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Unusual Reactivity of “Proton Sponge” as a Hydride Donor to Transition Metals: Synthesis and Structural Characterization of Fluoroalkyl(hydrido) Complexes of Iridium(III) and Rhodium(III)

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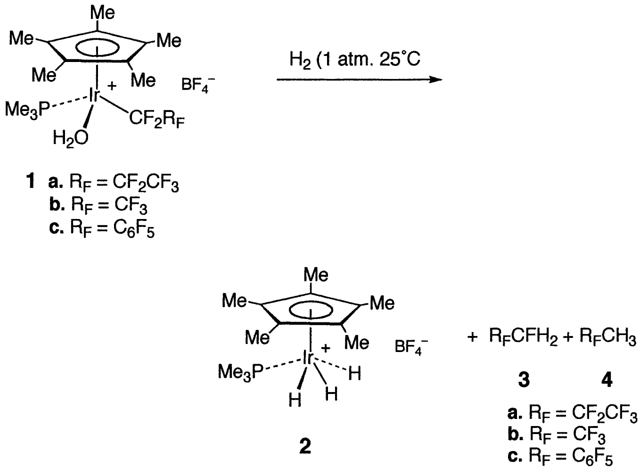
Attempts to prepare fluoroalkyl(hydrido) complexes of iridium by reactions of $[Ir(C_5Me_5)(PMe_3)(R_F)I]$ $\{R_F = CF_2CF_2CF_3, CF(CF_3)_2\}$ with either $NaBH_4$ or $LiAlH_4$ afford (inter alia) iridium hydrides $[Ir(C_5Me_5)(PMe_3)(CH{=}CFCF_3)H]$ or $[Ir(C_5Me_5)(PMe_3)(C\{CF_3\}{=}CF_2)H]$, in which the fluoroalkyl groups are converted to unsaturated ligands via apparent α-CF activation and elimination of HF. A clean and selective route to desired saturated fluoroalkyl(hydrido) complexes $[Ir(C_5Me_5)(PMe_3)(R_F)H]$ $\{R_F = CF_2CF_2CF_3, CF_2CF_3, CF(CF_3)_2\}$ is afforded by treatment of the aqua cations $[Ir(C_5Me_5)(PMe_3)(R_F)(H_2O)]BF_4$ with 1,8-bis(dimethylamino)naphthalene (“Proton Sponge”). The reaction also affords the corresponding rhodium analogue $[Rh(C_5Me_5)(PMe_3)(CF_2CF_2CF_3)H]$ from the corresponding aqua precursor. The source of the hydride is unambiguously defined as an $N{-}CH_3$ group by using the perdeuteromethylated analogue of Proton Sponge, which provides clean routes to the corresponding fluoroalkyl(deutero) complexes of iridium. Triethylamine or cobaltocene also effect this reaction, though not as cleanly as Proton Sponge. The mechanism of this novel transformation is discussed. The fluoroalkyl(hydrido) complexes are thermally robust, but do react with chlorinated solvents to give the corresponding chlorides. Single-crystal X-ray diffraction studies of the structures of $[Ir(C_5Me_5)(PMe_3)(CF_2CF_2CF_3)H]$, $[Rh(C_5Me_5)(PMe_3)(CF_2CF_2CF_3)H]$, and $[Rh(C_5Me_5)(PMe_3)(CF_2CF_2CF_3)Cl]$ are reported and compared.

Introduction

Recently we reported preliminary results on the hydrogenolysis of carbon fluorine bonds in a position α to iridium by reaction of the water complexes **1** with excess molecular hydrogen to give the trihydride **2** and the hydrofluorocarbons **3** and **4**.[1] Analogous results were observed for secondary fluoroalkyl ligands.[1] We speculated that a key intermediate in that process was the dihydrogen complex **5**. Clearly, the same intermediate could be generated by protonation of the corresponding iridium hydrides **6**, and we demonstrated that this was indeed the case.[1] To carry out isotopic labeling studies of this reaction, we required access to a series of primary and secondary fluoroalkyl iridium hydrides **6** and **7** and their deuterated analogues **8** and **9**. As described below, conventional approaches to these compounds were not always selective, and here we report more fully on a rather novel route to these compounds and a rhodium analogue.



Transition metal hydrides play important roles in many homogeneous catalytic cycles and are commonly prepared by oxidative addition of H_2 or H−heteroatom bonds to a low-valent metal center or by reduction of metal halides with hydride donors such as BH_4^-.[2−5] Perfluoroalkyl(hydrido) complexes of the transition metals are rare,[6−9] and we are unaware of any previously reported iridium(III) or rhodium(III) systems. Alkyl-

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[†] Dartmouth College.

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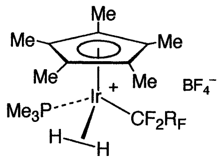
10.1021/om0102347 CCC: $20.00



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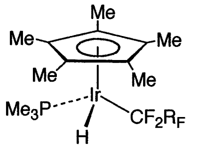
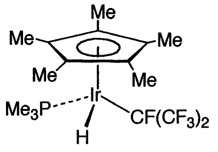


6 **a.** $R_F = CF_2CF_3$
b. $R_F = CF_3$



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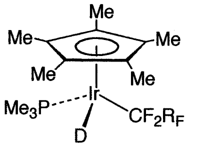
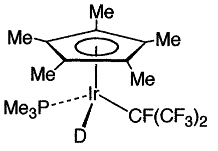


8 **a.** $R_F = CF_2CF_3$
b. $R_F = CF_3$



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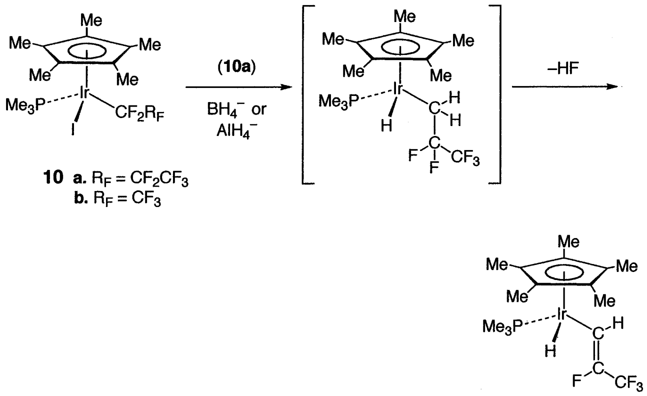
(hydrido) complexes of iridium(III)[10] and rhodium(III)[11] have also been approached by oxidative addition of alkane CH bonds to the MCp*(PMe_3) fragment, but can also be generated by alternative routes. One such approach is through alkylation of [Ir(η^5-C_5Me_5)(PMe_3)H]-Li using RX;[12,13] this kind of route is likely to be unsatisfactory for fluoroalkyl analogues R_F−I due to the unfavorable polarity of the C−I bond.[14] Another logical approach would be by reduction of Ir(η^5-C_5Me_5)(PMe_3)-(R)X (X = Br, Cl) by $NaBH_4$.[3] We have used this method to prepare a variety of fluoroalkyl(hydrido) complexes of platinum,[15] and it was our first choice in attempting to synthesize our target compounds **6**−**9**. Herein is described our woeful lack of success in this specific endeavor, along with our serendipitous discovery of a very clean and selective route to iridium and rhodium analogues.

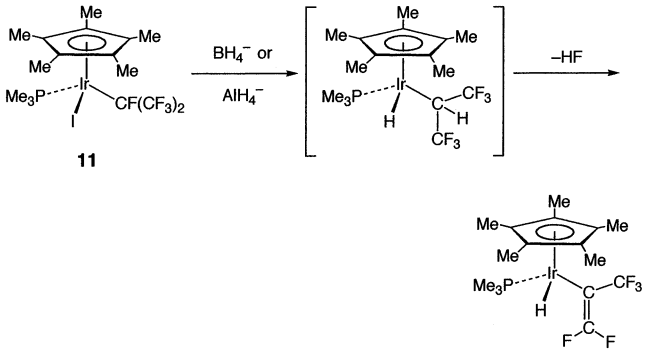
Results and Discussion

Synthesis of Hydrides. Treatment of the fluoroalkyl(iodo) complex **10a**[16] with $NaBH_4$ in refluxing THF for 2 days did produce the desired hydride **6a**, but the reaction frequently afforded product of variable purity, contaminated by other metal hydride species that were difficult to separate. Longer reaction times result in the formation of mixtures containing unsaturated fluoroalkenyl ligands, such as **12** from **10a**, and **13** from the corresponding reaction of **11**. These compounds are the principal fluorine containing products when $LiAlH_4$ is used instead of $NaBH_4$, along with the known dihydride IrCp*(PMe_3)($H)_2$. In addition, attempts to extend this using $NaBD_4$ usually resulted in a mixture of the desired deuteride **8a**, contaminated by sometimes significant amounts of the corresponding hydride **6a**. The source of the hydride may be the solvent; repetition of the reaction in THF-d_8 afforded the desired deuteride **8a**, but still contaminated with other metal deuterides.



10 **a.** $R_F = CF_2CF_3$
b. $R_F = CF_3$

12



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Compounds **12** and **13** were unambiguously characterized using NMR spectroscopy. Each shows characteristic Cp* and PMe_3 peaks in the ^1H NMR spectrum along with hydride resonances at δ −16.6 ppm (J_{PH} = 36 Hz) (**12**) and −17.2 ppm (J_{PH} = 37 Hz) (**13**). In addition, **12** exhibits a resonance at δ 7.7 ppm with a strong doublet coupling to a single fluorine (J_{FH} = 59 Hz); the corresponding fluorine resonates in the ^{19}F NMR spectrum at δ −122.4 as a doublet of quartets (J_{FH} = 59; J_{FF} = 14 Hz), along with the CF_3 group at δ −69.4 ppm. Compound **13** exhibits strongly coupled resonances at δ −64.4 and −74.6 due to the geminal CF_2 fluorines, with the higher field resonance also showing coupling to ^{31}P. The CF_3 appears as a doublet of doublets of doublets from coupling to each of the CF fluorines and also to the hydride. The ^{19}F−^{19}F NMR coupling pattern is analogous to that observed in β,β-difluoro-α-(trifluoromethyl)styrenes.[17] In their IR spectra, complexes **12**

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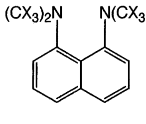
and **13** show hydride stretches at 2096 and 2123 cm^{-1} and C$=$C stretches at 1716 and 1673 cm^{-1}, respectively.

Any mechanisms for formation of **12** and **13** require conversion of the α-CF bonds to CH bonds, followed by elimination of HF, as shown. Clearly the α-CF bonds in these fluoroalkyl complexes of iridium are considerably more susceptible to this reaction than are those in platinum(II) analogues, in which BH_4^- reduction occurs only at the metal center, leaving the CF bonds intact. Reasons for this different reactivity are currently unclear, but, regardless of their nature, treatment of fluoroalkyl(iodo) complexes of iridium with conventional hydride reducing agents is not an unfailingly reliable method for formation of the desired fluoroalkyl(hydrido) complexes.

Salvation in this endeavor was provided from a most unexpected source. While attempting to deprotonate the cationic aqua complexes **1a**,**b**[1] with various bases, we attempted the reaction with 1,8-bis(dimethylamino)-naphthalene (**14**), commonly called "Proton Sponge" because of its unusually high basicity and low nucleophilicity.[18-22] The high basicity of Proton Sponge arises from a combination of the repulsion of the proximate lone pairs on the peri-dimethylamino groups and the high stability of the intramolecular hydrogen bond formed when the base is monoprotonated.[19,22,23] Instead of the expected behavior, we observed that treatment of **1a**,**b** with Proton Sponge in benzene solution resulted in clean formation of the desired fluoroalkyl(hydrido) complexes **6a**,**b** along with precipitation of the known 1,1,3-trimethyl-2,3-dihydroperymidinium tetrafluoroborate salt **15**,[24] easily identified by its NMR spectrum. The source of the hydrido ligand in the products was unambiguously defined as an *N*-methyl group of the Proton Sponge by using the fully perdeuteromethylated analogue **16**.[25] Reactions of **1a**,**b** with this reagent afforded **17** and the corresponding deuterides **8a**,**b**, thereby providing a very clean route to these isotopically labeled compounds. This method also works well for secondary fluoroalkyls, and the aqua complex **18** is cleanly converted into either **7** or **9**. One rhodium analogue has also been prepared by conversion of the aqua cation **19**[26] into hydrido complex **20**.

This constitutes a clean and selective method for formation of hydrides and deuterides of these fluoroalkyl complexes. Workup is especially easy: by using a slight molar deficiency of Proton Sponge the highly soluble hydrides can easily be separated from the slight excess of aqua complex starting material and product salt **15** by simple extraction into hexanes.



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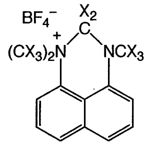
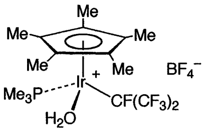
16 X = D



15 X = H
17 X = D



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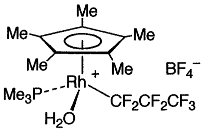

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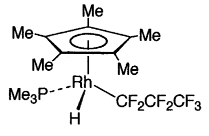

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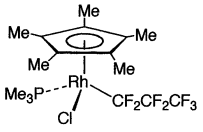

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Spectroscopic, Chemical, and Crystallographic Characterization of Hydrides. These new hydrido complexes have been characterized by a combination of crystallographic, chemical, and spectroscopic methods. All four complexes exhibited characteristically strong $\nu_{\mathrm{M-H}}$ bands at 2046 (**6a**), 2048 (**6b**), 2010 (**7**), and 2015 (**20**) cm^{-1}. All four complexes exhibited characteristic ^{1}H resonances for the hydride; that in the rhodium hydride complex **20** appears as a doublet of doublets at δ −13.20 ppm ($J_{\mathrm{PH}} = 46$ Hz, $J_{\mathrm{HRh}} = 29$ Hz), and those in the three iridium hydride complexes **6a**, **6b**, and **7** appear as doublets at δ −17.46 ppm ($J_{\mathrm{PH}} = 35$ Hz), −17.48 ppm ($J_{\mathrm{PH}} = 37$ Hz), and −17.72 ppm ($J_{\mathrm{PH}} = 38$ Hz), respectively. There is no significant coupling between the M−H and the fluorines of the fluoroalkyl group. In the corresponding deuterides **8** and **9** the ^{2}H NMR spectrum shows the deuterium resonance as a doublet with $J_{\mathrm{PD}} \approx 6$ Hz, as expected. Since the metal in each complex is a stereocenter, each CF_2 group in the perfluoro-*n*-alkyl complexes contains diastereotopic fluorines, each pair of which appears as a strongly coupled AX or AB spin system in the ^{19}F NMR spectra. In compounds **6a**,**b** and **20** one fluorine of the α-CF_2 group couples strongly to ^{31}P, and the other coupling is close to zero, such that the $^{31}P\{^1H\}$ NMR spectrum appears as a large doublet, sometimes with a very small additional doublet coupling. In the corresponding deuterides the $^{31}P\{^1H\}$ NMR spectrum appears as a doublet of (1:1:1) triplets due to coupling with one fluorine and one deuterium, as expected. In C_6D_6 the two diastereotopic CF_3 groups of **7** appear isochronously as a broad single ^{19}F resonance, but in CD_3OD the expected two ^{19}F resonances were observed.

The compounds are slightly air sensitive, particularly in the case of the rhodium compound **20**, but seem to be relatively robust thermally, since they can be heated at 90 °C for several days in C_6D_6 without noticeable signs of decomposition. However, chlorinated solvents will easily convert the metal hydride complexes into metal chloride complexes, as observed with many other metal hydrides.[2] This reaction is qualitatively faster for rhodium than for iridium and occurs quite quickly in methylene chloride solution. Addition of even a drop of CH_2Cl_2 to a benzene solution of **20** slowly, but quantitatively, converts it to the chloro complex **21**, which was characterized crystallographically (see below) and spec-

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

	6a	**20**	**21**
formula	$C_{16}H_{25}F_7IrP$	$C_{16}H_{25}F_7PRh$	$C_{16}H_{24}ClF_7PRh$
fw	573.53	484.24	518.68
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	8.9511(14)	8.92220(10	8.899(2)
b, Å	13.321(3)	13.3832(2)	13.5478(8)
c, Å	17.123(8)	17.26060(10)	16.974(1)
α, deg	90	90	90
β, deg	102.98(2)	102.7672(2)	92.57(1)
γ, deg	90	90	90
V, Å^3	1989.5(11)	2010.17(4)	2044.3(5)
Z	4	4	4
D(calcd), g/cm^3	1.915	1.600	1.685
abs coeff, cm^{-1}	68.50	9.87	11.03
temp, K	293(2)	223(2)	298(2)
diffractometer	Siemens P4	Siemens P4/CCD	Siemens P4
radiation		Mo Kα 0.71073 Å	
$R(F)$, %^{a}	4.65	4.14	3.24
$R(wF^2)$, %^{a}	9.70	12.72	7.70

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

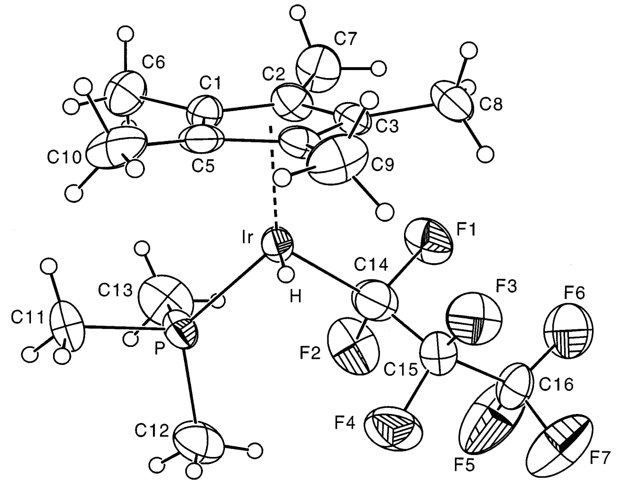


Figure 1. ORTEP diagram of the non-hydrogen atoms of **6a**, showing atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Ir−C(14), 2.09(2); Ir−P, 2.226(4); Ir−CNT, 1.896(3); C(14)−F(1), 1.43(2); C(14)−F(2), 1.40(2); CNT−Ir−P, 131.48(4); CNT−Ir−C(14), 127.17(3); C(14)−Ir−P, 89.8(6); F(2)−C(14)−F(1), 98.6(15); C(15)−C(14)−Ir, 119.3(18).

troscopically. This appears to be a rare example of such a reaction involving methylene chloride rather than the more common CCl_4 or $CHCl_3$.[2] The corresponding reactions of the iridium analogues are much slower, and we have not attempted to isolate the corresponding chlorides. The chloro complex **21** can also be prepared by treatment of the aqua precursor **19** with sodium chloride.

The molecular structures of hydrido complexes **6a** and **20** were also confirmed by single-crystal X-ray diffraction studies, along with that of the chloro complex **21**. Details of the structural determination are provided in Table 1, and ORTEP diagrams for each structure, along with selected bond lengths and angles, are presented in Figures 1−3. The positions of the hydride atoms were not located, but were fixed at 1.603 and 1.580 Å in **6a** and **20**, respectively. The metal−fluoropropyl distances are not significantly different [for **6a** Ir−C(14) = 2.09(2), for **20** Rh−C(11) = 2.076(4), and for **21** Rh−C(11) = 2.073(5)] and are also not significantly different from the corresponding Ir−C distance to the fluoropropyl ligand [2.098(8) Å] in the iodo complex **10a**.[16] The metal−phosphorus distances are significantly different, with that in the iridium complex **6a** [2.226(4) Å] being slightly shorter than in its rhodium analogue **20** [2.2437(9) Å], which in turn is slightly shorter than that in the corresponding chloride complex **21** [2.2971(13) Å]. That in **10a** is longer still, at 2.307(2) Å,[16] suggesting that steric interactions of the PMe_3 with the adjacent H, Cl, and I ligands may be responsible for these differences. The perfluoropropyl ligands exhibit the typical pattern of acute F−C−F angles at the α-CF_2

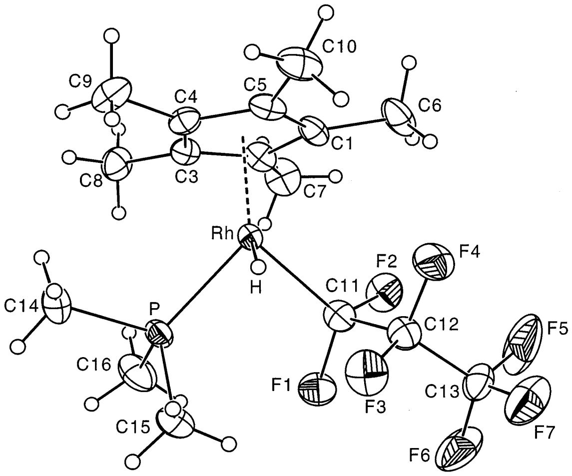


Figure 2. ORTEP diagram of the non-hydrogen atoms of **20**, showing atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Rh−C(11), 2.076(4); Rh−P, 2.2437(9); Rh−CNT, 1.914(4); C(11)−F(2), 1.389(5); C(11)−F(1), 1.401(4); CNT−Rh−C(11), 127.48(5); CNT−Rh−P, 131.27(5); C(11)−Rh−P, 91.29(12); F(2)−C(11)−F(1), 102.1(3); C(12)−C(11)−Rh, 116.9(3).

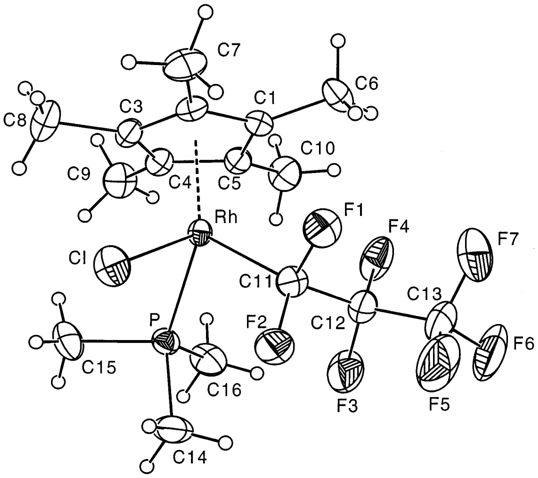
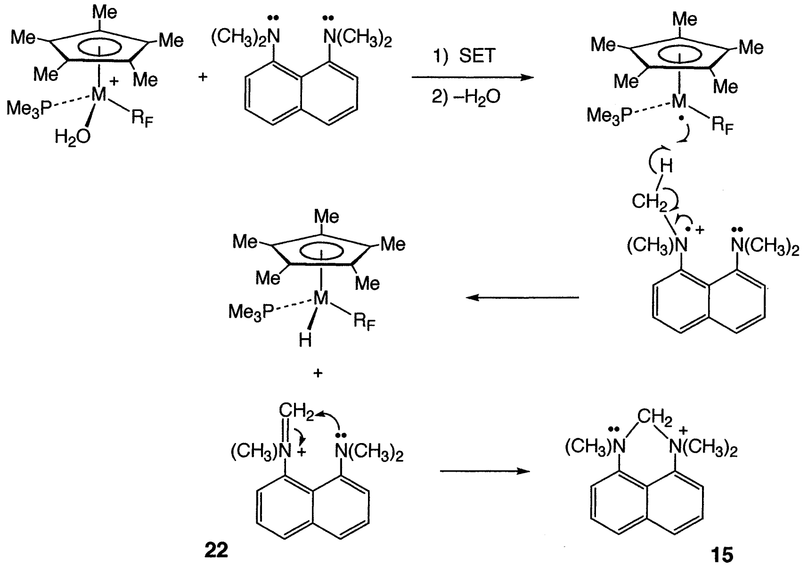


Figure 3. ORTEP diagram of the non-hydrogen atoms of **20**, showing atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Rh−C(11), 2.073(5); Rh−P, 2.2971(13); Rh−Cl, 2.252(4); Rh−CNT, 1.875(4); C(11)−F(1), 1.387(5); C(11)−F(2), 1.383(5); CNT−Rh−C(11), 127.60(5); CNT−Rh−P, 128.55(5); CNT−Rh−Cl, 119.31(5); C(11)−Rh−P, 93.93(14); C(11)−Rh−Cl, 95.0(2); F(2)−C(11)−F(1), 102.5(4); C(12)−C(11)−Rh, 120.4(3).

Scheme 1



[98.6(15)° for **6a**, 102.1(3)° for **20**, 102.5(4)° for **21**] and obtuse M−C−C angles [119.3(18)° for **6a**, 116.9(3)° for **20**, 120.4(3)° for **21**] previously observed and discussed for other fluoroalkyl compounds.[16,27] The perfluorinated ligand in the hydrido complexes **6a** and **20** adopts a conformation in which the β-carbon is syn to the hydride position, while that in the chloro analogue **21** adopts a conformation in which the β-carbon is anti to the chloro ligand, analogous to that observed in the iodo(iridium) analogue **10a**.[16] Once again this suggests that steric interactions dominate this conformational choice.

Mechanism of Hydride Formation. How does Proton Sponge effect this transformation? The literature contains a report of an apparently analogous reaction of Proton Sponge with *mer*-$RhCl_3(DMSO)_3$ which generates the cation of **15**, isolated as a salt with the anion *trans*-$[RhCl_4(DMSO)_2]^-$.[24] Although no Rh(I) species were isolated, the air sensitivity of the filtrate was taken by the authors to imply the presence of low-valent species. The same authors described a similar dehydrogenation reaction of *mer*-$RhCl_3(DMSO)_3$ in the presence of triethylamine that results in the formation of a ylidic enamine complex.[28] The authors suggest identical mechanisms for both transformations involving initial coordination of the amine to the metal, followed by deprotonation of an $N-CH_3$ group by free amine and a concerted electron transfer to the Rh(III).[24] In our case, this seems unlikely for several reasons. Coordination of an amine nitrogen to the metal appears to violate the very design features of Proton Sponge in that quaternization of nitrogen with anything more bulky than a proton is strongly disfavored. While the steric crowding of the *peri*-amino groups restricts its ability to act as a nucleophile through the nitrogen atoms,[29−31] it has been reported to act as a carbon nucleophile in certain instances; with very strong electrophiles[32,33] and coordinated alkenes,[34] nucleophilic substitution has been observed at the 4-position. We observe no such reactivity. Moreover, involvement of Proton Sponge in a deprotonation reaction would generate the conjugate acid of Proton Sponge in a reaction that is quite likely to be irreversible;[19,23] we observe no such product.

However, Proton Sponge has been reported to undergo fairly easy one-electron oxidation with an oxidation potential measured as +0.36 V with reference to the SCE in CH_3CN[35] (+0.10 V vs ferrocenium/ferrocene).[36] Consequently, an alternative mechanism might involve an outer sphere electron transfer reaction, as shown in Scheme 1, to give the 19-electron metal radical and the radical cation of the amine. Rapid loss of H_2O followed by H atom abstraction from the amine methyl group by iridium affords the metal−H bond and the iminium cation **22**, which is rapidly trapped intramolecularly by the remaining adjacent tertiary amine to produce the product **15**. A redox process to give metal hydrides from aqua complexes is not unprecedented, as the electrochemical or chemical reductions of $[Rh(\eta^5\text{-}C_5Me_5)(2,2'\text{-bipyridine})(H_2O)]^{2+}$ complexes have been shown to give metal hydrides as intermediates.[37]

We do not know the reduction potentials of these cationic aqua complexes, but the oxidation potential of Proton Sponge is lower than that for NEt_3, which is ca. 0.47 V vs $[FeCp_2]^+/[FeCp_2]$ in CH_3CN.[36] Not unexpectedly, NEt_3 also reacts with **1a** to afford the hydride **6a**, with the resultant iminium cation $[Et_2C{=}NHCH_3]^+$, which cannot be trapped intramolecularly as occurs with **22**, instead being hydrolyzed by the liberated water to produce acetaldehyde and the ammonium salt $Et_2NH_2^+$,

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each of which was unambiguously characterized. This mode of reactivity for NEt_3 has been described previously.[28] However, NEt_3 could react by an inner sphere mechanism with prior coordination, as suggested by previous authors.[28] To provide an unambiguous demonstration of the possibility of an outer sphere redox pathway, THF solutions of the iridium aqua complexes **1a** and **18** were treated with the reducing agent cobaltocene ($E° = -1.33$ V vs ferrocene/ferrocenium in CH_2Cl_2).[36] Cobaltocene typically reacts by an outer sphere mechanism and would not be expected to coordinate with the iridium complex.[36] Formation of the corresponding hydride complexes **6a** and **7** was observed, with the cobaltocene being oxidized to $[Co(\eta^5\text{-}C_5H_5)_2]BF_4$. The source of the hydride was not investigated in these systems, but is presumably the solvent. Consequently, we feel more comfortable in proposing an outer sphere pathway as a realistic option for the Proton Sponge reaction. It should be pointed out that while each of these alternative methods does indeed produce the hydride, the Proton Sponge method is far superior in terms of ease of workup (vide supra). In addition, the organometallic hydride products are acid sensitive and the ammonium salt produced from NEt_3 has a deleterious effect on the overall yields and purity of the product.

Conclusions

A selective and efficient method for the synthesis of fluoroalkyl(hydrido) complexes of rhodium and iridium, and some deuterated analogues, has been developed using Proton Sponge as the hydride source. It is far superior to conventional reagents such as $NaBH_4$ and $LiAlH_4$ for making the metal−hydride bonds in these particular systems.

Experimental Section

General Considerations. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen that has been deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun drybox. Methylene chloride, hexane, diethyl ether, and toluene were deoxygenated and dried over activated alumina using an apparatus modified from that described in the literature.[38] Benzene was distilled under nitrogen from potassium benzophenone ketyl. IR spectra were recorded on a Perkin-Elmer FTIR 1600 Series spectrometer. NMR spectra were recorded on a Varian Unity Plus 300 FT spectrometer. ^1H 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). $^{31}P\{^1H\}$ NMR spectra were referenced to 85% H_3PO_4 (0.00 ppm). $ICF(CF_3)_2$ and $ICF_2CF_2CF_3$ (Lancaster) were washed with sodium thiosulfate to remove residual iodine, then vacuum distilled and deoxygenated by several cycles of freeze−pump−thaw. Proton Sponge (Aldrich), cobaltocene (Strem), triethylamine (Aldrich), and $LiAlH_4$ and $NaBH_4$ (Aldrich) were used as received. Rhodium and iridium complexes $[MCp^*(PMe_3)(R_F)I]$ and $[MCp^*(PMe_3)(R_F)(H_2O)]BF_4$ were prepared according to literature procedures.[16,26] 1,8-Diaminonaphthalene and dimethyl sulfate-d_6 were purchased from Aldrich.

Proton Sponge-d_{12} was prepared by a modification of the published route.[25] 1,8-Diaminonaphthalene was purified by sublimation under vacuum (60 °C/10^{-3} mbar) onto a receiver cooled to −78 °C; Dimethyl sulfate-d_6 was used without further purification. 1,8-Diaminonaphthalene (2.178 g, 13.77 mmol) was dissolved in THF (40 mL). NaH (2.1 g, 87.51 mmol) was added, and the solution was heated to reflux. Dimethyl sulfate-d_6 (10 g, 99.82 mmol) was added dropwise during 45 min. The mixture was refluxed for an additional 2.5 h and then stirred overnight at ambient temperature. The solution was treated with MeOH (5 mL), a solution of NaOH (4 g) in H_2O (15 mL), and finally H_2O (10 mL). The solution was washed with pentane (150 mL) and ether (3 × 120 mL). The organic solutions were collected, dried over sodium carbonate, and evaporated. The product was purified by column chromatography (*n*-pentane/silica, 15 cm × 3 cm), followed by crystallization from pentane at −70 °C. If necessary, the product can be sublimed under vacuum (70 °C/10^{-3} mbar) onto a receiver cooled to −78 °C. Yield: 1.93 g (61%) of colorless crystals. ^2H NMR (CH_2Cl_2): δ 3.02 (6D, s, CD_3). ^1H NMR showed no discernible proton impurity in the *N*-methyl groups.

$Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(CF_2CF_2CF_3)H$ (6a). (a) Using Proton Sponge. Compound **1a** (50 mg, 0.087 mmol) was suspended in benzene (5 mL) to give a yellow slurry. Proton sponge (18 mg, 0.080 mmol) was added, and the mixture stirred for an hour. By this time, the color of the reaction mixture had darkened to orange with formation of a white precipitate. The precipitate was removed by filtration, and the solvent was removed from the filtrate in vacuo to give a dark solid. Extraction of the solid with hexanes, filtration, and evaporation of the filtrate afforded **6a** as a pale yellow solid (40 mg, 93%). A crystal suitable for X-ray diffraction was grown by slow evaporation of a hexane solution. ^1H NMR (C_6D_6): δ 1.76 (d, $J_{PH} = 2$, 15H, C_5Me_5), 1.18 (d, $J_{PH} = 11$, 9H, PMe_3), −17.46 (d, $J_{PH} = 35$, 1H, Ir-H). ^{19}F NMR (C_6D_6): δ −69.57 (d, $^2J_{FF} = 277$, 1F, $C_\alpha F_A$), −71.51 (d, $^2J_{FF} = 277$, 1F, $C_\alpha F_B$), −78.04 (t, $J_{FF} = 13$, 3F, CF_3), −113.41 (d, $^2J_{FF} = 281$, 1F, $C_\beta F_A$), −117.71 (d, $^2J_{FF} = 281$, 1F, $C_\beta F_B$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −39.01 (ddd, $J_{PF} = 46$, 3, 2, PMe_3). IR (KBr): ν(Ir−H) 2020 cm^{-1}. Anal. Calcd for $C_{22}H_{16}F_7IrP$ (573.53): C, 33.50; H, 4.39. Found: C, 33.29; H, 4.16.

(b) Using Cobaltocene. Compound **1a** (50 mg, 0.087 mmol) was suspended in benzene (5 mL) to give a yellow slurry. Cobaltocene (15 mg, 0.080 mmol) was added, and the mixture stirred for an hour. After an initial darkening the reaction mixture slowly changed in color to dark orange with formation of a yellow precipitate of $[CoCp_2]BF_4$. The solvent was removed by vacuum pumping to give a dark solid. Extraction with hexanes as above afforded **6a** (20 mg, 47%).

(c) Using $NaBH_4$. Compound **1a** (70 mg, 0.10 mmol) was dissolved in THF (5 mL), and $NaBH_4$ (18.9 mg, 0.50 mmol) in THF (10 mL) was added. The solution was freeze−pump−thawed, refluxed for 3 days, and then evaporated to dryness. Hexane was then used to extract the hydride, and filtrate was removed under vacuum to give impure **1a** as a pale yellow solid (59 mg, 97%).

$Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(CF_2CF_2CF_3)D$ (8a) was prepared similarly from **1a** and Proton Sponge-d_{12}. ^1H NMR (C_6D_6): δ 1.77 (d, $J_{PH} = 1.5$, 15H, C_5Me_5); 1.18 (d, $J_{PH} = 10.5$, 9H, PMe_3). ^2H NMR (C_6H_6): δ −17.3 (d, $J_{PD} = 5.1$, 1D, Ir-D). ^{19}F NMR (C_6D_6): δ −65.8 (dd, $^2J_{FF} = 277$, $J_{PF} = 48$, 1F, $C_\alpha F_A$); −68.8 (d, $^2J_{FF} = 277$, 1F, $C_\alpha F_B$); −78.4 (s, 3F, CF_3); −114.8 (d, $^2J_{FF} = 281$, 1F, $C_\beta F_A$); −117.0 (d, $^2J_{FF} = 281$, 1F, $C_\beta F_B$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −40.7 (dm, $J_{PF} = 48$, PMe_3).

$Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(CF_2CF_3)H$ (6b). Compound **1b** (100 mg, 0.16 mmol) was suspended in benzene (20 mL) and was subsequently treated with a solution of Proton Sponge (30.7 mg, 0.14 mmol) in benzene (5 mL). The reaction mixture was stirred for 2 h and then filtered. The solvent was removed from the filtrate in vacuo to give an orange-yellow solid residue. Hexane was used to extract the product. The hexane solution was filtered, and filtrate was pumped down to give **6b** as a pale yellow solid (66 mg, 88%). ^1H NMR (C_6D_6): δ 1.76 (d, J_{PH} = 2, 15H, C_5Me_5], 1.19 (d, $J_{PH} = 11$, 9H, PMe_3), −17.48 (br d,

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J_{PH} = 37, 1H, Ir-H). ^{19}F NMR (C_6D_6): δ −70.1 (dd, $^2J_{FF}$ = 273, J_{PF} = 48 Hz, 1F, $C_\beta F_A$), −72.5 (d, $^2J_{FF}$ = 273 Hz, 1F, $C_\beta F_B$), −84.5 (t, J_{FF} = 12 Hz, 3F, CF_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −39.1 (dd, J_{PF} = 45, J_{PF} = 11, PMe_3). IR (KBr): ν(Ir−H) = 2048 cm^{-1}. Anal. Calcd for $C_{15}H_{25}F_5IrP$ (523.55): C, 34.41; H, 4.81. Found: C, 34.26; H, 4.83.

Ir(η5-C_5Me_5)(PMe_3)(CF_2CF_3)D (8b) was prepared similarly from **1b** and Proton Sponge-d_{12}. ^{1}H NMR (C_6D_6): δ 1.21 (d, $^2J_{PH}$ = 10 Hz, 9H, PMe_3), 1.78 (d, $^3J_{PH}$ = 2, 15H, C_5Me_5). ^{2}H NMR (C_6H_6): δ −17.31 (d, $^2J_{PD}$ = 5, 1D, Ir-D); ^{19}F NMR (C_6D_6): δ −70.12 (dd, $^2J_{FF}$ = 274, $^3J_{PF}$ = 45, 1F, CF_2), −72.62 (d, $^2J_{FF}$ = 274, 1F, CF_2), −84.86 (s, 3F, CF_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −40.86 (dt, $^3J_{PF}$ = 45, $^2J_{PD}$ = 5, PMe_3).

Ir(η^5-C_5Me_5)(PMe_3)[CF(CF_3)$_2$]H (7). (a) Using Proton Sponge. Compound **18** (100 mg, 0.17 mmol) was suspended in benzene (5 mL), Proton Sponge (35 mg, 0.16 mmol) was added, and the mixture was stirred for an hour. By this time, the color of the reaction mixture had darkened to orange with formation of a white precipitate. The precipitate was filtered, and the solvent was removed from the filtrate in vacuo to give a dark solid. Hexane was added to the dark solid to extract the final product. The hexane solution was filtered, and filtrate was pumped down to give **7** as a pale yellow solid (51 mg, 62%). ^{1}H NMR (C_6D_6): δ 1.67 (s, 15H, C_5Me_5); 1.21 (d, J_{PH} = 11, 9H, PMe_3), −17.72 (d, J_{PH} = 38, 1H, Ir-H). ^{19}F NMR (C_6D_6): δ −71.23 (s, 6F, CF_3), −163.29 (br s, 1F, CF). ^{31}P{^{1}H} NMR (C_6D_6): −41.77 (br s, PMe_3). IR (KBr), ν(Ir−H) 2010 cm^{-1}. Anal. Calcd for $C_{22}H_{16}F_7IrP$ (573.53): C, 33.51; H, 4.39. Found: C, 33.86; H, 4.22.

(b) Using Cobaltocene. Compound **18** (100 mg, 0.17 mmol) was suspended in benzene (5 mL), cobaltocene (31 mg, 0.16 mol) was added, and the mixture was stirred for an hour. After an initial darkening, the reaction mixture slowly changed in color to dark orange with formation of a yellow precipitate of [$CoCp_2$](BF_4). The solution was filtered though an EtOAc-deactivated silica gel column to give a yellow solution, which was evaporated to afford **7** as a yellow solid (27 mg, 31%).

(c) Using Triethylamine. Compound **18** (20 mg, 30 μmol) was slurried in benzene (10 mL) and triethylamine (5 μL, 33 μmol) was added via a syringe. The reaction mixture was stirred at room temperature for an hour. The volatiles were then transferred under vacuum to another Schlenk flask cooled to −78 °C. The presence of acetaldehyde was confirmed by NMR spectroscopy and GC/MS. The residue was subjected to NMR analysis and showed the presence of **7** along with $Et_2NH_2^+BF_4^-$.

(d) Using $NaBH_4$. Compound **11** (70 mg, 0.10 mmol) was dissolved in THF (5 mL). $NaBH_4$ (17.8 mg, 0.47 mmol)/THF (10 mL) was added into the iridium complex solution. The solution was refluxed overnight. Then the solution was pumped down. Hexane was added to extract the product. Hexane solution was filtered, and filtrate was pumped down to give some pale yellow solid (38 mg, 62%), which proved to be almost pure **7** contaminated with traces of **13**.

Ir(η^5-C_5Me_5)(PMe_3)[CF(CF_3)$_2$]D (9) was prepared similarly from **18** and Proton Sponge-d_{12}. ^{1}H NMR (C_6D_6): δ 1.65 (s, 15H, C_5Me_5); 1.18 (d, J_{PH} = 11, 9H, PMe_3). ^{2}H NMR (C_6H_6): δ −17.5 (d, J_{PD} = 6.1, 1D, Ir-D). ^{19}F NMR (C_6D_6): δ −71.2 (s, 6F, CF_3), −163.3 (br s, 1F, CF). ^{31}P{^{1}H} NMR (C_6D_6): −42.6 (m, PMe_3).

Rh(η^5-C_5Me_5)(PMe_3)($CF_2CF_2CF_3$)H (20). Using Proton Sponge. A suspension of compound **19** (96 mg, 0.16 mmol) in benzene (5 mL) was treated with a solution of Proton Sponge (34 mg, 0.16 mmol) in benzene (5 mL). The mixture was stirred for 1 h at room temperature, during which time the color changed from orange-yellow to pale yellow with the formation of some white precipitate. The solution was filtered, the filtrate evaporated, and the residue was extracted with ether and filtered. The ether was removed under vacuum to give **20** as a yellow solid (63 mg, 80%). ^{1}H NMR (C_6D_6): δ 1.73 (s, C_5Me_5), 1.02 (d, J_{PH} = 10.3, PMe_3), −13.20 (dd, J_{PH} = 46, J_{RhH} = 29, Rh-H). ^{19}F NMR (C_6D_6): δ −71.4 (dd, $^2J_{FF}$ = 270, J_{PF} = 48, 1F, α-CF_2), −74.4 (d, $^2J_{FF}$ = 270, 1F, α-CF_2), −78.6 (t, J_{FF} = 12, 3F, CF_3), −115.3 (d, $^2J_{FF}$ = 283, 1F, β-CF_2), −117.2 (d, $^2J_{FF}$ = 283, 1F, β-CF_2). ^{31}P{^{1}H} NMR (C_6D_6): δ 8.3 (ddt, J_{RhP} = 153, J_{PF} = 49, J_{PF} = 12, PMe_3). IR (CH_2Cl_2): ν(Rh−H) 2015 cm^{-1}.

Rh(η^5-C_5Me_5)(PMe_3)($CF_2CF_2CF_3$)Cl (21). (a) Compound **19** (10 mg, 0.017 mmol) was dissolved in $CDCl_3$ (0.5 mL) and transferred to an NMR tube. Proton Sponge (4 mg, 0.019 mmol) was added as a solid. The color of the solution changed immediately from an orange-yellow to yellow, and the NMR spectrum showed quantitative conversion to **21**.

(b) Compound **20** (20 mg, 0.041 mmol) was partially dissolved in C_6D_6 (0.7 mL) in an NMR tube, and CH_2Cl_2 (1 drop) was added. After 72 h, the hydride **20** had converted completely to the chloride **21**. Evaporation and extraction of the residue with ether, filtration, and evaporation afforded **21** as orange needles in 55% yield. ^{1}H NMR (C_6D_6): δ 1.36 (d, J_{RhH} = 3.2, C_5Me_5), 1.15 (d, J_{PH} = 11.0, PMe_3). ^{19}F NMR (C_6D_6): δ −74.7 (dm, $^2J_{FF}$ = 270, 1F, $C_\alpha F_A$), −78.8 (t, J_{FF} = 11, CF_3), −81.0 (dm, $^2J_{FF}$ = 273, 1F, $C_\alpha F_A$), −114.1 (dt, $^2J_{FF}$ = 285, J_{FF} = 13, 1F, $C_\beta F_A$), −116.3 (dt, $^2J_{FF}$ = 283, J_{FF} = 8, 1F, $C_\beta F_B$). ^{31}P{^{1}H} NMR (C_6D_6): δ 7.8 (ddd, J_{PRh} = 148, J_{PF} = 15, J_{PF} = 5, PMe_3). Anal. Calcd for $C_{16}H_{24}ClF_7PRh$: C, 37.05; H, 4.66. Found: C, 36.91; H, 4.83.

Preparation of (η^5-C_5Me_5)Ir[CH═CF(CF_3)](PMe_3)H (12). A mixture of (η^5-C_5Me_5)Ir(PMe_3)($^n C_3F_7$)I (**10a**) (33 mg, 0.047 mmol) and $LiAlH_4$ (8.2 mg, 0.215 mmol) in THF (5 mL) was stirred for an hour, during which time the solution changed from yellow to very pale yellow. $Na_2SO_4 \cdot 12H_2O$ was added to quench the excess $LiAlH_4$, the solution was filtered, and the solvent was evaporated. The residue was extracted with hexane and filtered, and the filtrate was evaporated to give a yellow solid, shown by its NMR spectra to contain mostly **12**, along with other unidentified metal hydrides. ^{1}H NMR (C_6D_6): δ 7.7 (d, J_{FH} = 59, ═CH), 1.8 (d, J_{PH} = 2, 15H, C_5Me_5), 1.1 (d, J_{PH} = 10, 9H, PMe_3), −16.6 (d, J_{PH} = 36, 1H, Ir-H). ^{19}F NMR (C_6D_6): δ −69.4 (d, J_{FF} = 13.8, 3F, CF_3), −122.4 (dq, J_{FH} = 59.8, J_{FF} = 13.8, 1F, ═CF). ^{31}P{^{1}H} NMR (C_6D_6): δ −43 (m, PMe_3). IR: (C_6H_6) ν_{Ir-H} 2096 cm^{-1}, $\nu_{C=C}$ 1716 cm^{-1}.

Preparation of (η^5-C_5Me_5)Ir[C(CF_3)═CF_2](PMe_3)H (13). A mixture of (η^5-C_5Me_5)Ir(PMe_3)($^i C_3F_7$)I (**11**) (33 mg, 0.047 mmol) and $NaBH_4$ (17.8 mg, 0.47 mmol) in ethanol (10 mL) was refluxed for 3 days. The solvent was removed under vacuum, and the residue was extracted with hexanes. Filtration and evaporation of the filtrate afforded a yellow solid containing several metal hydrides, the principal component of which was identified as **13** based on its NMR spectra. ^{1}H NMR (C_6D_6): δ 1.73 (d, J_{HP} = 2, 15H, C_5Me_5), 1.11 (dd, J_{PH} = 10, J_{HF} = 2, 9H, PMe_3), −17.2 (d, J_{PH} = 37, J_{FH} = 2, 1H, Ir-H). ^{19}F NMR (C_6D_6): δ −52.5 (ddd, J_{FF} = 26.4, J_{FF} = 12.0, J_{FH} = 2.0, 3F, CF_3), −64.4 (dq, J_{FF} = 52, J_{FF} = 26.5, 1F, ═CF), −74.6 (dqd, J_{FF} = 52, J_{FF} = 12.0, J_{PF} = 5.1, 1F, ═CF). ^{31}P{^{1}H} NMR (C_6D_6): δ −42.7 (d, J_{PF} = 4.7, PMe_3). IR: (C_6H_6) ν_{Ir-H} 2123 cm^{-1}, $\nu_{C=C}$ 1673 cm^{-1}.

Crystallographic Studies. The single-crystal X-ray diffraction experiments were performed on a Siemens P4 diffractometer for **6a** and **21** and on a Siemens P4/CCD diffractometer for **20**. Details of the data collection and refinement are presented in Table 1. The systematic absences in the diffraction data are uniquely consistent with the reported space groups. The structures were solved using direct methods, completed by difference Fourier synthesis, and refined by full-matrix least-squares methods. For **21** semiempirical absorption corrections were applied, and for **6a** the semiempirical absorption correction data were collected by the ψ-scan technique. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All non-hydride hydrogens were treated as idealized contributions. For **6a** and **20** the metal−hydrogen distances were fixed to 1.603 and 1.580 Å, respectively, and the thermal parameters of these hydrogen atoms were allowed to refine.

All software and sources of scattering factors are contained in the SHELXTL (version 5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: Fractional atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **6a**, **20**, and **21** are available free of charge via the Internet at http://pubs.acs.org.

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