Cationic Iridium−Perfluoroalkyl Complexes with NH_3 and PH_3 Ligands. Activation of Carbon−Fluorine Bonds by H_2S To Give Bis(trifluoromethyl)dithiametallacyclobutane and Bis(trifluoromethyl)trithiametallacyclohexane Complexes

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The cationic fluoroalkyl(aqua) complexes $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)(H_2O)][BF_4]$ (R_F = $CF(CF_3)_2$, CF_2CF_3) react with NH_3 and PH_3 to afford the corresponding ammonia and phosphine complexes $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)L][BF_4]$ (R_F = $CF(CF_3)_2$, CF_2CF_3; L = NH_3, PH_3). No reaction of NH_3 or PH_3 with the fluoroalkyl ligand is observed. The molecular structure of $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)\{CF(CF_3)_2\}(NH_3)][BF_4]$ has been determined and shows hydrogen-bonded interactions between the coordinated NH_3 ligand and the BF_4^- counterion. The molecular structure of the phosphine complex $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)\{CF(CF_3)_2\}(PH_3][B\{C_6H_3(CF_3)_2\}_4]$ has also been determined. Close intramolecular contacts between the NH_3 or PH_3 ligands and the fluorocarbon ligand in these two complexes are interpreted as resulting from steric requirements rather than intramolecular hydrogen bonding. Dimethyl sulfide reacts similarly to afford $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)(Me_2S)][BF_4]$ (R_F = $CF(CF_3)_2$, CF_2CF_3). In contrast, H_2S reacts with the secondary fluoroalkyl complex $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)\{CF(CF_3)_2\}(H_2O][BF_4]$ to give the sulfhydryl complex $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)\{CF(CF_3)_2\}(SH)]$ and with $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(CF_2CF_3)(H_2O][BF_4]$ to give carbon−fluorine bond activation with formation of a mixture of compounds containing two new classes of fluorinated ligands. The molecular structures of representatives of each class, the 2,3-dithiametallacyclobutane complex $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(\textit{syn}\text{-}S_2CHCF_3)]$ and the 2,4,6-trithiametallacyclohexane complex $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(\textit{anti,anti}\text{-}S_3\{CHCF_3\}_2)]$, have been determined. Both syn and anti stereoisomers of the dithiametallacyclobutane complex and all three stereoisomers (*syn,syn*, *syn,anti*, and *anti,anti*) of the trithiametallacyclohexane complex are observed in solution as products of the reaction, and their configurations have been confirmed by NOE experiments.

Introduction

While many fluorocarbons play beneficial roles in the lives of human beings, the negative environmental effects of some fluorocarbons, particularly atmospheric ozone depletion and global warming potentials, are also well-documented. Volatile chlorofluorocarbons (CFCs), now banned under the Montréal Protocol as agents of ozone depletion and global warming,[1−3] have been replaced as refrigerants, cleaning solvents, and foaming agents with environmentally benign hydrofluorocarbons (HFCs), which have zero ozone depleting potential compared to CFCs.[4] The unique solvent properties of perfluorocarbons (PFCs) were recognized long ago,[5−7] and these solvents, now christened as "fluorous",[8,9] are now utilized extensively in stoichiometric and catalytic organic and organometallic transformations[8] and in separations and combinatorial chemistry,[10−14] resulting in a significantly increased use of PFCs. However, while they are inert under ambient conditions, PFCs also have high global warming potential and atmospheric lifetimes of thousands of years; therefore, increased usage brings potential liability if they are not recycled carefully.[1−4]

As a result of these factors, a major research thrust in our group has been to develop methodology using

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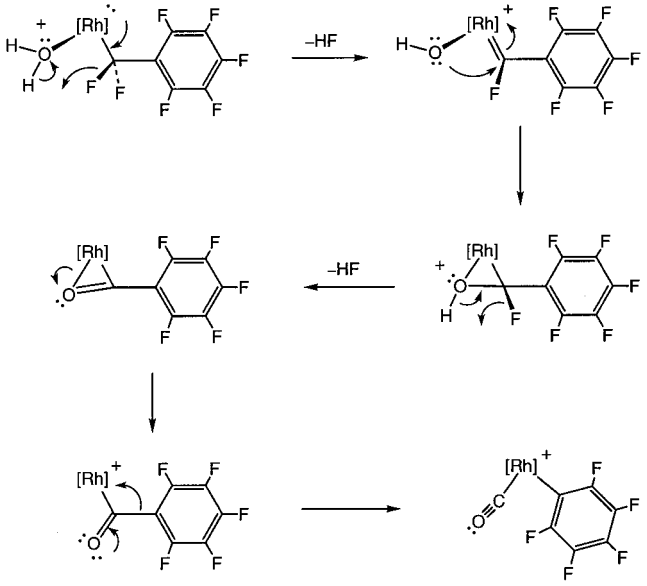
transition-metal compounds to activate normally unreactive aliphatic C−F bonds with a longer term goal of developing stoichiometric and catalytic methods for the production of HFCs from PFCs and other halofluorocarbons. The activation of inert C−F bonds is an area of considerable recent interest among transition-metal chemists.[15−19]

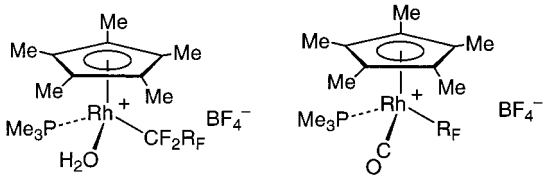
While fluoroalkyl−organometallic compounds have been known since the early days of organotransition-metal chemistry,[20−24] studies of their reactivity have been limited. Greater reactivity has been noted previously for fluoroalkyl ligands directly bonded to metal centers; the α-fluorines in such compounds are unusually reactive in the presence of Lewis acids such as BX_3.[25−32] Exogenous protic acids have also been shown to act as fluoride acceptors,[33−36] and more recently, reversible migrations of fluorine from the α-carbon to transition-metal centers have been demonstrated.[37,38] The unusual lability of the α-fluorines in these compounds may well be due to the participation of metal electrons in stabilizing a carbocation intermediate; organic chemists would view this as negative hyperconjugation,[39,40] while inorganic chemists might prefer to categorize such stabilization as back-bonding from metal d into CF σ* orbitals.[41−45]

Scheme 1[a]



[a] [Rh] = Rh(η^5-C_5Me_5)(PMe_3).

We have uncovered a series of reactions in which aliphatic C−F bond activation is remarkably facile under ambient conditions.[46−48] In particular, reaction of coordinated water in complexes **1** results in hydrolysis



1 **a.** $R_F = CF_2CF_3$ **b.** $R_F = C_6F_5$ **2** **a.** $R_F = CF_2CF_3$ **b.** $R_F = C_6F_5$

of the α-CF_2 groups of primary perfluoroalkyl complexes of rhodium to give carbonyl complexes **2**; the sequence of steps shown in Scheme 1 was proposed to account for this transformation.[47] Displacement of water from iridium analogues of complexes **1** by dihydrogen is also facile and results in hydrogenolysis of α-CF bonds in primary and secondary fluoroalkyl ligands to release hydrofluorocarbons.[48]

Consequently, we were interested in understanding the properties of such small molecules required in determining their reactivity with perfluoroalkyl ligands. We have suggested that in the case of water (Scheme 1)[47] and dihydrogen,[48] it is the enhancement of acidity expected via coordination that may be responsible for the facile hydrolysis of CF bonds in adjacent ligands. Coordinated hydrogen sulfide is expected to be more acidic than coordinated water, and phosphine is more

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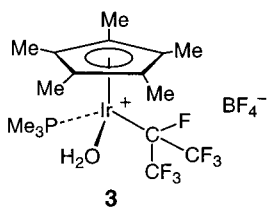
Table 1. Crystal Data and Summary of X-ray Data Collection

	5	7b	12	14
formula	$C_{16.50}H_{28}BClF_{11}IrNP$	$C_{49}H_{41}BCl_2F_{31}IrP_2$	$C_{15}H_{25}F_3IrPS_2$	$C_{17}H_{26}F_6IrPS_3$
fw	718.83	1554.67	549.64	663.73
space group	$C222_1$	$P2_1/n$	$P2_12_12_1$	$P2_1/m$
a, Å	19.2575(2)	12.8656(2)	9.510(4)	8.674(5)
b, Å	19.2517(2)	34.5644(3)	12.873(5)	13.983(5)
c, Å	26.5964(2)	13.5744(2)	15.620(6)	9.683(4)
α, deg	90	90	90	90
β, deg	90	98.6409(7)	90	105.83(5)
γ, deg	90	90	90	90
V, Å^3	9860.30(12)	5967.89(12)	1912.2(17)	1129.9(9)
Z	16	4	4	2
D(calcd), g/cm^3	1.937	1.730	1.909	1.951
abs coeff, mm^{-1}	empirical	DIFABS	empirical	empirical
temp, K	173(2) K	298(2)	235(2)	241(2)
diffractometer		Siemens P4		
radiation		Mo Kα (λ = 0.710 73 Å)		
R(*F*), %[a]	3.46	5.95	4.41	4.58
$R_w(F^2)$, %[a]	8.64	21.76	9.79	8.23

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

acidic than water but less acidic than H_2S, while ammonia is the least acidic.[49,50] As with water, the reactivity of NH_3 and PH_3 has been shown to be enhanced[51−56] on coordination to metals. In this paper, we describe studies of the reactions of NH_3, PH_3, and SH_2 with cationic water complexes of iridium containing perfluoroisopropyl (**3**) or perfluoroethyl (**4**) ligands.



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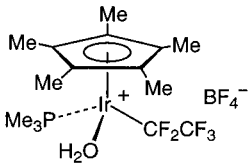
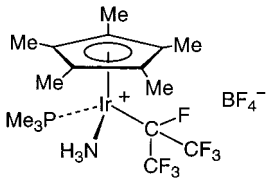


4

Results and Discussion

Ammonia Complexes. Preparation of the cationic ammonia complexes **5** and **6** was readily achieved by bubbling ammonia through methylene chloride solutions of the respective water complexes **3** and **4**. The solid-



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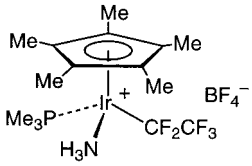

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state structure of **5** was confirmed by X-ray crystallography. Details of all crystallographic determinations

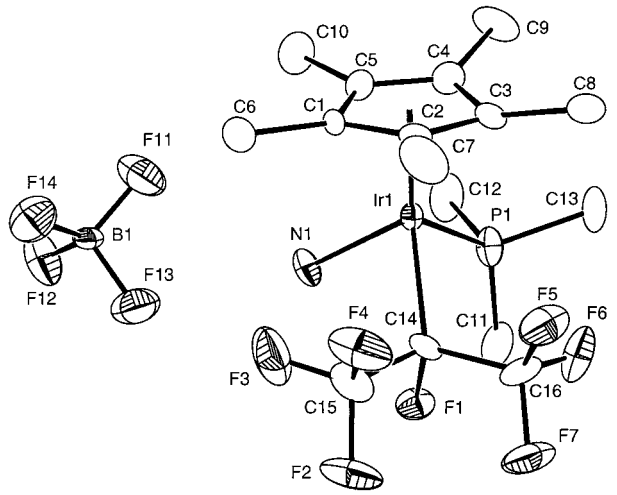

Figure 1. ORTEP diagram of the non-hydrogen atoms of one of the crystallographically independent cation/anion molecules of **5**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg): Ir(1)−C(14) = 2.149(10), Ir(1′)−C(14′) = 2.120(10), Ir(1)−N(1) = 2.171(7), Ir(1′)−N(1′) = 2.185(7), Ir(1)−P(1) = 2.330(3), Ir(1′)−P(1′) = 2.333(3), Ir(1)−CNT(1) = 1.879(9), Ir(1′)−CNT(1′) = 1.869(9); C(14)−Ir(1)−N(1) = 84.5(4), C(14′)−Ir(1′)−N(1′) = 84.6(4), N(1)−Ir(1)−P(1) = 87.8(3), N(1′)−Ir(1′)−P(1′) = 87.8(2), C(14)−Ir(1)−P(1) = 92.1(3), C(14′)−Ir(1′)−P(1′) = 92.8(3), CNT(1)−Ir(1)−N(1) = 123.29(3), CNT(1)−Ir(1)−P(1) = 125.16(3), CNT(1)−Ir(1)−C(14) = 130.88(3), CNT(1′)−Ir(1′)−N(1′) = 123.38(3), CNT(1′)−Ir(1′)−P(1′) = 125.04(3), CNT(1′)−Ir(1′)−C(14′) = 130.08(3).

are provided in Table 1. There are two crystallographically independent molecules in the unit cell. The ORTEP diagram and atom-labeling scheme for one cation/anion pair is shown in Figure 1, along with some selected bond distances and angles. The coordination geometry around the iridium atom is pseudo-octahedral, with three *fac* sites occupied by the pentamethylcyclopentadienyl ligand, as observed previously for aqua complex **3**.[57] The conformation of the perfluoroisopropyl ligand is the same in **3** and **5**, with the CF_3 groups gauche to the Cp*

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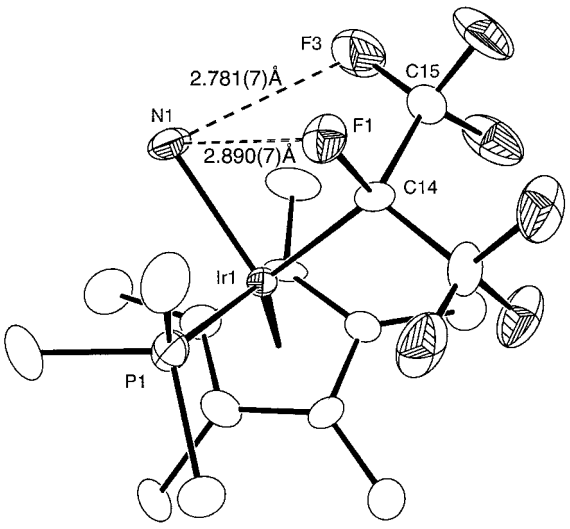


Figure 2. ORTEP diagram of the non-hydrogen atoms of one of the independent cations of **5**, showing close intramolecular contacts between the NH_3 ligand and CF bonds in the perfluoroisopropyl ligand. Thermal ellipsoids are shown at the 30% level.

and the tertiary CF bond approximately bisecting the N−Ir−P bond angle. The average Ir−N bond length of 2.178(7) Å is understandably longer than the corresponding Ir−O bond in aqua precursor **3**[57] (2.052(7) Å) but significantly shorter than those in $[Ir(PEt_3)_2(H)(NH_3)(\mu\text{-}NH_2)]_2$ (2.244(4) Å)[58] or $[IrCl_2(NH_3)(H)(PCy_3)_2]$ (2.259(3) Å).[59] The average Ir−C bond length of 2.135(10) Å is not significantly different from that in **3** (2.09(2) Å) or the Rh analogue of **3** (2.113(4) Å); likewise, the average Ir−P distance (2.332(3) Å) is the same as found in **3** (2.333(3) Å).[57]

Like the precursor water complex **3** and its relatives, close contacts between the ammonia ligand and the BF_4^- counterion are observed.[47,57] Each crystallographically independent cation forms a "dimer" in the solid state with a cation of like structure, with each cation pair apparently bridged in a slightly unsymmetrical fashion by BF_4^- anions. The closest contacts to the anions are those between N(1) and F(13) (3.087(7) and 3.429(7) Å). Unlike the corresponding contacts in the aqua analogue **3**,[57] these are slightly larger than the sum of the van der Waals radii of N (1.55 Å) and F (1.47 Å),[60] suggestive of weaker hydrogen bonding in **5**. Similar interactions of ammonia ligands that are within hydrogen-bonding distance to other species have been reported for other metal complexes.[61]

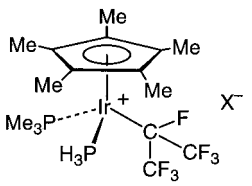
Intramolecular close contacts between the ammonia ligand and the fluoroalkyl group that are significantly smaller than the sum of the van der Waals radii are also observed, as shown in Figure 2, with N(1)−F(1) being 2.890(7) Å and N(1)−F(3) being 2.781(7) Å. In fact, these are indistinguishable from the corresponding values of 2.898 and 2.792 Å observed between the analogous F atoms and the O atom of ligated water in **3**.[57] We had initially suggested that these close contacts in **3** might be due to weak intramolecular hydrogen bonding between the water and the C−F bonds,[57] but the similarity of these values in both **3** and **5** suggests that these contacts are dictated by the sterics of enforced proximity, as discussed further in the case of the PH_3 analogue below.

The solution structure of **5** is consistent with the solid-state result. The presence of the ammonia ligand is detected in the IR spectrum by antisymmetric and symmetric N−H stretching bands at 3362 and 3298 cm^{-1}. In the ^1H NMR spectrum, the NH_3 ligand is observed as a broad singlet at δ 3.22. Unlike the water analogue **3** and its relatives,[47,57] the NMR spectra show no evidence of ammonia dissociation and epimerization at iridium on the NMR time scale, since the CF_3 groups remain diastereotopically nonequivalent, resonating at δ −70.34 and −70.65 in the ^{19}F NMR spectrum.

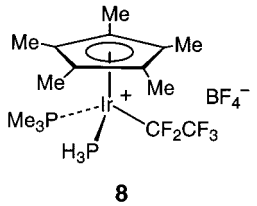
The structure of the perfluoroethyl analogue **6** is also clearly apparent from its solution spectroscopy. The N−H stretches of the ammonia ligand are observed in the IR at 3384 and 3302 cm^{-1}, while in the ^1H NMR spectrum the ammonia ligand is observed as a broad singlet δ 3.26. Similarly the NH_3 ligand of **6** does not dissociate on the NMR time scale, with resultant epimerization at iridium, as the ^{19}F NMR spectrum shows diastereotopic fluorines of the α-CF_2 group of the perfluoroethyl ligand as an AB quartet at δ −81.52 and −84.47 (J_{AB} = 290 Hz).

In contrast to other reported ammonia complexes,[51,58,59,62] complexes **5** and **6** are notably unreactive, even to loss of ammonia.[63] Heating the complexes to 150 °C resulted in no changes by NMR, although further prolonged heating resulted in extensive decomposition to unidentified products. Unlike its aqua analogues,[47,57] there is no sign of any reaction between the NH_3 ligand and the primary perfluoroethyl ligand.

Phosphine Complexes. Similarly, bubbling PH_3 (generated by acidification of Zn_3P_2)[64] through methylene chloride solutions of the water complexes **3** and **4** resulted in formation of the phosphine complexes **7a** and **8**. While we were unable to obtain diffraction-quality



7 **a.** X = BF_4
b. X = $B\{C_6H_3(CF_3)_2\}_4$



8

crystals of the tetrafluoroborate complex **7a**, metathesis to the BAr_F counterion afforded crystals of **7b** suitable for diffraction. The basic geometry of the cationic portion of the complex, presented as an ORTEP diagram in Figure 3, is similar to that of **5**. The Ir−P bond lengths are 2.328(4) Å (PMe_3) and 2.278(3) Å (PH_3). The

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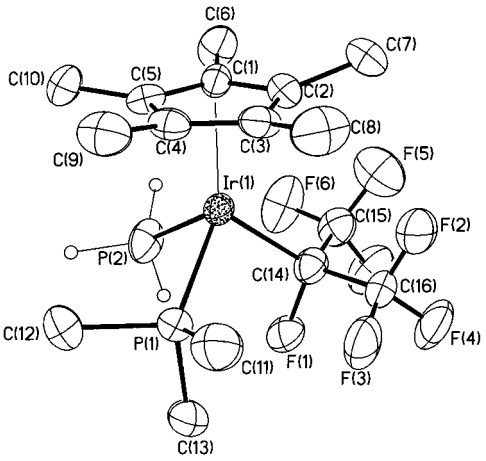


Figure 3. ORTEP diagram of the non-hydrogen atoms of the cation of **7b**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg): Ir(1)−C(14) = 2.157(11), Ir(1)−P(1) = 2.328(4), Ir(1)−P(2) = 2.278(3), CNT(1)−Ir(1) = 1.915(10), P(1)−C(12) = 1.814(13), P(1)−C(13) = 1.815(13), P(1)−C(11) = 1.848(17), P(2)−H(3) = 1.32(5), P(2)−H(2) = 1.39(11), P(2)−H(1) = 1.5(2); C(14)−Ir(1)−P(2) = 88.2(3), C(14)−Ir(1)−P(1) = 93.4(3), C(14)−Ir(1)−P(2) = 88.2(3), P(2)−Ir(1)−P(1) = 89.37(15), CNT(1)−Ir(1)−P(2) = 120.50(3), CNT(1)−Ir(1)−P(1) = 124.59(3), CNT(1)−Ir(1)−C(14) = 129.38(3).

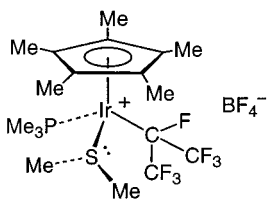
latter is quite consistent with other iridium−PH_3 bond lengths, which have been shown to vary from 2.274(4) to 2.398(5) Å.[49,65−67] The Ir−C(14) distance of 2.157(11) Å is not significantly different from that in **5**, and the conformation of the perfluoroisopropyl ligand is the same as in **5**. The tetraarylborate ligand is not capable of significant hydrogen bonding with the cation, and the distance from Ir to the nearest B atom is 8.154 Å.

Are there intramolecular hydrogen-bonding contacts in **7b**? The sum of the van der Waals radii of P and F is 3.27 Å,[60] and the P(2)−F(6) and P(2)−F(1) distances of 2.890 and 3.065 Å, respectively, lie well within this sum. However, the corresponding PMe_3 phosphorus, clearly incapable of hydrogen bonding, shows distances of P(1)−F(1) and P(1)−F(6) of 3.260 and 3.111 Å, respectively, also within the sum of the van der Waals radii. These close contacts are presumably the result of steric constraints, and it seems clear that it may be dangerous to conclude, as we[57] and others have done, that significant close contacts between carbon−fluorine bonds and potential hydrogen-bond donors are positive evidence for hydrogen bonding. This point has also been made in other more comprehensive analyses of the structures of fluorinated compounds.[68,69]

In solution, the PH_3 ligand of **7a** was observed in the ^{1}H NMR spectrum as a doublet at δ 4.04 (J_{PH} = 400 Hz). In the $^{31}P\{^1H\}$ NMR spectrum, the PH_3 ligand was observed at δ −126.0, coupled to the PMe_3 phosphorus (J_{PP} = 29 Hz), the CF group (J_{PF} = 42 Hz), and one CF_3 group (J_{PF} = 22 Hz) of the perfluoroisopropyl ligand. The PMe_3 phosphorus resonates at δ −38.5, coupled to the PH_3 phosphorus (J_{PP} = 29 Hz) and to the other CF_3 group of the perfluoroisopropyl ligand (J_{PF} = 6 Hz). The spectra of **7b** show analogous features. It is interesting that the tertiary CF fluorine couples only to the phosphorus of the PH_3 ligand and not to that of the PMe_3. In the molecular structure of **7b,** this fluorine F(1) is significantly closer to the PH_3 phosphorus (3.065 Å) than to that of the PMe_3 group (3.260 Å), suggesting that the P−F coupling observed in these systems may be inversely correlated with the P−F distances. Likewise, each phosphine couples only to that CF_3 group to which it is closest in space. Similar correlations between ^{1}H−^{19}F and ^{19}F−^{19}F couplings have been made in other systems.[70]

In the corresponding perfluoroethyl complex **8**, the protons of the PH_3 ligand are observed at δ 4.13 (J_{PH} = 407 Hz) in the ^{1}H NMR spectrum, while the phosphorus atom resonates as a multiplet at δ −130.90 in the $^{31}P\{^1H\}$ NMR spectrum. The fluorine spectrum shows diastereotopic fluorines in the CF_2 group, as expected. Like its ammonia analogue **5**, but unlike its aqua analogues,[47,57] there is no sign of any reaction between the PH_3 ligand and the primary perfluoroethyl ligand.

Reactions with Sulfur Ligands. The dimethyl sulfide complexes **9** and **10** were easily prepared in excellent yield by treating the corresponding iodo complexes [Ir(η^5-C_5Me_5)(PMe_3)(R_F)I] with $AgBF_4$ in the presence of Me_2S. The complexes were characterized by



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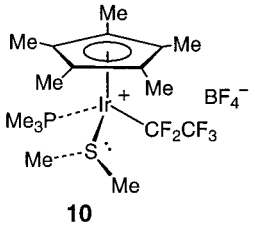

10

NMR spectroscopy and elemental analysis. For each complex, the inequivalent methyl groups of the dimethyl sulfide ligand resonate as two peaks around δ 2.5 in the ^{1}H NMR spectrum, indicating that inversion at S coupled with rotation about the Ir−S bond must be slow on the NMR time scale. The other spectral features of these complexes are similar to those of previously reported (perfluoroalkyl)iridium compounds. Thus, in **10** the diastereotopic α-CF_2 group resonates as an AB quartet (J_{AB} = 277 Hz) in the ^{19}F NMR spectrum, while the inequivalent CF_3 groups of **9** give two peaks at δ −65.54 and −69.98. In the $^{31}P\{^1H\}$ spectrum, the phosphorus atom of **9** couples to one CF_3 group (J_{PF} = 12 Hz) and the CF (J_{PF} = 5 Hz) of the perfluoroisopropyl ligand.

In contrast, treatment of the perfluoroisopropyl complex **3** with H_2S resulted in formation of the neutral

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(70) We have observed analogous correlations in a variety of complexes containing fluoroalkyl and fluoroaryl ligands and phosphines and will publish these observations in due course.

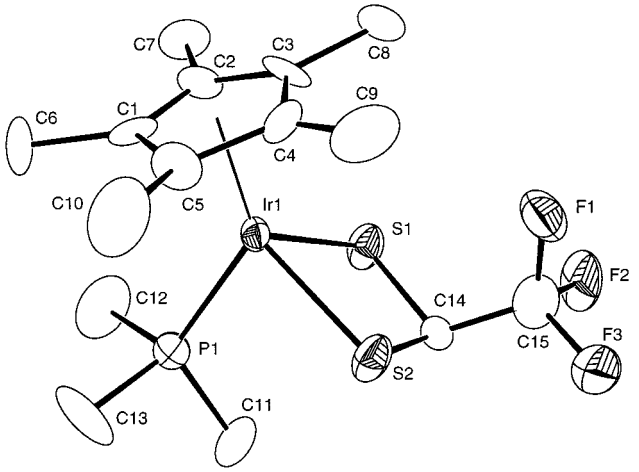
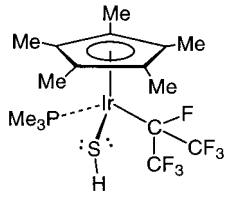


Figure 4. ORTEP diagram of the non-hydrogen atoms of **12**, showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg): Ir(1)−P(1) = 2.248(6), Ir(1)−S(2) = 2.368(5), Ir(1)−S(1) = 2.362(5), CNT(1)−Ir(1) = 1.873(9), S(1)−C(14) = 1.80(2), S(2)−C(14) = 1.84(2); P(1)−Ir(1)−S(2) = 88.4(2), P(1)−Ir(1)−S(1) = 88.7(2), S(2)−Ir(1)−S(1) = 74.71(19), CNT(1)−Ir(1)−P(1) = 132.07(3), CNT(1)−Ir(1)−S(1) = 126.32(3), CNT(1)−Ir(1)−S(2) = 128.40(3).

sulfhydryl complex **11**, in 61% yield, which was characterized by NMR spectroscopy and microanalysis. The

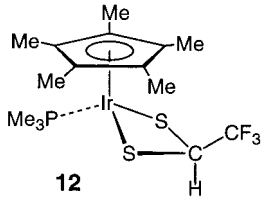


11

sulfhydryl group is characterized in the ^{1}H NMR spectrum by a doublet (J_{PH} = 1.2 Hz) at δ −2.21 and in the IR spectrum by a weak band at 2556 cm^{-1}. These NMR data are similar to those reported for [Ir(η^5-C_5Me_5)(PMe_3)(SH)(X)] complexes, where δ(SH) is around −1.9 to −2.2 and J_{PH} varies from 3.7 to 4.8 Hz.[71−73] The perfluoroisopropyl ligand is observed as three single peaks at δ −66.91 (CF_3), −70.80 (CF_3), and −171.11 (CF) in the ^{19}F NMR spectrum, while the PMe_3 group gives a singlet at δ −33.88 in the ^{31}P{^{1}H} NMR spectrum.

Presumably, formation of **11** proceeds via formation of a cationic H_2S complex, followed by deprotonation of the acidic hydrogen sulfide ligand by excess H_2S. As observed for coordinated water complexes with secondary fluoroalkyl groups, there is no evidence of a reaction between the coordinated hydrogen sulfide and the perfluoroisopropyl ligand.[47,57]

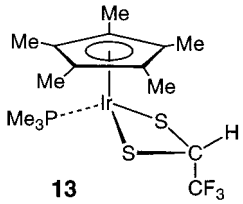
In further contrast, reaction of the perfluoroethyl water complex **4** with H_2S does not result in the formation of a neutral sulfhydryl analogue of **11** or a cationic H_2S complex. Instead, a mixture of five fluorine-containing complexes is obtained in about 60% overall yield, along with some insoluble residue, which was not characterized. These compounds have been separated into two structural classes, and one representative of each type of structure has been characterized by X-ray crystallography. The first structural type contains a 2,4-dithiametallacyclobutane ring as shown in complex **12**, for which an ORTEP diagram appears in Figure 4.



12

The structure clearly shows the CF_3 substituent to be syn to the Cp* ligand. This complex is structurally very similar to the compound [Ir(η^5-C_5Me_5)(PMe_3)(η^2-$S_2C(CH_3)_2$)] reported by Bergman,[71] and the metric parameters of the metallacyclic ring are very similar to those of other reported 2,4-dithiametallacyclobutane complexes.[74−77]

The solution NMR data for **12** illustrate that this is a minor isomer formed in the reaction, with the corresponding anti isomer **13** being formed in significantly larger amounts; the ratio of **12** to **13** formed in the initial reaction is 1:4. The CH group of the dithio ligand of **12**



13

resonates as a doublet of quartets at δ 5.95 (J_{HF} = 8 Hz, J_{PH} = 2 Hz), while the CF_3 group is observed as a doublet at δ −77.78 (J_{HF} = 8 Hz) in the ^{19}F NMR spectrum. The ^{1}H NOESY spectrum showed no NOE between the CH group and the pentamethylcyclopentadienyl ligand, consistent with this complex having the configuration observed in the solid state. For the major isomer, **13**, the CH group of the dithio ligand resonates as a doublet of quartets at δ 6.14 (J_{HF} = 8 Hz, J_{PH} = 1 Hz), with the CF_3 group appearing as a doublet at δ −78.86 (J_{HF} = 8 Hz) in the ^{19}F NMR spectrum. A NOESY spectrum of this complex revealed an NOE between the CH group and the pentamethylcyclopentadienyl ring, consistent with a structure having the CF_3 and C_5Me_5 groups in an anti disposition.

The second set of compounds obtained in this reaction is characterized by the X-ray structure of one of the

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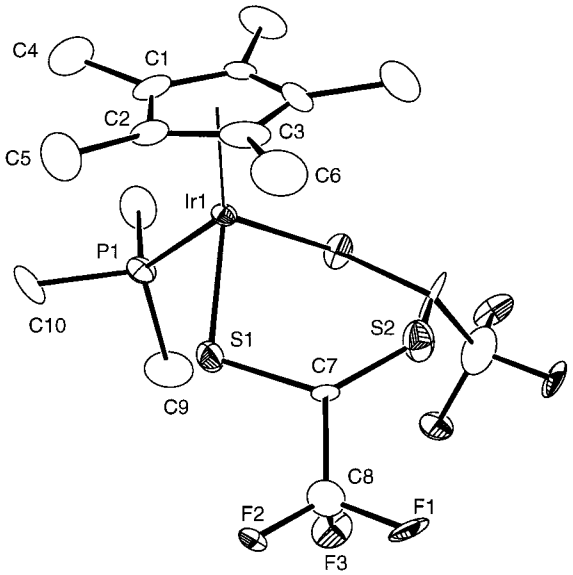
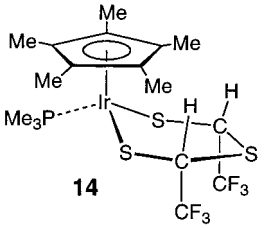
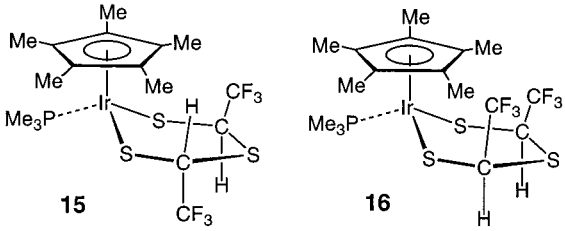


Figure 5. ORTEP diagram of the non-hydrogen atoms of **14**, showing the atom-labeling scheme. Only the major occupancy sites are shown. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg) for the majority occupancy structure: Ir(1)−P(1) = 2.248(2), Ir(1)−S(1) = 2.3470(16), CNT(1)−Ir(1) = 1.851-(9), S(1)−C(7) = 1.868(10), S(2)−C(7) = 1.672(13). P(1)−Ir(1)−S(1) = 85.81(6), S(1)#1−Ir(1)−S(1) = 96.80(8), C(7)−S(1)−Ir(1) = 109.0(4), S(2)−C(7)−S(1) = 119.0(7), CNT(1)−Ir(1)−P(1) = 130.72(4), CNT(1)−Ir(1)−S(1) = 123.22(3).

components, **14**, the ORTEP diagram for which is shown



in Figure 5. The complex contains what appears to be the first example of a mononuclear 2,4,6-trithiametallacyclohexane ring. The only related transition-metal structure reported appears to be the dinuclear iron complex $[Fe_2(CO)_6\{\mu\text{-}(CH_2S)CH_2SCH_2\text{-}\mu\text{-}S)]$,[78] in which the sulfur atoms also bridge two iron atoms. The structures of two main-group examples with 1-phospha-2,4,6-trithiacyclohexane rings have been reported.[79,80] The crystallographically determined isomer **14** has both CF_3 groups anti to the Cp* ring but is a minor isomer formed in the reaction. Its ^1H NMR spectrum shows the two equivalent SCH groups as a quartet (J_{HF} = 8 Hz) at δ 4.27, and the two equivalent CF_3 groups give rise to a doublet at δ −66.43 (J_{HF} = 9 Hz). The anti/anti assignment of the CF_3 groups with respect to the pentamethylcyclopentadienyl ring is confirmed by observation of an NOE between the CH groups and the pentamethylcyclopentadienyl ring. The major isomer shows two overlapping quartets due to the nonequivalent SCH groups at δ 4.83 (J_{HF} = 9 Hz) and δ 4.82 (J_{HF} = 9 Hz) in a 1:1 ratio, while two CF_3 groups are observed as two doublets in a 1:1 ratio at δ −65.72 (J_{HF} = 8 Hz) and −69.41 (J_{HF} = 9 Hz). Its NOESY spectrum shows an NOE between one of the SCH protons and the Cp* ring. Clearly, this must be the corresponding syn/anti isomer **15**. The third minor component must therefore be the syn/syn isomer **16**, which shows similar spectral features similar to those of **14,** except that no NOE was observed from the CH groups to the Cp* ring.



The mechanism of formation of these sulfur heterocycles is not clear. A possible mechanism for formation of the dithiametallacyclobutane ligand is shown in Scheme 2, based on that proposed previously for the hydrolysis of primary fluoroalkyl ligands by coordinated water (Scheme 1). Elimination of HF from the H_2S intermediate **17**, followed by formation of the C−S bond and elimination of a second equivalent of HF, affords the thioacyl intermediate **18**. At this stage in reaction with water, migration of the fluoroalkyl group to the metal occurs, but in the case of **18** it is not unreasonable that excess H_2S can react further, as shown, to produce **13** as the observed result. The stereochemistry of attack of H_2S at **18** would determine whether **12** or **13** was produced. Formation of the trithiacyclohexane product is more difficult to explain and clearly requires participation by two iridium centers to produce the observed compound containing two CF_3 groups.

Concluding Remarks

The reactivity of small, potentially protic, ligands toward α-CF bonds in adjacent ligands does not seem to be a simple function of their acidity. Water and H_2S are reactive in C−F bond activation reactions, while NH_3 and PH_3 are not. Further studies aimed at elucidating reasons for these differences in reactivity are in progress.

Experimental Section

General Considerations. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over molecular sieves or in a Braun drybox. Ethers, pentane, and hexanes were distilled under nitrogen from K/benzophenone and chlorinated solvents from CaH_2. ^1H (300 MHz), ^{19}F (282 MHz), and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian Unity-300 spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of TMS (^1H, referenced to solvent) or internal $CFCl_3$ (^{19}F) and external 85% H_3PO_4 (^{31}P). Coupling constants are reported in hertz. Elemental analyses were performed by Schwartzkopf (Woodside, NY).

Ammonia and hydrogen sulfide were obtained from Matheson, and phosphine was prepared by treating Zn_3P_2 (obtained from Strem) with dilute H_2SO_4.[64] $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)(H_2O)][BF_4]$ (R_F = $CF(CF_3)_2$ (**3**), CF_2CF_3 (**4**))[57,81] and $NaB\{C_6H_3(CF_3)_2\}_4$[82] were prepared as previously reported.

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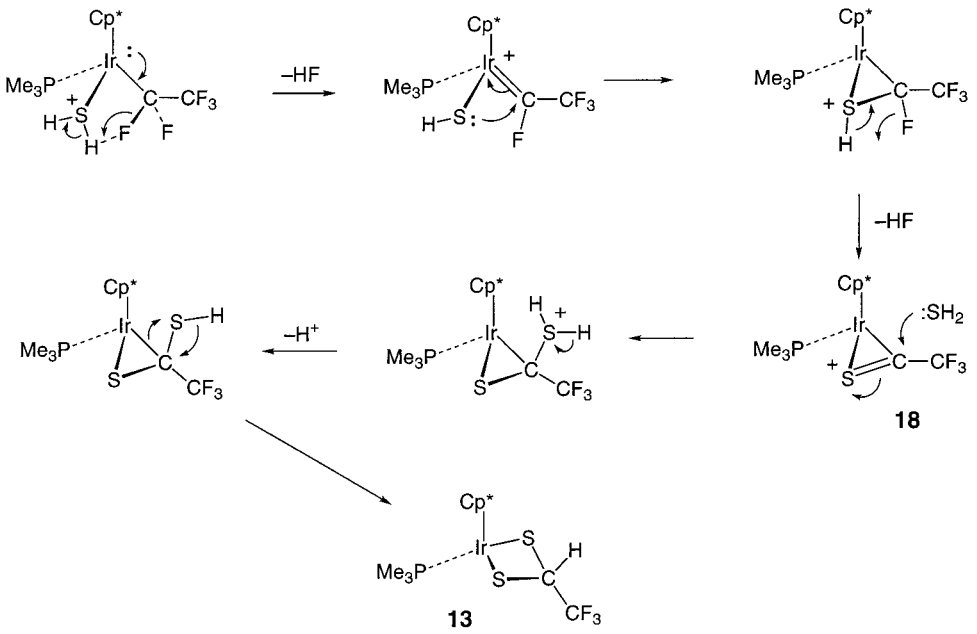
(80) Hesserodt, J.; Pritzkow, H.; Sundermeyer, W. *Chem. Ber.* **1993**, *126*, 1701−1706.

Scheme 2



[Ir(η^5-C_5Me_5)(PMe_3){$CF(CF_3)_2$}(NH_3)][BF_4] (5). Dry NH_3 was bubbled through a yellow solution of [Ir(η^5-C_5Me_5)(PMe_3)-($CF(CF_3)_2$)(H_2O)]BF_4 (**3**; 50 mg, 74 μmol) in CH_2Cl_2 (10 mL). The solution faded to pale yellow. After 30 min, the solvent was pumped off to give a pale yellow solid, which was dried in vacuo to give a cream-colored powder that was crystallized from CH_2Cl_2/hexane to give pale yellow crystals (43 mg, 86%). ^{1}H NMR (CD_2Cl_2): δ 3.22 (br s, 3H, NH_3); 1.69 (s, 15H, C_5Me_5); 1.64 (d, J_{PH} = 10.2, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −70.34 (m, 3F, CF_3); −70.65 (m, 3F, CF_3); −150.06 (s, 4F, BF_4); −179.68 (s, 1F, CF). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −32.23 (m, PMe_3). IR (KBr): ν_{NH} 3362, 3298 cm^{-1}. The compound crystallizes with $^1/_2$ molecule of CH_2Cl_2. Anal. Calcd for $C_{16}H_{28}BF_{11}$-IrNP·0.5CH_2Cl_2 (676.37): C, 27.57; H, 3.93; N, 1.95. Found: C, 27.66; H, 3.89; N, 2.06.

[Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(NH_3)][BF_4] (6). In a Schlenk flask, [Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(H_2O)][BF_4] (**4**; 200 mg, 319 μmol) was dissolved in CH_2Cl_2 (20 mL) to give a bright yellow solution. Dry NH_3 was bubbled through the yellow solution, the color of which immediately faded. After 30 min, the volatiles were removed by vacuum pumping to give a lemon yellow solid, which was dried under vacuum and crystallized from CH_2Cl_2/hexane to give yellow crystals (153 mg, 77%). ^{1}H NMR ($CDCl_3$): δ 3.26 (br s, 3H, NH_3); 1.79 (d, J_{PH} = 1.8, 15H, C_5Me_5); 1.68 (d, J_{PH} = 10.8, 9H, PMe_3). ^{19}F NMR ($CDCl_3$): δ −81.52 (dd, J_{AB} = 289.6, J_{PF} = 24.3, 1F, $C_\alpha F_A$); −82.89 (s, 3F, CF_3); −84.47 (d, J_{AB} = 289.6, 1F, $C_\alpha F_B$); −150.60 (s, 4F, BF_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −32.72 (dq, J_{PF} = 26.0; J_{PF} = 9.2). IR (KBr): ν_{NH} = 3384, 3302 cm^{-1}. Anal. Calcd for $C_{15}H_{27}BF_{11}$-IrNP (626.36): C, 28.76; H, 4.35; N, 2.24. Found: C, 29.53; H, 4.57; N, 2.19.

[Ir(η^5-C_5Me_5)(PMe_3){$CF(CF_3)_2$}(PH_3)][BF_4] (7a). Dry PH_3 (generated from 0.5 g of Zn_3P_2) was bubbled through a solution of [Ir(η^5-C_5Me_5)(PMe_3)($CF(CF_3)_2$)(H_2O)]BF_4 (**3**; 100 mg, 148 μmol) in CH_2Cl_2 (15 mL). The color of the solution faded to clear, and after 2 h the reaction was stopped. The solvent was pumped off to give a white solid, which was dried in vacuo and crystallized from CH_2Cl_2/hexane to give colorless crystals (80 mg, 75%). ^{1}H NMR (CD_2Cl_2): δ 4.04 (d, J_{PH} = 400, 3H, PH_3); 1.86 (d, J_{PH} = 1.8, 15H, C_5Me_5); 1.69 (d, J_{PH} = 10.5, 9H, PMe_3). ^{1}H{^{31}P} NMR (CD_2Cl_2): δ 4.04 (s, 3H, PH_3); 1.86 (s, 15H, C_5Me_5); 1.69 (s, 9H, PMe_3). ^{19}F (CD_2Cl_2); δ −69.80 (m, 3F, CF_3); −70.48 (m, 3F, CF_3); −151.70 (s, 4F, BF_4); −164.88 (d, 1F, J_{PF} = 42, CF). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −38.49 (dq, J_{PP} = 29, J_{PF} = 6, 1P, PMe_3); −125.97 (ddq, J_{PP} = 29, J_{PF} = 42, J_{PF} = 22, 1P, PH_3). The molecule crystallizes with one molecule of CH_2Cl_2. Anal. Calcd for $C_{16}H_{27}BF_{11}IrP_2$·CH_2Cl_2 (725.33): C, 26.23; H 3.76. Found: C, 26.68; H, 3.55.

[Ir(η^5-C_5Me_5)(PMe_3){$CF(CF_3)_2$}(PH_3)][B{$C_6H_3(CF_3)_2$}$_4$] (7b). Complex **7a** (10 mg, 14 μmol) was dissolved in CH_2Cl_2 (5 mL) to give a pale yellow solution. To this was added a solution of NaB{$C_6H_3(CF_3)_2$}$_4$ (14 mg, 16 μmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature for 20 min, the solvent removed by rotary evaporation, and the residue extracted with diethyl ether. The solvent was removed from the extract by rotary evaporation and the residue dissolved in methylene chloride/hexanes and allowed to crystallize by evaporation to give cream-colored crystals (15 mg, 71%). ^{1}H NMR (CD_2Cl_2): δ 7.71 (s, 8H, *o*-H); 7.56 (s, 4H, *p*-H); 3.90 (d, J_{PH} = 398, 3H, PH_3); 1.82 (dd, J_{PH} = 3.9, J_{HF} = 2.1, 15H, C_5Me_5); 1.64 (dd, J_{PH} = 10.5, J_{PH} = 1.8, 9H, PMe_3). ^{1}H{^{31}P} NMR (CD_2Cl_2): δ 7.71 (s, 8H, *o*-H); 7.56 (s, 4H, *p*-H); 3.90 (s, 3H, PH_3); 1.82 (s, 15H, C_5Me_5); 1.64 (s, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −63.22 (s, 24F, *m*-CF_3); −69.76 (s, 3F, CF_3); −70.62 (s, 3F, CF_3); −163.87 (s, 1F, CF). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −38.47 (dq, J_{PP} = 28.5, J_{PF} = 6.7, 1P, PMe_3); −125.21 (dq, J_{PP} = 28.5, J_{PF} = 41.3, 1P, PH_3). Anal. Calcd for $C_{48}H_{39}F_{31}$-$BIrP_2$·CH_2Cl_2 (1554.67): C, 37.85; H 2.66. Found: C, 38.19; H, 2.71.

[Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(PH_3)][BF_4] (8). Dry PH_3 (generated from 0.5 g of Zn_3P_2) was bubbled through a solution of [Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(H_2O)]BF_4 (**4**; 40 mg, 64 μmol) in CH_2Cl_2 (15 mL). The color of the solution faded to clear, and after 2 h, the reaction was stopped. The solvent was pumped off to give a pale yellow solid, which was dried in vacuo and crystallized from CH_2Cl_2/hexane to give colorless crystals (25 mg, 56%). ^{1}H NMR ($CDCl_3$): δ 4.13 (d, J_{PH} = 407, 3H, PH_3); 1.93 (s, 15H, C_5Me_5); 1.74 (d, J_{PH} = 10.8, 9H, PMe_3). ^{1}H{^{31}P} NMR ($CDCl_3$): δ 4.13 (s, 3H, PH_3); 1.93 (s, 15H, C_5Me_5); 1.74 (s, 9H, PMe_3). ^{19}F NMR ($CDCl_3$): δ −72.87 (d, J_{AB} = 290, 1F, $C_\alpha F_A$); −73.44 (dd, J_{AB} = 290, J_{PF} = 35, 1F, $C_\alpha F_B$); −82.56 (s, 3F, CF_3); −151.25 (s, 4F, BF_4). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −38.82 (dt, J_{PP} = 25, J_{PF} = 8, 1P, PMe_3); −130.90 (m, 1P, PH_3).

[Ir(η^5-C_5Me_5)(PMe_3)(R_F)(SMe_2)][BF_4]. A solution of Ir(η^5-C_5Me_5)(PMe_3)(R_F)I (100 mg) in CH_2Cl_2 (10 mL) containing

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Me_2S (1 mL) was added to a slurry of $AgBF_4$ (1.1 equiv) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature overnight to give a yellow slurry/solution, which was filtered to give a yellow solution. The volatiles were removed by rotary evaporation to give a cream-colored powder, which was dried under vacuum and crystallized from CH_2Cl_2/hexane to give yellow crystals.

[Ir(η^5-C_5Me_5)(PMe_3){$CF(CF_3)_2$}(SMe_2)][BF_4] (9): 94 mg, 91%. ^1H NMR ($CDCl_3$): δ 2.45 (s, 3H, MeS); 2.45 (s, 3H, MeS); 1.78 (d, J_{PH} = 12.0, 9H, PMe_3); 1.75 (s, 15H, C_5Me_5). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 2.45 (s, 3H, MeS); 2.45 (s, 3H, MeS); 1.78 (s, 9H, PMe_3); 1.75 (s, 15H, C_5Me_5). ^{19}F NMR ($CDCl_3$): δ −65.54 (m, 3F, CF_3); −69.98 (m, 3F, CF_3); −152.78 (s, 4F, BF_4); −164.62 (s, 1F, CF). $^{19}F\{^{31}P\}$ NMR ($CDCl_3$): δ −65.54 (m, 3F, CF_3); −69.98 (m, J_{FF} = 10.7, 3F, CF_3); −152.78 (s, 4F, BF_4); −164.62 (s, 1F, CF). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −37.08 (dq, J_{PF} = 12.0, J_{PF} = 5.0, PMe_3). Anal. Calcd for $C_{18}H_{30}BF_9IrPS$ (721.46): C, 29.96; H, 4.19. Found: C, 29.51; H, 3.87.

[Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(SMe_2)][BF_4] (10): 100 mg, 97%. ^1H NMR ($CDCl_3$): δ 2.58 (s, 3H, MeS); 2.55 (s, 3H, MeS); 1.85 (d, J_{PH} = 2.1, 15H, C_5Me_5); 1.70 (d, J_{PH} = 10.5, 9H, PMe_3). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 2.58 (s, 3H, MeS); 2.55 (s, 3H, MeS); 1.86 (s, 15H, C_5Me_5); 1.70 (s, 9H, PMe_3). ^{19}F NMR ($CDCl_3$): δ −74.05 (dd, J_{AB} = 276.9, J_{PF} = 8.8, $C_\alpha F_A$); −80.95 (d, J_{AB} = 276.9, $C_\alpha F_B$); −81.90 (s, CF_3); −152.99 (s, 4F, BF_4). $^{19}F\{^{31}P\}$ NMR ($CDCl_3$): δ −74.05 (d, J_{AB} = 276.9, $C_\alpha F_A$); −80.95 (d, J_{AB} = 276.9, $C_\alpha F_B$); −81.90 (s, CF_3); −152.99 (s, 4F, BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −35.59 (m, PMe_3). Anal. Calcd for $C_{17}H_{30}BF_9IrPS$ (671.46): C, 30.31; H, 4.50. Found: C, 30.40; H, 4.11.

[Ir(η^5-C_5Me_5)(PMe_3){$CF(CF_3)_2$}SH] (11). [Ir(η^5-C_5Me_5)(PMe_3){$CF(CF_3)_2$}(H_2O)][BF_4] (**3**; 100 mg, 148 μmol) was dissolved in CH_2Cl_2 (15 mL) to give a yellow solution. The solution was freeze−pump−thawed and backfilled with H_2S. The yellow color of the solution faded almost immediately. The reaction was stirred at room temperature for 1 h, and the volatiles were removed by vacuum pumping to give a yellow residue. The residue was extracted with benzene to give a yellow solution that almost immediately started turning greenish. The solvent was removed by vacuum pumping to give a greenish yellow residue, which was crystallized from CH_2Cl_2/hexane to give greenish yellow crystals (55 mg, 61%). ^1H NMR ($CDCl_3$): δ 1.70 (d, J_{PH} = 2.1, 15H, C_5Me_5); 1.59 (dd, J_{PH} = 10.5, J_{PH} = 2.4, 9H, PMe_3); −2.21 (d, J_{PH} = 1.2, 1H, SH). ^{19}F NMR ($CDCl_3$): δ −66.91 (s, 3F, CF_3); −70.80 (s, 3F, CF_3); −171.11 (s, 1F, CF). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −33.88 (s, PMe_3). IR (KBr): ν_{SH} 2556 cm^{-1}. Anal. Calcd for $C_{16}H_{25}F_7IrPS$: C, 31.73; H, 4.16. Found: C, 32.02; H, 4.14.

Reaction of [Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(H_2O)][BF_4] with H_2S. [Ir(η^5-C_5Me_5)(PMe_3)(CF_2CF_3)(H_2O)][BF_4] (**4**; 50 mg, 80 μmol) was dissolved in CH_2Cl_2 (10 mL) to give a yellow solution. The solution was freeze−pump−thawed and backfilled with H_2S. The yellow color of the solution faded slightly. The reaction was stirred at room temperature for 3 h, and the volatiles were removed by vacuum pumping to give a yellow residue (50 mg). The residue was extracted with benzene to give a yellow solution. The two benzene-soluble complexes could be separated by fractional crystallization from CH_2Cl_2/hexanes. An isomeric mixture of **12** and **13** and an isomeric mixture of **14**, **15**, and **16** were each obtained in ca. 30% yield.

[Ir(η^5-C_5Me_5)(PMe_3){η^2-$S_2C(H)(CF_3)$}] (Isomers 12 and 13). Data for minor isomer **12** are as follows. ^1H NMR ($CDCl_3$): δ 5.95 (dq, J_{HF} = 8, J_{PH} = 2, 1H, CH); 1.86 (d, J_{PH} = 2, 15H, C_5Me_5); 1.73 (d, J_{PH} = 10.2, 9H, PMe_3). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 5.95 (q, J_{HF} = 8, 1H, CH); 1.86 (s, 15H, C_5Me_5); 1.73 (s, 9H, PMe_3). ^{19}F NMR ($CDCl_3$): δ −77.78 (d, J_{HF} = 8, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −30.48 (s, PMe_3).

Data for major isomer **13** are as follows. ^1H NMR ($CDCl_3$): δ 6.14 (dq, J_{HF} = 8, J_{PH} = 1, 1H, CH); 1.83 (d, J_{PH} = 10.2, 9H, PMe_3); 1.79 (d, J_{PH} = 2, 15H, C_5Me_5). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 6.14 (q, J_{HF} = 8, 1H, CH); 1.83 (s, 9H, PMe_3); 1.79 (s, 15H, C_5Me_5). ^{19}F NMR ($CDCl_3$): δ −78.86 (d, J_{HF} = 8, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.62 (s, PMe_3).

Anal. Calcd for $C_{15}H_{25}F_3IrPS_2$ (549.64): C, 32.78; H, 4.58. Found: C, 32.63; H, 4.66.

[Ir(η^5-C_5Me_5)(PMe_3)(η^2-SC(H)(CF_3)SC(H)(CF_3)S)] (Isomers 14−16). Data for minor isomer **14** are as follows. ^1H NMR (CD_2Cl_2): δ 4.27 (q, J_{HF} = 8, 2H, SCH); 1.64 (d, J_{PH} = 11, 9H, PMe_3); 1.44 (s, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2): δ −66.43 (d, J_{HF} = 9, 6F, CF_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −22.91 (s, PMe_3).

Data for major isomer **15** are as follows. ^1H NMR (CD_2Cl_2): δ 4.83 (q, J_{HF} = 9, 1H, SCH); 4.82 (q, J_{HF} = 9, 1H, SCH); 1.80 (s, 15H, C_5Me_5); 1.61 (d, J_{PH} = 11, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −65.72 (d, J_{HF} = 9, 3F, CF_3); −69.41 (d, J_{HF} = 9, 3F, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −27.64 (s, PMe_3).

Data for minor isomer **16** are as follows. ^1H NMR (CD_2Cl_2): δ 4.87 (q, J_{HF} = 8, 2H, SCH); 1.77 (d, J_{PH} = 14, 9H, PMe_3); 1.72 (s, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2): δ −67.23 (d, J_{HF} = 8, 6F, CF_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −29.87 (s, PMe_3).

Anal. Calcd for $C_{17}H_{26}F_6IrPS_3$ (663.73): C, 30.76; H, 3.95. Found: C, 30.97; H, 4.06.

Crystallographic Structural Determinations. Crystal data and data collection and refinement parameters are collected in Table 1. Unless otherwise stated, the systematic absences in the diffraction data 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. DIFABS absorption corrections[83] were applied to all structures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions unless otherwise stated.

Compound **5** crystallized with two independent molecules in the asymmetric unit, each with half a molecule of disordered CH_2Cl_2.

For compound **7b** the three hydrogen atoms of the PH_3 ligand were located from the difference map and refined. The $B\{C_6H_3(CF_3)_2\}_4^-$ counterion possesses unresolvable positional disorder of the CF_3 groups, which gives rise to large thermal parameters of the offending fluorine atoms. The molecule crystallizes with one severely disordered molecule of CH_2Cl_2.

For compound **14 s**ystematic absences indicated either of the monoclinic space groups $P2_1$ and $P2_1/m$. The latter was chosen initially due to the presence of a symmetry plane in the structure and was confirmed by the results of refinement. The disorder described below is not affected by the space group choice. The structure was solved by direct methods and completed by a series of difference Fourier syntheses. Two regions of the structure were found to be disordered, the CF_3 groups (two orientations, ca. 41 and 59% occupancies) and the methylene group, C(7) (two orientations, ca. 44 and 56% occupancies). All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms, except those associated with C(7), were placed in idealized locations.

All software is contained in the SHELXTL program libraries (various versions, G. Sheldrick, Bruker AXS, Madison, WI).

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Supporting Information Available: Tables of atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for complexes **5**, **7b**, **12**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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