.83(5)	
C(20)−M−X	86.29(6)	89.91(11)	91.89(9)					
M−C(1)−C(4)	176.8(6)	173.4(5)	178.0(5)	169.1(6)	169.1(6)	176.1(5)	170.5(5)	177.9(5), 176.2(5)
Ct(01)−M−C(1)−C(2)[c]	103.8(6)	96.6(5)	93.2(5)	91.6(5)	91.5(5)	75.4(5)	88.7(5)	80.8(5), 84.2(5)
Ct(01)−M−C(1)−C(6)[c]	76.2(6)	75.7(6)	84.2(5)	73.9(5)	74.5(5)	99.3(5)	79.8(5)	94.2(6), 90.7(6)

[a] Ct(01) = centroid of [C(7) − C(11)]. [b] Two independent molecules in asymmetric unit. [c] Torsion angle.

in a dramatic reduction in the Ct(01)−M−C(1)−C(2) angle, from 104° to 76°, but without a significant reduction in the Ct(01)−M−C(1)−C(6) angle, which remains at 76°. The distortion is accommodated not by a simple rotation of the aryl ring about the M−C(1) bond, as might be expected, but instead by a distortion of the whole aryl ring, up toward the Cp*, as shown in Figure 9, and quantified by the contraction of the M−C(1)−C(4) angle from 177° to 173°. An almost identical distortion is observed in the structure of **9**. In the absence of a fluorine on C(6), as in **18**, the aryl ring can cant away from PMe_3 toward iodide, but there is still a analogous out-of-plane distortion of the aryl ring toward Cp*. In the chloro and hydrido complexes **18** and **14**, reduced steric interaction between C(6), which does not bear a fluorine, and the adjacent Cl or H ligands leads to structures in which the aryl ring cants toward the smaller ligand and shows a much smaller out-of-plane distortion.

(b) Benzyne Complexes. The structure of the iridium complex of tetrafluorobenzyne **6** was reported in our original communication,[24] and those of the rhodium analogue **11** and the iridium benzyne complex **15** are described here. ORTEP plots are provided in Figures 10 and 11; the atom-numbering system is different from that of the previously described phenyl complexes (vide supra) but, to facilitate comparisons, is identical with that already published for **6**.[24] The rhodium complex **11** exists as two independent molecules in the asymmetric unit, thereby providing two independent sets of metric parameters, but complex **15**, containing the parent benzyne ligand, lies on a crystallographic plane of symmetry, reducing the number of independent parameters. Details of the crystallographic determinations are provided in Table 1, and selected bond lengths and angles for **11** and **15** along with comparison values for **6** are provided in Table 3.

The distances from the metal to the ligated benzyne carbon atoms C(11) and C(12) are not significantly different between the tetrafluorobenzyne complex **6** and its hydrocarbon analogue **15**, with averaged values being identical at 2.062(5) and 2.062(3) Å, respectively. In the rhodium−tetrafluorobenzyne analogue **11** there is significant asymmetry between the two Rh−C distances in each independent molecule, with each structure having the P−C(17) bond eclipsing the Rh−C(12) bond. In structure **6**, the phosphine adopts a conformation in which the corresponding P−C(17) bond eclipses the Ir−C(12) bond less, while in **11** the crystallographically imposed symmetry makes this point moot. Consequently, it seems likely that significant differences in M−C bond lengths in **11** are the result of steric effects with the phosphine ligand.

Although the M−C distances are not significantly different between **6** and **15**, one effect of fluorination in the benzyne ligand appears to be a slight decrease in the M−P(1) distance and a slight increase in the M−Ct(01) distance in **15**, compared to those in **6**, and also in rhodium analogue **11**. These crystallographic differences are slight and are not likely to be chemically significant. In our communication concerning the structure of **6**, we noted the different pattern of bond lengths around the tetrafluorobenzyne ring in comparison to those of other benzyne complexes,[24] with C(14)−C(15) being the shortest bond. The pattern of bond distances around the hydrocarbon benzyne ligand in **15** and in the tetrafluorobenzyne ligands of the two independent molecules of **11** are not as significantly different as those in **6**. Moreover, the distance between the coordinated benzyne carbon atoms C(11)−C(12) is significantly longer in **6** than in either the hydrocarbon complex **15** or the fluorocarbon analogue **11**, which are insignificantly different from one another. The interpretation of bond distances in these compounds in terms of effects induced by fluorine seems to have been premature.

The temptation to overinterpret metric parameters obtained from crystallographic studies of these compounds is illustrated by a comparison of the planarity of the M−benzyne system in each compound, as quantified by the dihedral angle between the least-squares planes M−C(11)−C(12) and C(11) through C(16). For complex **6** this angle is 171.5(4)°, significantly different from that of 175.6(4)° in **15**. However, the two independent molecules of compound **11** show values of 170.4(3) and 176.1(3)°, a larger spread than for the two other compounds, and one that must be attributed to crystal packing forces,[45] rather than to differences between the fluorinated and hydrocarbon ligands. Clearly, the M−benzyne bond is easily deformed by such puckering.

(45) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

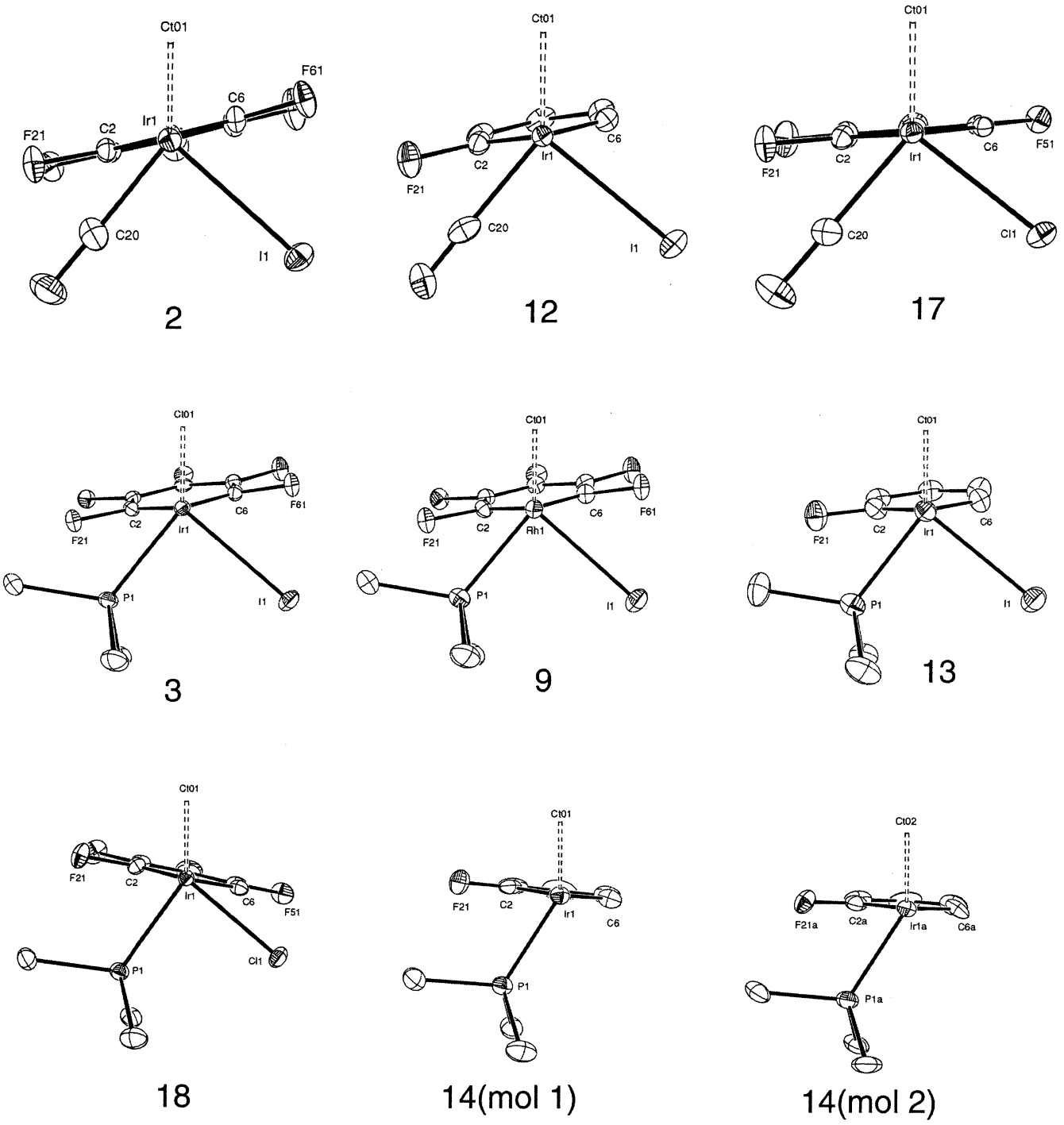

Figure 9. Partial ORTEP diagrams showing projections of compounds **2**, **12**, **17**, **3**, **9**, **13**, **18**, and **14** as viewed down the M−C(1) bond. The cyclopentadienyl rings are omitted, and only the centroid of these rings (Ct(01)) is shown, oriented perpendicular to the M−C(1) bond.

Concluding Remarks

The synthesis of fluorinated and nonfluorinated benzyne ligands from fluoroaryl hydrido complexes has been extended. The reaction appears to be general, at least for compounds of Ir and Rh. Detailed interpretations of structural differences between benzyne and tetrafluorobenzyne complexes using crystallographic means are inappropriate, as crystal-packing forces clearly have a greater impact on their structures than do chemical differences between the fluorinated and nonfluorinated ligands.

Experimental Section

All reactions were performed in oven-dried glassware, using standard Schlenk techniques under an atmosphere of nitrogen that had been deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun Drybox. Methylene chloride, hexane, diethyl ether, and toluene were dried over an alumina column under nitrogen. IR spectra were recorded on a Perkin-Elmer FTIR 1600 series spectrometer. NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT spectrometer. ^{1}H NMR spectra were referenced to the protio impurity in the solvent; C_6D_6 (δ 7.16 ppm), $CDCl_3$ (δ 7.27 ppm), CD_2Cl_2 (δ 5.32 ppm). ^{19}F NMR spectra were referenced to $CFCl_3$ (0.00 ppm), and

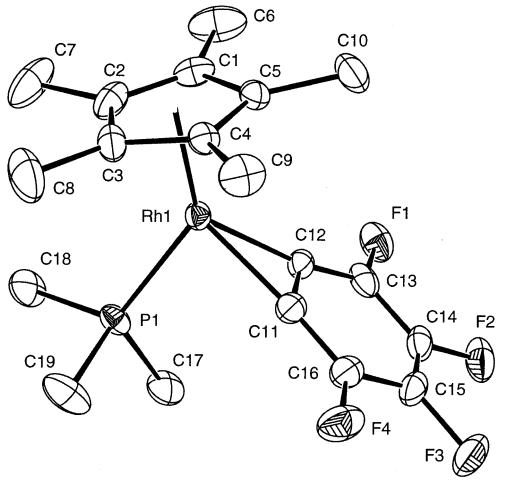

Figure 10. ORTEP diagram of the non-hydrogen atoms of one of the crystallographically independent molecules of compound **11**, with thermal ellipsoids shown at the 30% level.

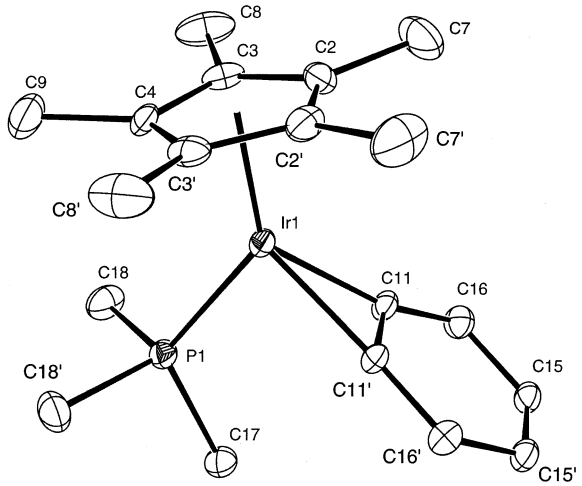

Figure 11. ORTEP diagram of the non-hydrogen atoms of compound **15**, with thermal ellipsoids shown at the 30% level. Atoms labeled with a prime (′) are crystallographically related to their unprimed analogues by a plane of symmetry containing P(1), Ir(1), and C(4).

$^{31}P\{^{1}H\}$ NMR spectra were referenced to 85% H_3PO_4 (0.00 ppm). Coupling constants are reported in hertz. Elemental analyses were performed by Schwartzkopf (Woodside, NY). Iodopentafluorobenzene and 2,3,4,5-tetrafluorobenzoyl chloride (Lancaster) and pentamethylcyclopentadiene and ethyltetramethylcyclopentadiene (Aldrich) were used as received. Cp*M(CO)$_2$ (M = Ir, Rh)[44] and $[Ir(C_5Me_4Et)Cl_2]_2$[46] were prepared by the literature methods.

IrCp*(C_6F_5)(CO)I (2). To a solution of IrCp*$(CO)_2$ (756 mg, 1.97 mmol) in benzene (40 mL) was added C_6F_5I (0.30 mL, 2.25 mmol), and the resultant solution was gently refluxed for 40 h to give an orange-purple solution. Removal of solvent, followed by recrystallization of the solid residue from CH_2Cl_2/hexanes, gave a brown crystalline solid (1.090 g), containing the desired product, contaminated with about 5% of IrCp*$(CO)I_2$. Complete purification was achieved by passing through a Florisil column (CH_2Cl_2/hexanes, 50:50) to give **2** as a yellow crystalline solid (80%). Anal. Calcd for $C_{17}H_{15}F_5IIrO$: C, 31.44; H, 2.33. Found: C, 31.47; H, 2.22. ^1H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 2.06 (s, 15H, Cp*). ^{19}F NMR ($CDCl_3$, 282.2 MHz, 21 °C): δ −163.0 (br, *m*-C_6F_5), −159.8 (dd, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 20.0 Hz, *p*-C_6F_5), −111.1 (br, *o*-C_6F_5), −108.6 (br, *o*-C_6F_5).

IrCp*(C_6F_5)(PMe_3)I (3). To a solution of IrCp*$(C_6F_5)(CO)I$ (**2**; 137.5 mg, 0.212 mmol) in toluene (15 mL) was added PMe_3 (0.030 mL, 0.29 mmol). The resultant solution was refluxed for 3.5 h, cooled to room temperature, and filtered through Celite. The solvent was removed in vacuo from the filtrate and the residual solid recrystallized from CH_2Cl_2/hexanes. Yield: 127 mg, 86%. Anal. Calcd for $C_{19}H_{24}F_5IIrP$: C, 32.72; H, 3.47. Found: C, 32.52; H, 3.23. ^1H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 1.78 (dd, $^2J_{HP}$ = 10.2 Hz, $^6J_{HF}$ = 1.5 Hz, 9H, PMe_3), 1.81 (d, $^4J_{HP}$ = 2.4 Hz, 15H, Cp*). ^{19}F NMR ($CDCl_3$, 282.2 MHz, 21 °C): δ − 165.7 (dddd, $^3J_{FF}$ = 32.0 Hz, $^3J_{FF}$ = 20.0 Hz, $^5J_{FF}$ = 8.5 Hz, $^4J_{FF}$ = 4.0 Hz, *m*-C_6F_5), −163.4 (dddd, $^3J_{FF}$ = 29.0 Hz, $^3J_{FF}$ = 20.0 Hz, $^5J_{FF}$ = 7.5 Hz, $^4J_{FF}$ = 4.0 Hz, *m*-C_6F_5), −162.4 (dd, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 20.0 Hz, *p*-C_6F_5), −113.6 (dd, $^3J_{FF}$ = 32.0 Hz, $^4J_{FP}$ = 19.0 Hz, *o*-C_6F_5), −102.3 (ddd, $^3J_{FF}$ = 29.0 Hz, $^5J_{FF}$ = 8.5 Hz, $^4J_{FF}$ = 6.0 Hz, *o*-C_6F_5). $^{31}P\{^1H\}$NMR ($CDCl_3$, 121.4 MHz, 21 °C) δ −43.3 (d, $^4J_{PF}$ = 19.0 Hz, PMe_3).

[IrCp*(C_6F_5)(PMe_3)(OH_2)]O_3SCF_3 (4a) and IrCp*(C_6F_5)(PMe_3)O_3SCF_3 (4b). A solution of IrCp*$(C_6F_5)(PMe_3)I$ (**3**; 500 mg, 0.717 mmol) in toluene (20 mL) was added slowly dropwise to rapidly stirred AgO_3SCF_3 (221 mg, 0.860 mmol), and the resultant suspension was stirred for 30 min. The mixture was filtered through Celite and the filtrate reduced in vacuo to a yellow solid, which was recrystallized from CH_2Cl_2/hexanes. Yield: 519 mg, 98%. Anal. Calcd for $C_{20}H_{26}F_8IrO_4PS$: C, 33.38; H, 3.64. Found: C, 33.33; H, 3.16. [IrCp*$(C_6F_5)(PMe_3)(OH_2)]O_3SCF_3$ (**4a**): ^1H NMR (CD_2Cl_2, 500 MHz, −40 °C) δ 1.51 (d, $^2J_{HP}$ = 11.0 Hz, 9H, PMe_3), 1.62 (d, $^4J_{HP}$ = 1.5 Hz, 15H, Cp*); ^{19}F NMR (CD_2Cl_2, 470.3 MHz, −40 °C) δ − 160.9 (ddd, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 30.5 Hz, $^5J_{FF}$ = 7.0 Hz, *m*-C_6F_5), −160.6 (ddd, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 29.0 Hz, $^5J_{FF}$ = 7.5 Hz, *m*-C_6F_5), −158.5 (dd, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 20.0 Hz, *p*-C_6F_5), −121.8 (d, $^3J_{FF}$ = 29.0 Hz, *o*-C_6F_5), −112.8 (ddd, $^3J_{FF}$ = 30.5 Hz, $^5J_{FF}$ = 7.5 Hz, $^4J_{FP}$ = 11.0 Hz, *o*-C_6F_5), −77.7 (s, O_3SCF_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz, −75 °C) δ −22.9 (d, $^4J_{PF}$ = 11.1 Hz, PMe_3). IrCp*$(C_6F_5)(PMe_3)O_3SCF_3$ (**4b**): ^1H NMR (CD_2Cl_2, 300 MHz, 21 °C) δ 1.62 (d, $^2J_{HP}$ = 10.8 Hz, 9H, PMe_3), 1.69 (t, $^4J_{HP}$ = 2.1 Hz, 15H, Cp*); ^{19}F NMR (CD_2Cl_2, 470.3 MHz, −75 °C) δ − 162.5 (m, *m*-C_6F_5), −161.7 (m, *m*-C_6F_5), −159.8 (dd, $^3J_{FF}$ = 20.5 Hz, $^3J_{FF}$ = 20.5 Hz, *p*-C_6F_5), −114.7 (d, $^3J_{FF}$ = 30 Hz, *o*-C_6F_5), −113.8 (d, $^3J_{FF}$ = 27 Hz, *o*-C_6F_5), −77.6 (s, O_3SCF_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz, −75 °C) δ −18.9 (m).

Table 3. Selected Distances (Å) and Angles (deg) in Benzyne Complexes

	11[b]	**6**[24]	**15**[c]
M−C(11)	2.023(3), 2.015(3)	2.0q58(5)	2.062(3)
M−C(12)	2.067(3), 2.049(3)	2.046(5)	2.062(3)
M−P(1)	2.2671(9), 2.2614(9)	2.2573(13)	2.2347(13)
M−Ct(01)[a]	1.860(3), 1.858(3)	1.858(3)	1.877(4)
C(11)−C(12)	1.349(5), 1.343(5)	1.374(7)	1.350(7)
C(12)−C(13)	1.350(5), 1.343(5)	1.357(7)	1.376(5)
C(13)−C(14	1.409(6), 1.402(6)	1.393(8)	1.415(5)
C(14)−C(15)	1.363(6), 1.382(7)	1.355(9)	1.372(8)
C(15)−C(16)	1.390(6), 1.374(6)	1.418(9)	1.415(5)
C(16)−C(11)	1.353(5), 1.357(5)	1.360(7)	1.376(5)
C(11)−C(12)−C(13)	120.6(3), 122.3(4)	122.4(5)	123.2(2)
C(12)−C(13)−C(14)	118.1(4), 117.2(4)	117.5(5)	115.2(4)
C(13)−C(14)−C(15)	120.0(4), 120.3(4)	121.2(5)	121.6(2)
C(14)−C(15)−C(16)	121.0(4), 120.2(4)	120.3(5)	121.6(2)
C(15)−C(16)−C(11)	116.8(4), 117.9(4)	117.8(5)	115.2(4)
C(16)−C(11)−C(12)	123.6(4), 122.1(4)	120.6(5)	123.2(2)
Ct(01)−M−P(1)	133.4(4), 133.3(4)	133.9(4)	132.9(4)

[a] Ct(01) = centroid of Cp* [C(1) − C(5)]. [b] Two independent molecules in asymmetric unit. [c] For consistency within this table, atoms in compound **15** that are related by the crystallographic symmetry plane have been numbered differently, to be consistent with the numbering scheme in the other two structures: i.e., C(12) = C(11)′, C(13) = C(16)′, C(14) = C(15)′.

(46) Dooley, T.; Fairhurst, G.; Chalk, C. D.; Tabatabaian, K.; White, C. *Transition Met. Chem.* **1978**, *3*, 299−302.

IrCp*(C_6F_5)(PMe_3)H (5). (a) A solution of [IrCp*(C_6F_5)(PMe_3)(OH_2)]O_3SCF_3 (**4a**; 280 mg, 0.380 mmol) and 1,8-bis(dimethylamino)naphthalene (79 mg, 0.369 mmol) in toluene (20 mL) was stirred for 3 h. The solvent was removed in vacuo the residual solid suspended in hexanes (15 mL), and the suspension stirred vigorously for 5 min. The solvent was removed in vacuo, the residual solid was extracted into hexanes (15 mL), and the suspension was filtered. The colorless filtrate was reduced in vacuo to a white solid. Yield: 190 mg, 88%.

(b) A less pure sample was obtained by reaction of IrCp*(C_6F_5)(PMe_3)I (**3**) and $NaBH_4$ in refluxing 2-propanol: a mixture of IrCp*(C_6F_5)(PMe_3)I (70 mg, 0.100 mmol) and $NaBH_4$ (50 mg, 1.32 mmol) in 2-propanol (15 mL) was heated under reflux for 4 h. The solvent was removed, the solid residue extracted into hexanes, and the mixture filtered. The colorless filtrate was reduced in vacuo to a yellow oil, which solidified on standing to a tan solid. The product was contaminated with entrained 2-propanol. ^{1}H NMR (C_6D_6, 300 MHz, 21 °C): δ −16.48 (dd, $^2J_{HP}$ = 37.8 Hz, $^4J_{HF}$ = 10.8 Hz, 1H, Ir−H), 0.97 (d, $^2J_{HP}$ = 9.9 Hz, 9H, PMe_3), 1.70 (dd, $^4J_{HP}$ = 1.8 Hz, $^4J_{HH}$ = 0.8 Hz, 15H, Cp*). ^{19}F NMR (C_6D_6, 282.2 MHz, 21 °C): δ − 165.7 (dddd, $^3J_{FF}$ = 35.0 Hz, $^3J_{FF}$ = 20.5 Hz, $^5J_{FF}$ = 9.5 Hz, $^4J_{FF}$ = 4.0 Hz, *m*-C_6F_5), −164.6 (dddd, $^3J_{FF}$ = 31.5 Hz, $^3J_{FF}$ = 20.5 Hz, $^5J_{FF}$ = 9.0 Hz, $^4J_{FF}$ = 4.0 Hz, *m*-C_6F_5), −164.2 (dd, $^3J_{FF}$ = 20.5 Hz, $^3J_{FF}$ = 20.5 Hz, *p*-C_6F_5), −111.8 (dm, $^3J_{FF}$ = 35.0 Hz, *o*-C_6F_5), −107.6 (dd., $^3J_{FF}$ = 31.5 Hz, $^5J_{FF}$ = 9.5 Hz, $^4J_{FH}$ = 11.0 Hz, *o*-C_6F_5). ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz, 21 °C): δ −44.5 (dd, $^4J_{PF}$ = 6.8 Hz, $^4J_{PF}$ = 2.9 Hz, PMe_3).

IrCp*(η^2-C_6F_4)(PMe_3) (6). To a solution of IrCp*(C_6F_5)(PMe_3)H (190 mg, 0.332 mmol) in hexanes (20 mL) at −78 °C was added a solution of *n*-BuLi in hexanes (1.0 mL, 3.8 M, 3.8 mmol). The resultant yellow solution was warmed to room temperature and was stirred for 20 h. The resultant murky yellow solution was cooled in an ice bath, and ca. 2 mL of MeOH was added to the stirred solution. Removal of volatiles in vacuo gave a yellow solid, which was extracted into hexanes and the mixture filtered. Removal of solvent in vacuo gave an off-white solid. Yield: 181 mg, 99%. X-ray-quality crystals were grown by slow evaporation of a hexane solution; details of the structural determination appear elsewhere.[24] Anal. Calcd for $C_{19}H_{24}F_4IrP$: C, 41.37; H, 4.39. Found: C, 41.48; H, 4.31. ^{1}H NMR (C_6D_6, 300 MHz, 21 °C): δ 0.67 (d, $^2J_{HP}$ = 9.9 Hz, 9H, PMe_3), 1.65 (d, $^4J_{HP}$ = 1.5 Hz, 15H, Cp*). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 21 °C): δ 10.15 (d, $^3J_{CP}$ = 0.75 Hz, C_5Me_5), 17.90 (d, $^1J_{CP}$ = 38.2 Hz, PMe_3), 84.2 (m, *i*-C_6F_4), 92.46 (d, $^2J_{CP}$ = 3.5 Hz, C_5Me_5), 135.28 (dm, $^1J_{CF}$ = 252 Hz, *o*- or *m*-C_6F_4), 142.8 (dm, $^1J_{CF}$ = 253 Hz, *o*- or *m*-C_6F_4). ^{19}F NMR (C_6D_6, 282.2 MHz, 21 °C): δ −151.5 (m ($F_AF_{A'}F_XF_{X'}$), $^3J_{F(XX')}$ = 40.8 Hz, $^3J_{F(AX)}$ = 29.3 Hz, $^5J_{F(AA')}$ = 11.5 Hz, $J_{F(AX')}$ = 1.2 Hz, *m*-C_6F_4), −143.5 (dm ($F_AF_{A'}F_XF_{X'}$), $^4J_{FP}$ = 1.4 Hz, $^3J_{F(XX')}$ = 40.8 Hz, $^3J_{F(AX)}$ = 29.3 Hz, $^5J_{F(AA')}$ = 11.5 Hz, $J_{F(AX')}$ = 1.2 Hz, *o*-C_6F_4). ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz, 21 °C): δ −37.2 (PMe_3). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz, 21 °C): δ 10.15 (d, $^3J_{CP}$ = 0.75 Hz, C_5Me_5), 17.90 (d, $^1J_{CP}$ = 38.2 Hz, PMe_3), 84.2 (m, *i*-C_6F_4), 92.46 (d, $^2J_{CP}$ = 3.5 Hz, C_5Me_5), 135.28 (dm, $^1J_{CF}$ = 252 Hz, *o*- or *m*-C_6F_4), 142.8 (dm, $^1J_{CF}$ = 253 Hz, *o*- or *m*-C_6F_4).

RhCp*(C_6F_5)(CO)I (8). To a sample of RhCp*$(CO)_2$ (238 mg, 0.809 mmol) in toluene (20 mL) was added C_6F_5I (0.14 mL, 1.05 mmol) and the solution stirred in an oil bath at 80 °C for 48 h. The volume of the resultant red solution was reduced in vacuo and the mixture passed through a column (silica, toluene). The first, orange band was discarded, and the second, red band was collected. The solvent was removed to give a brown-orange solid, which was recrystallized from CH_2Cl_2/hexanes. Yield: 345 mg, 76%. Anal. Calcd for $C_{17}H_{15}F_5IORh$: C, 36.45; H, 2.70. Found: C, 36.20; H, 2.79. ^{1}H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 2.01 (s, 15H, Cp*). ^{19}F NMR ($CDCl_3$, 282.2 MHz, 21 °C): δ −162.2 (br, *m*-C_6F_5), −159.1 (dd, $^3J_{FF}$ = 19.5 Hz, $^3J_{FF}$ = 19.5 Hz, *p*-C_6F_5), −110 (br, *o*-C_6F_5), −105 (br, *o*-C_6F_5).

RhCp*(C_6F_5)(PMe_3)I (9). To a solution of IrCp*(C_6F_5)(CO)I (**8**; 284 mg, 0.507 mmol) in toluene (20 mL) was added PMe_3 (0.068 mL, 0.66 mmol) and the resultant solution stirred at room temperature for 2.5 h to give a vibrant orange solution. The volatiles were removed in vacuo and the residual orange solid recrystallized from CH_2Cl_2/hexanes. Yield: 299 mg, 97%. Anal. Calcd for $C_{19}H_{24}F_5IPRh$: C, 37.52; H, 3.98. Found: C, 37.67; H, 3.87. ^{1}H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 1.68 (d, $^2J_{HP}$ = 10.2 Hz, 9H, PMe_3), 1.79 (d, $^4J_{HP}$ = 3.3 Hz, 15H, Cp*). ^{19}F NMR ($CDCl_3$, 282.2 MHz, 21 °C): δ − 164.7 (ddddd, $^3J_{FF}$ = 34.2 Hz, $^3J_{FF}$ = 21 Hz, $^5J_{FF}$ = 8.5 Hz, $^4J_{FF}$ = 4.0 Hz, $^4J_{FRh}$ = 3.7 Hz, *m*-C_6F_5), −162.5 (ddm, $^3J_{FF}$ = 31.3 Hz, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5), −161.3 (dd, $^3J_{FF}$ = 21 Hz, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −112.5 (ddddd, $^3J_{FF}$ = 34.2 Hz, $^4J_{FP}$ = 25.3 Hz, $^5J_{FF}$ = 7 Hz, $^4J_{FF}$ = 8 Hz, $^3J_{FRh}$ = 7 Hz, *o*-C_6F_5), −98.0 (dddd, $^3J_{FF}$ = 31.3 Hz, $^5J_{FF}$ = 8.5 Hz, $^4J_{FF}$ = 8 Hz, $^3J_{FRh}$ = 2.5 Hz, *o*-C_6F_5). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz, 21 °C): δ 0.6 (dd, $^1J_{PRh}$ = 144.3 Hz, $^4J_{PF}$ = 25.3 Hz, PMe_3).

RhCp*(C_6F_5)(PMe_3)H (10). A mixture of RhCp*(C_6F_5)(PMe_3)I (**9**; 10 mg, 0.016 mmol) and $NaBH_4$ (10 mg, 0.26 mmol) in d_8-THF (0.7 mL) was heated in an evacuated J. Young NMR tube in an oil bath at 50 °C for 16 h. The solution slowly changed from orange to colorless. NMR showed complete conversion to the desired product. Yield: quantitative. ^{1}H NMR (d_8-THF, 500 MHz, 21 °C): δ −12.80 (ddd, $^2J_{HP}$ = 48.5 Hz, $^1J_{HRh}$ = 25.5 Hz, $^4J_{HF}$ = 10.5 Hz, 1H, Rh−H), 1.23 (d, $^2J_{HP}$ = 10.5 Hz, 9H, PMe_3), 1.85 (d, $^4J_{HP}$ = 2.5 Hz, 15H, Cp*). ^{19}F NMR (d_8-THF, 470.4 MHz, 21 °C): δ −163.0 (m, *m*-C_6F_5), −162.4 (m, *m*-C_6F_5), −162.0 (dd, $^3J_{FF}$ = 20 Hz, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −107.4 (dm, $^3J_{FF}$ = 37 Hz, *o*-C_6F_5), −102.4 (m, *o*-C_6F_5). ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz, 21 °C): δ 9.3 (ddd, $^1J_{PRh}$ = 142.2 Hz, $^4J_{PF}$ = 9.3 Hz, $^4J_{PF}$ = 9.3 Hz, PMe_3).

RhCp*(η^2-C_6F_4)(PMe_3) (11). To a solution of RhCp*(C_6F_5)(PMe_3)H (**10**; freshly prepared from RhCp*(C_6F_5)(PMe_3)I (76 mg, 0.0125 mmol) and $NaBH_4$) in hexanes (15 mL) at −78 °C was added a solution of *n*-BuLi in hexanes (0.06 mL, 2.8 M, 0.017 mmol). The resultant yellow solution was warmed to room temperature and was stirred for 1 h. An orange-yellow cloudy solution was produced. Cooling to 0 °C and addition of 1 mL of MeOH to the stirred solution, followed by removal of volatiles in vacuo, extraction into hexanes, and filtration, gave a pale yellow filtrate which was reduced in vacuo to a pale yellow solid. Yield: 48 mg, 84%. X-ray-quality crystals were grown by slow evaporation of a hexane solution and subsequent washing with hexanes. Anal. Calcd for $C_{19}H_{24}F_4PRh$: C, 49.37; H, 5.23. Found: C, 48.74; H, 5.34. ^{1}H NMR (C_6D_6, 300 MHz, 21 °C): δ 0.49 (dd, $^2J_{HP}$ = 9.9 Hz, $^3J_{HRh}$= 1.2 Hz, 9H, PMe_3), 1.59 (dd, $^4J_{HP}$ = 2.7 Hz, $^3J_{HRh}$ = 0.6 Hz, 15H, Cp*). ^{19}F NMR (C_6D_6, 282.2 MHz, 21 °C): δ −149.4 (m ($F_AF_{A'}F_XF_{X'}$), $^3J_{F(XX')}$ = 41.3 Hz, $^3J_{F(AX)}$ = 30.0 Hz, $^5J_{F(AA')}$ = 11.8 Hz, $J_{F(AX')}$ = 1.4 Hz, *m*-C_6F_4), −141.6 (dm ($F_AF_{A'}F_XF_{X'}$), $^4J_{FRh}$ = 4.5 Hz, $^3J_{F(XX')}$ = 41.3 Hz, $^3J_{F(AX)}$ = 30.0 Hz, $^5J_{F(AA')}$ = 11.8 Hz, $J_{F(AX')}$ = 1.4 Hz, *o*-C_6F_4). ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz, 21 °C): δ −1.46 (d, $^1J_{PRh}$ = 167 Hz, PMe_3).

IrCp*(2-C_6FH_4)(CO)I (12). To a solution of IrCp*$(CO)_2$ (545 mg, 1.42 mmol) in toluene (50 mL) was added 2-fluoro-1-iodobenzene (0.35 mL, 0.665 g, 3.0 mmol). The mixture was heated in an oil bath at 140 °C for 48 h. A reddish brown solution was produced, and this was cooled to room temperature. The solvent was removed in vacuo to produce a brown solid, which was purified by column chromatography (silica; toluene). The resultant yellow solution was reduced in vacuo to a yellow solid, which was recrystallized from CH_2Cl_2/hexanes to give X-ray-quality crystals. Yield: 535 mg, 65%. Anal. Calcd for $C_{17}H_{19}FIIrO$: C, 35.36; H, 3.32. Found: C, 35.48; H, 3.17. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 1.95 (s, 15H, Cp*), 6.85 (m, 2H, C_6H_4F), 6.94 (m, 1H, C_6H_4F), 7.67 (m, 1H, C_6H_4F). ^{19}F NMR ($CDCl_3$, 300 MHz, 22 °C): δ 87.79 (m, C_6H_4F).

IrCp*(2-C_6FH_4)(PMe_3)I (13). A solution of IrCp*(CO)(C_6H_4F)I (**12**; 215 mg, 0.37 mmol) in dry toluene (50 mL) was

degassed, and PMe_3 (0.06 mL, 0.042 g, 0.56 mmol) was added by syringe. The reaction mixture was heated under reflux for 3 h and cooled to room temperature. All volatiles were removed under vacuum, and the residue was crystallized from CH_2Cl_2/hexanes to give crystals of X-ray quality. Yield: 217 mg, 92%. Anal. Calcd for $C_{19}H_{28}FIIrP$: C, 36.48; H, 4.51. Found: C, 36.58; H, 4.38. ^1H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 1.67 (d, $^2J_{HP} = 10.5$ Hz, 9H, PMe_3), 1.74 (d, $^4J_{HP} = 1.8$ Hz, 15H, Cp*), 6.72 (m, 2H, C_6H_4F), 6.83 (m, 1H, C_6H_4F), 8.08 (m, 1H, C_6H_4F). ^{19}F NMR ($CDCl_3$, 282.2 MHz, 22 °C): δ 88.27 (m, $^4J_{FP} = 10.5$ Hz, 1F, C_6H_4F). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz, 22 °C): δ 43.66 (d, $^4J_{FP} = 10.5$ Hz, PMe_3)

IrCp*(PMe$_3$)(2-C$_6$FH$_4$)H (14). IrCp*(PMe_3)(C_6H_4F)I (**13**; 215 mg, 0.37 mmol) was placed in a Schlenk flask, and ethanol (50 mL of 95%) and $NaBH_4$ (130 mg, 3.4 mmol) were added. The reaction mixture was heated to 60−70 °C, and the resultant yellow solution was stirred for 30 min until it became colorless. All volatiles were removed under vacuum. The residue was extracted with dry hexane, the resultant solution was filtered, and almost all the hexane was removed under vacuum. The solution was cooled, and crystals of X-ray quality were obtained. Yield: 148 mg, 87%. Anal. Calcd for $C_{19}H_{29}FIrP$: C, 45.68; H, 5.85. Found: C, 45.96; H, 5.75. Major rotamer: ^1H NMR (CD_2Cl_2, 500 MHz, −60 °C) δ −17.44 (d, $^2J_{HP} = 35.5$ Hz, 1H, Ir−H), 1.28 (d, $^2J_{HP} = 10.0$ Hz, 9H, PMe_3), 1.81 (m, 15H, Cp*), 6.50 (m, 1H, C_6H_4F), 6.58 (m, 1H, C_6H_4F), 6.75 (m, 1H, C_6H_4F), 7.49 (m, 1H, C_6H_4F); ^{19}F NMR (CD_2Cl_2, 470.3 MHz, −60 °C) δ 87.79 (br, 1F, C_6H_4F); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.35 MHz, −60 °C) δ −41.33 (d, $^4J_{FP} = 4.4$ Hz, 1P, PMe_3). Minor rotamer: ^1H NMR (CD_2Cl_2, 500 MHz, −60 °C) δ −16.73 (dd, $^2J_{HP} = 37.3$ Hz, $^4J_{HF} = 10.3$ Hz, 1H, Ir−H), 1.25 (d, $^2J_{HP} = 10.0$ Hz, 9H, PMe_3), 1.81 (m, 15H, Cp*), 6.58 (m, 1H, C_6H_4F), 6.63 (m, 1H, C_6H_4F), 6.75 (m, 1H, C_6H_4F), 7.29 (m, 1H, C_6H_4F); ^{19}F NMR (CD_2Cl_2, 470.3 MHz, −60 °C) δ 84.82 (s, 1F, C_6H_4F); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.35 MHz, −60 °C) δ −38.57 (s, 1P, PMe_3).

IrCp*(η^2-C$_6$H$_4$)(PMe$_3$) (15). To a solution of IrCp*(PMe_3)(2-C_6FH_4)H (**14**; 110 mg, 0.220 mmol) in hexanes (25 mL) was added a solution of *n*-BuLi in hexane (1.0 mL, 2.8 M, 2.2 mmol). The resultant yellow solution was stirred for 4 h at room temperature. Cooling to 0 °C and addition of ∼0.3 mL of MeOH to the stirred solution, followed by removal of volatiles in vacuo, gave an off-white solid which was extracted into hexanes and filtered. Pale yellow crystals were grown by slow evaporation of a hexane solution. Yield: 65 mg, 62%. Anal. Calcd for $C_{19}H_{28}IrP$: C, 47.58; H, 5.88. Found: C, 47.29; H, 5.79. ^1H NMR (C_6D_6, 300 MHz, 22 °C): δ 0.85 (d, $^2J_{HP} = 9.9$ Hz, 9H, PMe_3), 1.85 (d, $^4J_{HP} = 1.8$ Hz, 15H, Cp*), 7.08 (m ($H_AH_{A'}H_XH_{X'}$), $^3J_{H(XX)} = 7.0$ Hz, $^3J_{H(AX)} = 6.1$ Hz, $^5J_{H(AA')} = 1.7$ Hz, $^4J_{H(AX')} = 0.5$ Hz), 7.40 (m ($H_AH_{A'}H_XH_{X'}$), $^3J_{H(XX)} = 7.0$ Hz, $^3J_{H(AX)} = 6.1$ Hz, $^5J_{H(AA')} = 1.7$ Hz, $^4J_{H(AX')} = 0.5$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.7 MHz, 22 °C): δ 10.84 (d, $^3J_{CP} = 1.15$ Hz, C_5Me_5), 18.70 (d, $^1J_{CP} = 37.6$ Hz, PMe_3), 92.38 (d, $^2J_{CP} = 3.8$ Hz, C_5Me_5), 107.88 (d, $^2J_{CP} = 9.2$ Hz, *i*-C_6H_4), 116.27 (s, *o*- or *m*-C_6H_4), 126.85 (s, *o*- or *m*-C_6H_4). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz, 22 °C): δ −37.52 (s, PMe_3).

IrCp*(C$_6$H$_5$)(PMe$_3$)(*n*-Bu) (16). To a solution of IrCp*(PMe_3)(2-C_6FH_4)H (**14**; 40 mg, 0.08 mmol) in hexanes (20 mL) was added a solution of *n*-BuLi in hexane (0.3 mL, 2.8 M, 0.8 mmol). The resultant yellow solution was stirred for 2 h at 60 °C. Cooling to 0 °C and addition of ∼0.3 mL of MeOH to the stirred solution, followed by removal of volatiles in vacuo, gave an off-white solid which was extracted with hexanes and filtered. Removal of solvent in vacuo gave a colorless oil, which was purified by column chromatography (silica, hexanes). Yield: 20 mg, 48%. Adequate microanalysis results could not be obtained, and the complex was characterized only spectroscopically. ^1H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 0.91 (t, $^3J_{HH} = 7.2$ Hz, 3H, CH_3), 1.35 (d, $^2J_{HP} = 9.6$ Hz, 9H, PMe_3), 1.59 (d, $^4J_{HP} = 2.1$ Hz, 15H, Cp*), 6.75 (tm, $^3J_{HH} = 7.0$ Hz, 1H, *p*-C_6H_5), 6.80 (tm, $^3J_{HH} = 7.0$ Hz, 2H, *m*-C_6H_5), 7.16 (dm, $^3J_{HH} = 8.0$ Hz, 2H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz, 22 °C) δ 1.36 (d, $^2J_{CP} = 9.3$ Hz, α-CH_2), 9.09 (d, $^3J_{CP} = 0.75$ Hz, C_5Me_5), 14.07 (s, δ-CH_2), 15.53 (d, $^1J_{CP} = 35.8$ Hz, PMe_3), 29.2 (s, 1C, γ-CH_2), 39.06 (d, $^3J_{CP} = 4.9$ Hz, β-CH_2), 93.00 (d, $^2J_{CP} = 3.6$ Hz, C_5Me_5), 120.21 (s, *p*-C_6H_5), 126.34 (s, *m*-C_6H_5), 137.79 (d, $^2J_{CP} = 12.6$ Hz, *i*-C_6H_5), 139.63 (d, $^3J_{CP} = 3.3$ Hz, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz, 22 °C): δ −39.8 (s, PMe_3).

Ir(C$_5$Me$_4$Et)(CO)$_2$. A solution of $[Ir(C_5Me_4Et)Cl_2]_2$ (301 mg, 0.730 mmol) and $Fe_3(CO)_{12}$ (methanol stabilized, 300 mg, 0.59 mmol) in benzene (50 mL) was heated under reflux in air for 16 h to give a brown murky solution. The mixture was cooled to room temperature and then filtered through Celite. If any green color remained in the solution, it was allowed to stand in air for 24 h. The solvent was then removed in vacuo and the solid residue extracted into hexanes and then filtered through Celite. The solvent was removed to give a brown oil, which became a waxy dark yellow solid on standing. Yield: 243 mg, 84%. ^1H NMR ($CDCl_3$, 500 MHz, 21 °C): δ 1.09 (t, $^3J_{HH} = 7.5$ Hz, 3H, CH_2CH_3), 2.17 (s, 6H, C_5Me_4Et), 2.18 (s, 6H, C_5Me_4Et), 2.46 (q, $^3J_{HH} = 7.5$ Hz, 2H, CH_2CH_3).

Ir(C$_5$Me$_4$Et)(2,3,4,5-C$_6$F$_4$H)(CO)Cl (17). A solution of Ir(C_5Me_4Et)$(CO)_2$ (**16**; 243 mg, 0.611 mmol) and 2,3,4,5-tetrafluorobenzoyl chloride (0.16 mL, 1.2 mmol) in toluene (15 mL) was heated in an oil bath at 110 °C for 48 h to give a yellow solution. The solvent was removed in vacuo and the solid residue purified by column chromatography (silica, 1:1 toluene/CH_2Cl_2). The yellow band was collected and the solvent removed in vacuo to give a yellow solid, which was recrystallized from CH_2Cl_2/hexanes. Yield: 252 mg, 74%. Anal. Calcd for $C_{18}H_{18}ClF_4IrO$: C, 39.02; H, 3.28. Found: C, 38.92; H, 3.32. ^1H NMR (C_6D_6, 500 MHz, 21 °C): δ 0.87 (t, $^3J_{HH} = 8.0$ Hz, 3H, CH_2CH_3), 1.76 (s, 3H, C_5Me_4Et), 1.78 (s, 3H, C_5Me_4Et), 1.86 (s, 3H, C_5Me_4Et), 1.90 (s, 3H, C_5Me_4Et), 2.17 (q, $^3J_{HH} = 8.0$ Hz, 2H, CH_2CH_3), 6.57 (dddd, $^3J_{HF} = 10.8$ Hz, $^4J_{HF} = 8.9$ Hz, $^5J_{HF} = 2.8$ Hz, $^4J_{HF} = 1.9$ Hz, 1H, C_6F_4H). ^{19}F NMR ($CDCl_3$, 470.3 MHz, 21 °C): δ −162.6 (ddd, $^3J_{FF} = 21.2$ Hz, $^3J_{FF} = 18.8$ Hz, $^4J_{FH} = 8.9$ Hz, *p*-C_6F_4H), −158.4 (ddd, $^3J_{FF} = 26.8$ Hz, $^3J_{FF} = 18.8$ Hz, $^5J_{FH} = 2.8$ Hz, *m*-C_6F_4H), −141.9 (ddd, $^3J_{FF} = 21.2$ Hz, $^5J_{FF} = 12.7$ Hz, $^3J_{FH} = 10.8$ Hz, *m*-C_6F_4H), −115.9 (ddd, $^3J_{FF} = 26.8$ Hz, $^5J_{FF} = 12.7$ Hz, $^4J_{FH} = 1.9$ Hz, *o*-C_6F_4H).

Ir(C$_5$Me$_4$Et)(2,3,4,5-C$_6$F$_4$H)(PMe$_3$)Cl (18). A solution of Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(CO)Cl (**17**; 241 mg, 0.435 mmol) and PMe_3 (0.06 mL, 0.58 mmol) in toluene (15 mL) was heated in an oil bath at 95 °C for 16 h. The resultant yellow solution was reduced in vacuo to a yellow solid, which was recrystallized from CH_2Cl_2/hexanes. Yield: 244 mg, 93%. Anal. Calcd for $C_{20}H_{27}ClF_4IrP$: C, 39.90; H, 4.52. Found: C, 40.02; H, 4.54. ^1H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 1.04 (t, $^3J_{HH} = 7.5$ Hz, 3H, CH_2CH_3), 1.46 (d, $^2J_{HP} = 10.8$ Hz, 9H, PMe_3), 1.61 (d, $^4J_{HP} = 2.4$ Hz, 6H, C_5Me_4Et), 1.67 (d, $^4J_{HP} = 2.4$ Hz, 3H, C_5Me_4Et), 1.68 (d, $^4J_{HP} = 1.8$ Hz, 3H, C_5Me_4Et), 2.01 (q, $^3J_{HH} = 7.5$ Hz, 2H, CH_2CH_3), 6.62 (ddddd, $^3J_{HF} = 12.0$ Hz, $^4J_{HF} = 9.6$ Hz, $^4J_{HF} = 3$ Hz, $^5J_{HF} = 3$ Hz, $^4J_{HP} = 1.2$ Hz, 1H, C_6F_4H). ^{19}F NMR ($CDCl_3$, 470.3 MHz, 21 °C): δ −165.7 (ddd, $^3J_{FF} = 21.2$ Hz, $^3J_{FF} = 18.9$ Hz, $^3J_{FH} = 9.6$ Hz, *p*-C_6F_4H), −160.6 (ddd, $^3J_{FF} = 30.5$ Hz, $^3J_{FF} = 18.9$ Hz, $^5J_{FH} = 3$ Hz, *m*-C_6F_4H), −143.7 (ddd, $^3J_{FF} = 21.2$ Hz, $^5J_{FF} = 13.5$ Hz, $^3J_{FH} = 12.0$ Hz, *o*-C_6F_4H), −117.2 (dddd, $^3J_{FF} = 30.5$ Hz, $^5J_{FF} = 13.5$ Hz, $^4J_{FH} = 3$ Hz, $^4J_{FP} = 6.1$ Hz, *o*-C_6F_4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.3 MHz, 21 °C): δ − 35.0 (d, $^4J_{PF} = 6.1$ Hz).

[Ir(C$_5$Me$_4$Et)(2,3,4,5-C$_6$F$_4$H)(PMe$_3$)(OH$_2$)]O$_3$SCF$_3$ (19). A solution of Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(PMe_3)Cl (**18**; 244 mg, 0.333 mmol) in toluene (20 mL) was added dropwise to rapidly stirred AgO_3SCF_3 (114 mg, 0.444 mmol) to form a yellow solution with a white precipitate. The mixture was stirred for 1.5 h and then filtered through Celite to give a yellow filtrate. The solvent was removed in vacuo from the filtrate, the residual solid dissolved in CH_2Cl_2, and this solution filtered again through Celite. Addition of hexanes to the filtrate and removal of the CH_2Cl_2 in vacuo gave an orange precipitate. Yield: 281 mg, 95%. Anal. Calcd for $C_{21}H_{29}F_7IrO_4PS$: C, 34.38;

H, 3.98. Found: C, 34.46; H, 3.91. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.05 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_2CH_3), 1.53 (d, $^2J_{HP}$ = 10.8 Hz, 9H, PMe_3), 1.63 (br, 3H, C_5Me_4Et), 1.67 (br, 3H, C_5Me_4Et), 1.70 (br, 6H, C_5Me_4Et), 2.08 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CH_3), 7.11 (ddddd, $^3J_{HF}$ = 11.4 Hz, $^4J_{HF}$ = 9.3 Hz, $^4J_{HF}$ = 3.3 Hz, $^5J_{HF}$ = 3.3 Hz, $^4J_{HP}$ = 1 Hz, 1H, C_6F_4H). ^{19}F NMR ($CDCl_3$, 470.4 MHz, 21 °C): δ −163.8 (br, *p*-C_6F_4H), −158.3 (br, *m*-C_6F_4H), −141.8 (br, *m*-C_6F_4H), −116.7 (br, *o*-C_6F_4H), −79.2 (s, O_3SCF_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz, 21 °C): δ −22.0 (br).

Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(PMe_3)H (20). A solution of [Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(PMe_3)(OH_2)]O_3SCF_3 (**19**; 263 mg, 0.358 mmol) and Proton Sponge (74 mg, 0.35 mmol) in toluene (15 mL) was stirred for 2.5 h. The solvent was removed in vacuo, the residue extracted into hexanes, and the extract filtered. The solvent was removed from the filtrate to give an off-white solid. The solid was dissolved in hexanes (15 mL) and left to stand at −30 °C for 3 h. A yellow precipitate developed, which was removed by filtration. Removal of solvent from the filtrate gave a pale yellow oil, which solidified on standing. Yield: 198 mg, 97%. Crystals were grown by standing a concentrated hexane solution at −30 °C for 16 h. Anal. Calcd for $C_{20}H_{28}F_4IrP$: C, 42.32; H, 4.97. Found: C, 42.33; H, 4.88. ^{1}H NMR (C_6D_6, 300 MHz, 21 °C): δ −17.17 (br, d, $^2J_{HP}$ = 35 Hz, 1H, Ir−H), 0.88 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_2CH_3), 0.98 (d, br, $^2J_{HP}$ = 9.9 Hz, 9H, PMe_3), 1.66 (br, 3H, C_5Me_4Et), 1.67 (br, 3H, C_5Me_4Et), 1.70 (br, 3H, C_5Me_4Et), 1.71 (br, 3H, C_5Me_4Et), 2.08 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CH_3), 7.43 (br, 1H, C_6F_4H); a minor isomer was distinguishable only as a broad hump at −16.2 ppm. ^{19}F NMR (C_6D_6, 282.2 MHz, 21 °C): δ −167.1 (br, *p*-C_6F_4H), −160.6 (br, *m*-C_6F_4H), −145.2 (br, *m*-C_6F_4H), −113.9 (br, *o*-C_6F_4H); a minor isomer was distinguishable as small broad peaks at −159.4, −146.0, and −109.0 ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz, 21 °C): δ −44.2 (br); a minor isomer was distinguishable as a broad hump at −42.5 ppm.

Ir(C_5Me_4Et)(η^2-3,4,5-C_6F_3H)(PMe_3) (21). To a solution of Ir(C_5Me_4Et)(2,3,4,5-C_6F_4H)(PMe_3)H (**20**; 126 mg, 0.222 mmol) in hexanes (15 mL) was added a solution of *n*-BuLi in hexanes (0.8 mL, 2.8 M, 2.2 mmol). The mixture was stirred for 22 h to give a yellow cloudy solution. The mixture was cooled in an ice bath, MeOH (2 mL) was added, and then the volatiles were removed in vacuo. The solid residue was extracted into hexanes and filtered. The filtrate was reduced in vacuo to a pale brown oil. Yield: 120 mg, 99%. Crystals were obtained by allowing a concentrated hexanes solution to stand at −30 °C for 24 h. Anal. Calcd for $C_{20}H_{27}F_3IrP$: C, 43.87; H, 4.97. Found: C, 43.96; H, 5.09. ^{1}H NMR (C_6D_6, 300 MHz, 21 °C): δ 0.72 (d, $^2J_{HP}$ = 9.9 Hz, 9H, PMe_3), 0.93 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_2CH_3), 1.67 (d, $^4J_{HP}$ = 1.8 Hz, 3H, C_5Me_4Et), 1.68 (d, $^4J_{HP}$ = 1.8 Hz, 3H, C_5Me_4Et), 1.71 (d, $^4J_{HP}$ = 1.8 Hz, 6H, C_5Me_4Et), 2.06 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CH_3), 7.43 (dddd, $^3J_{HF}$ = 3 Hz, $^4J_{HF}$ = 3 Hz, $^5J_{HF}$ = 3 Hz, $^4J_{HP}$ = 0.9 Hz, 1H, C_6F_3H). ^{19}F NMR (C_6D_6, 282.2 MHz, 21 °C): δ −161.2 (ddd, $^3J_{FF}$ = 29.1 Hz, $^3J_{FF}$ = 10.7 Hz, $^4J_{FH}$ = 3.1 Hz, *m*-C_6F_3H), −141.2 (d, $^3J_{FF}$ = 29.1 Hz, *o*-C_6F_3H), −136.8 (dd, $^3J_{FF}$ = 10.7 Hz, $^3J_{FH}$ = 3 Hz, *m*-C_6F_3H). ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz, 21 °C): δ − 35.8 (d, $^4J_{PF}$ = 1.6 Hz).

Crystallographic Structural Determinations. Crystal data and data collection and refinement parameters are collected in Table 1. Systematic absences in the diffraction data for **2** and **11**−**13** and statistics of intensity for **3**, **9**, **14**, **15**, **18**, and **19** are uniquely consistent for the reported space groups and yielded chemically reasonable and computationally stable results on refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. SADABS absorption corrections[47] were applied to all structures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions.

Compounds **11** and **14** crystallized with two independent molecules in the asymmetric unit. In compound **14** the single ortho fluorine is disordered in each molecule between locations F(21) and F(61). The disorder was successfully modeled with an F(21)/F(61) occupancy ratio of 0.70/0.30 in molecule 1 and 0.59/0.41 in molecule 2.

All software and sources of scattering factors are contained in the SHELXTL program libraries (various versions, G. Sheldrick, Bruker AXS, Madison, WI).

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Supporting Information Available: Tables giving atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for complexes **2**, **3**, **9**, **11**−**15**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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