Synthesis and Structural Characterization of (Perfluoroalkyl)fluoroiridium(III) and (Perfluoroalkyl)methyliridium(III) Compounds

Cheryl J. Bourgeois,[†] Shaun A. Garratt,[†] Russell P. Hughes,*[,†] Roman B. Larichev,[†] Jeremy M. Smith,[†] Antony J. Ward,[†] Stefan Willemsen,[†] Donghui Zhang,[†] Antonio G. DiPasquale,[‡] Lev N. Zakharov,[‡] and Arnold L. Rheingold[‡]

Departments of Chemistry, 6128 Burke Laboratories, Dartmouth College, Hanover, New Hampshire 03755, and University of California, San Diego, California 92093

Received March 24, 2006

A new family of metal perfluoroalkyl fluoro compounds has been obtained by treatment of the iodo precursors $Cp^*Ir(PMe_3)(R_F)I$ with AgF in CH_2Cl_2 solution in the dark to give $Cp^*Ir(PMe_3)(R_F)F$ (R_F = CF_3, CF_2CF_3, $CF_2CF_2CF_3$, $CF(CF_3)_2$, $CF(CF_3)(CF_2CF_3)$). The molecular structures of the compounds with R_F = CF_2CF_3, $CF_2CF_2CF_3$, $CF(CF_3)_2$ have been determined crystallographically. These fluoro compounds provide a ready and reproducible route to the analogous methyl complexes $Cp^*Ir(PMe_3)(R_F)CH_3$, by treatment with exactly 0.5 equiv of $Zn(CH_3)_2$ at low temperatures in toluene. Alkylation with other reagents such as CH_3Li and $Cp_2Zr(CH_3)_2$ leads to inseparable mixtures. This metathesis of Ir−F and Zn−CH_3 represents the only way to date for the clean reproducible synthesis of $Cp^*Ir(PMe_3)(R_F)CH_3$ compounds containing primary perfluoroalkyl groups. The molecular structures of $Cp^*Ir(PMe_3)(R_F)CH_3$ (R_F = CF_2CF_3, $CF_2CF_2CF_3$) have been determined crystallographically.

Introduction

There has been much interest among organometallic chemists in finding new ways of functionalizing normally unreactive and strong bonds, such as those between carbon and hydrogen or between carbon and fluorine. Breaking the C−F bond, the strongest single bond to carbon,[1] has been the focus of many studies.[2−26] It is clear that aliphatic C−F bonds are significantly labilized when placed α to certain transition metals; C−F bond activation has thus been readily achieved using a variety of exogenous protic[27−30] and Lewis acids.[31−35] In some cases, this process occurs in tandem with migration of a hydride group from the metal to the α-C.[36−38]

We have shown that the primary fluoroalkyl hydrido and fluoroalkyl methyl complexes $Cp^*Ir(PMe_3)(R_F)R$ (R = H,[39]

* To whom correspondence should be addressed. E-mail: rph@dartmouth.edu.

[†] Dartmouth College.

[‡] University of California at San Diego.

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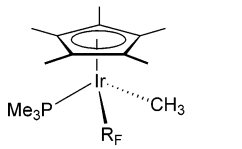
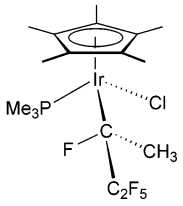
10.1021/om060267s CCC: $33.50
Publication on Web 06/09/2006

CH_3[40]) undergo such a reaction diastereoselectively on treatment with weak acids HX. Protonation of an α-C−F bond in a primary fluoroalkyl ligand by external acid occurs with migration of R from Ir to C and trapping at the metal by the conjugate base of HX. For example, treatment of compound **1a** with lutidinium chloride affords only the (R_C,R_{Ir})(S_C,S_{Ir}) diastereomer of compound **2**.[40] In addition to being completely diastereoselective, this reaction is remarkable in that protonation of the methyl group to give methane is not observed.



1a. $R_F = CF_2CF_2CF_3$
1b. $R_F = CF_2CF_3$
1c. $R_F = CF_3$
1d. $R_F = CF(CF_3)_2$
1e. $R_F = CF(CF_3)(CF_2CF_3)$



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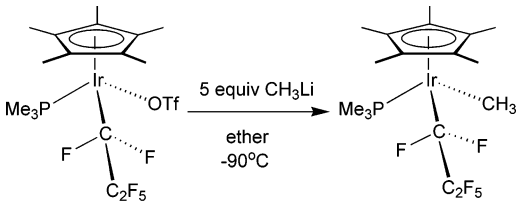
In this paper, we present much improved syntheses of the methyl complex **1a** and some analogues, the original procedures for which[40] were found to be much less reproducible than initially reported. The precursors are a new family of fluoroalkyl fluoro compounds, which have been characterized spectroscopically and in some cases crystallographically.

Results and Discussion

a. Synthesis of Fluoroalkyl Fluoro Complexes. The previously employed synthesis of **1a** via reaction of triflate precursor **3** with an excess of ethereal CH_3Li at low temperature[40] was found in some cases to give very pure samples of product but proved to be frustratingly irreproducible by a number of workers attempting the reaction. The problem appears to stem from the very property that was so desirable in the product, in that the fluorines α to Ir are sensitive to exogenous protic or Lewis acids, so that even soluble lithium byproducts from methylation may be sufficiently reactive to promote C−F activation. Thus, these CH_3Li reactions often lead to samples of **1a** contaminated by impurities with solubilities similar enough to preclude selective crystallization. Due to the high reactivity of the α-fluorines in **1a**, attempts to purify the mixture of products by chromatography on silica gel or alumina using a variety of solvents also led to decomposition. Grignard reagents are also unsuccessful, as the halide (Cl, Br, I) reacts rapidly with **3** to displace triflate and give the corresponding Ir−halide complexes, which are unreactive toward alkylation.



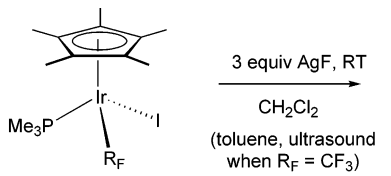
3 **1a**

Consequently, to carry out detailed kinetic studies of the conversion of **1a** to **2**, a more reproducible route to pure samples of **1a** was required.

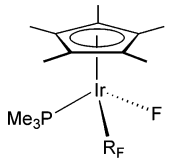
Interestingly, this synthetic difficulty is not encountered in the synthesis of corresponding secondary perfluoroalkyl methyl compounds such as **1d**,**e**.[41] In these cases the secondary perfluoroalkyl ligand in the product does not undergo C−F activation with weak acids. For example, treatment of Cp*Ir(PMe$_3$)(i-C_3F_7)OTf with excess ethereal CH_3Li at low temperature, 1 equiv of $ZnMe_2$ in toluene at low temperature, or 0.5 equiv of Cp_2ZrMe_2 in toluene at room temperature all afford the pure methyl product **1d** in high yield and high purity. However, attempts to utilize these procedures to form **1a** from complex **3** were unsuccessful. With both the Zn and Zr reagents, some of the desired methyl complex **1a** was formed (ca. 50%), along with a new collection of inseparable impurities in each case.

It thus became apparent that the triflate complex **3** was not the optimum precursor for the methyl complex **1a**. We had previously found that iridium halide complexes such as the iodide **4** (and its chloride and bromide analogues) did not react with alkylating agents, thereby necessitating the use of **3**.[40,41] As an alternative we sought routes to the corresponding fluoride analogues **5**, reasoning that fluoride displacement from iridium might open up the possibility of using other types of alkylating agents.

Two techniques for accomplishing iodide for fluoride exchange were attempted as routes to compound **5a**. One was based on the method previously reported by Grushin[42] to make palladium fluorides and involved treatment of the iodide complex **4a** with excess AgF in C_6H_6 in an ultrasonic bath for up to 1 day. Filtration of the AgI precipitate, removal of solvent, and extraction with hexane afforded **5a** in good yield, but always with 5−10% of an unidentified impurity. Attempts to recrystallize the samples were unsuccessful. No attempts were made to optimize this ultrasonic approach, because clean **5a** was obtained upon treatment of **4a** with 3 equiv of AgF in CH_2Cl_2 in the dark for 17−24 h (a method used by Vigalok for synthesis of palladium fluorides[43]). By the same protocol clean **5b**,**d**,**e** can be easily obtained in almost quantitative yields from the corresponding iodide precursors. Simply filtering the product



4a-e



a. $R_F = CF_2CF_2CF_3$
b. $R_F = CF_2CF_3$
c. $R_F = CF_3$
d. $R_F = CF(CF_3)_2$
e. $R_F = CF(CF_3)(CF_2CF_3)$

5a-e

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mixture through Celite was sufficient to isolate the products from silver salts. Unfortunately, when the same procedure was applied to prepare the trifluoromethyl compound **5c**, it was always obtained with several impurities that could be neither separated nor identified. Application of Grushin's conditions (toluene as a solvent, ultrasound bath, 3 equiv of AgF, 12 h reaction) gave **5c** as a mixture with **4c**, but only with about 70% conversion; longer reaction times led again to formation of unidentified impurities.

Compounds **5** were characterized crystallographically (see below) and also showed a signature high-field resonance in the ^{19}F NMR spectrum in the region δ −440 ppm, characteristic of a fluorine atom directly bound to a transition metal, specifically Ir(III).[44] While the ^{31}P{^{1}H} NMR spectra in C_6D_6 or CD_2Cl_2 clearly showed a strong doublet coupling (ca. 50 Hz) to the ligated fluoride, in addition to smaller couplings from fluorines on the α-carbon atom of the fluoroalkyl ligand, the ^{19}F NMR peak for the fluoride appeared as a very broad, featureless resonance. This has been observed in other fluoride complexes and is presumably due to hydrogen bonding of the fluoride with adventitious water present in the solvents used for NMR experiments.[42,45,46]Addition of anhydrous CsF to the NMR samples to scavenge traces of moisture produced no significant effects for the C_6D_6 spectra, but the samples in CD_2Cl_2 showed significant sharpening. In these cases the original broad singlet resolved into a broad doublet, showing the corresponding coupling to ^{31}P, as well as couplings to other fluorines in the fluoroalkyl ligands. For example, in the perfluoroethyl fluoro complex **5b** the fluoride resonance appears at δ −446.8 as a broad doublet of quartets with coupling to ^{31}P (50 Hz) and to the CF_3 group in the fluoroalkyl ligand (10 Hz). In the specific case of **5e** the presence of stereocenters at Ir and at C led to formation of two diastereomers in a 2:1 ratio. A ^{19}F{^{1}H} HOESY experiment[41] (C_6D_6, 21 °C, mixing time 3 s) showed that the major diastereomer had the relative configurations (R_{Ir},S_C)(S_{Ir},R_C).

b. Synthesis of Fluoroalkyl Methyl Complexes. With fluoro complexes **5** in hand, attention was refocused on the synthesis of methyl complexes **1**. Initially, **5a** was treated with excess ethereal CH_3Li at low temperature (−90 to −78 °C) in a manner analogous to our earlier procedure using **3**.[40] NMR spectroscopy of the product showed mixtures of five to six iridium complexes, but the proportion of desired **1a** (60−80%) was higher than that typically formed from reaction of **3** with CH_3-Li. Again, separation of the mixture proved impossible, but identification of some of the undesired products by NMR was possible by comparison to authentic samples. Once again, C−F activation of **1a** after its formation seems to be the main problem. A competing pathway appears to be reduction of the iridium by the lithium reagent to give quantities of Cp*Ir(PMe_3)-(n-C_3F_7)H[47] as well as some unidentified species giving rise to broad peaks in the ^{31}P and ^{19}F NMR spectra. The proportion of the latter increased with increasing amounts of CH_3Li.

Alkylation using $Cp_2Zr(CH_3)_2$ was also unsatisfactory: reactions were carried out with 0.5 and 1 equiv at both −78 °C and ambient temperature in toluene. The cleanest reactions were at ambient temperature, but even then only ca. 50% of **1a** was formed. The product mixture could not be separated by crystallization.

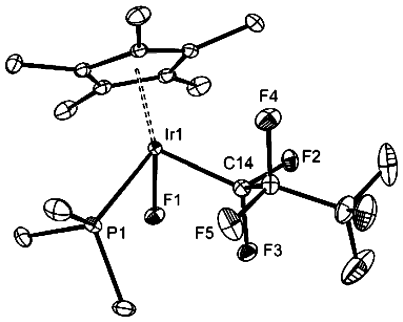
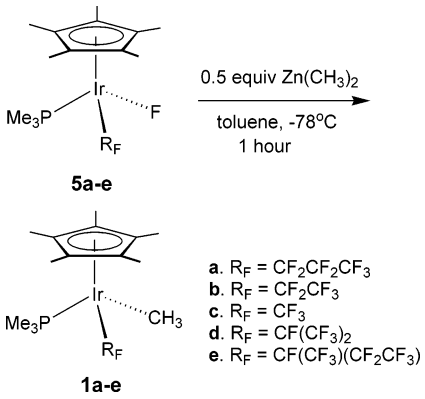


Figure 1. ORTEP diagram of **5a** with ellipsoids drawn at the 30% probability level. All hydrogen atoms are excluded. Selected bond lengths and angles are presented in Table 1.

The breakthrough in the synthesis of **1a** came when $Zn(CH_3)_2$ was used as the methylating agent. Treatment of **5a** with exactly 0.5 equiv of $Zn(CH_3)_2$ in toluene at −78 °C and slowly warming the solution to room temperature cleanly and reproducibly afford **1a** in high yield (>90%). By the same procedure compounds



1b,**d**,**e** were synthesized from **5b**,**d**,**e** in high yields, while **5c** was used for the reaction as a mixture with iodide **4c**, which is unreactive toward $Zn(CH_3)_2$. Complexes **1** are separated from the ZnF_2 byproduct and, in the case of **1c**, from unreacted **4c** by extraction with hexane; removal of the solvent gives pale yellow crystalline solids. Deviation from these conditions leads to mixtures of products. Addition of 0.5 equiv of $Zn(CH_3)_2$ to **5a** in toluene at room temperature results in a 3:1 mixture of **1a** and the hydride Cp*Ir(PMe_3)(n-C_3F_7)H. When 1 equiv of $Zn(CH_3)_2$ was used at −78 °C for 1 h, a mixture of three products was obtained in a 5:4:1 ratio. The major product was the desired **1a**, but the identities of the other species were unclear and were not explored further.

Structural Studies on Compounds 5 and 1. Compounds **5a**,**b**,**d** formed crystals that were suitable for X-ray structure determination; Figures 1−3 show ORTEP representations of the structures of **5a**,**b**,**d**, respectively. Selected bond lengths and angles are presented in Table 1 along with corresponding data for the methyl derivatives **1a**,**b** and previously published data for **1d**[41] and the iodide precursors **4a**,**b**,**d**.[48] Details of the crystallographic determinations of all compounds in this paper are presented in Table 2.

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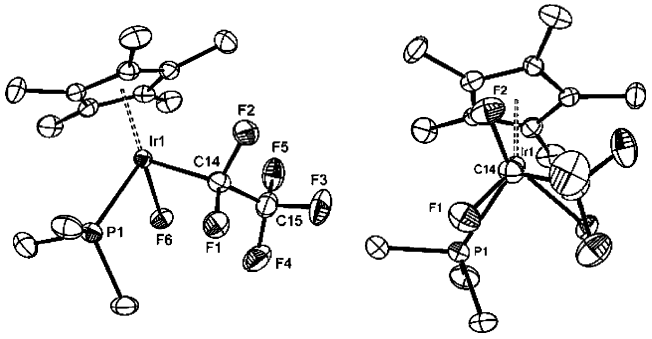


Figure 2. ORTEP diagrams of one of the two independent molecules of **5b** from two different perspectives with ellipsoids drawn at the 30% probability level. All hydrogen atoms are excluded. Selected bond lengths and angles are presented in Table 1.

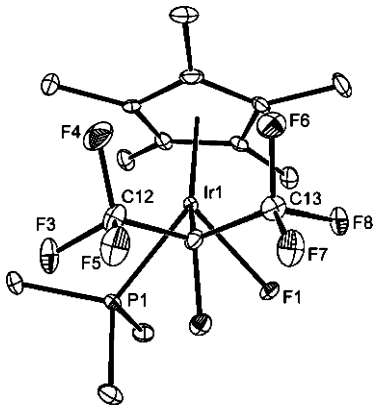


Figure 3. ORTEP diagram of **5d** with ellipsoids drawn at the 30% probability level. All hydrogen atoms are excluded. Selected bond lengths and angles are presented in Table 1.

The Ir−F distances of 2.070(2) Å (in **5a**), 2.055(3) and 2.060(4) Å (in two independent molecules of **5b**), and 2.074(3) Å (in **5d**) are all essentially identical with each other and with the Ir−F distance in the previously reported complex $Cp^{Et}Ir(PMe_3)(Ph)F$ (2.069(4) Å).[44] In **5a** the expected conformation[41] of the fluoroalkyl group is observed, with the β-CF_2 group oriented in the region of space between the Cp* and PMe_3 ligands. Curiously, the crystal structure of **5b** reveals that an unusual solid-state conformation is adopted by the perfluoroethyl ligand (Figure 2), which is the same in each of the two independent molecules in the asymmetric unit. It can be described as an almost eclipsed conformation with the bulkiest CF_3 group pointed toward the fluoride, a sterically less demanding ligand compared to Cp* and PMe_3. The corresponding perfluoroethyl iodo analogue **4b**[48] adopts the usual staggered conformation with the CF_3 group oriented in the region of space between the Cp* and PMe_3 ligands, as also observed for **5a**. This indicates that there is a fine line between conformational stabilities of rotamers and that the ground-state conformation is dependent on the nature of the neighboring halide group and the size of the perfluoroalkyl ligand. The secondary perfluoroisopropyl ligand in **5d** adopts the same conformation as that observed for iodo analogue **4d**.[48] The Ir−C_α distances to the ligated carbon of the fluoroalkyl ligand are the same within experimental error for **5a** (2.062(4) Å) and **5b** (2.072(6), 2.069(7) Å), but a longer distance is found (2.125(5) Å) for the secondary fluoroalkyl in **5d**.

Similarly, methyl compounds **1a**,**b** were subjected to crystallographic analysis. ORTEP diagrams are provided in Figures 4 and 5. Details of the crystallographic analyses are presented in Table 2, and selected bond distances and angles are given in Table 1, along with previously determined parameters for **1d**.[41] The corresponding trifluoromethyl derivative **1c** was also subjected to a crystallographic evaluation, but the CH_3 and CF_3 groups were completely disordered, and no useful metric information was obtained.

It is curious that the Ir−CH_3 bonds in **1a**,**b** differ by more than 0.1 Å yet all the angles at the iridium metal center are the same within experimental error for both molecules. The Ir−α-C_F bond in **1d** (2.150(16) Å)[41] is significantly longer than the analogous bonds in **1a**,**b** (2.044(4) and 2.074(5) Å, respectively), most likely due to the different steric properties of secondary vs primary perfluoroalkyl groups, as described above for the fluoro analogues **5a**,**b**. The fluoroalkyl ligands in **1a**,**b** adopt the usual staggered conformations with the β-CF_x carbon sitting in the region of space between the Cp* and PMe_3 ligands.

To explore whether the solid-state structure was maintained in solution, $^{19}F\{^1H\}$ HOESY experiments were carried out. We have recently demonstrated that this is a reliable technique for analysis of solution structures of iridium−fluoroalkyl complexes, confirming that the structure in solution usually matches up with that in the crystal.[41] The $^{19}F\{^1H\}$ HOESY spectrum obtained for **1a** is shown in Figure 6.

The following qualitative observations can be made: (1) α-F_A is close in space to Cp* and CH_3; (2) β-CF_3 is close in space to Cp* and PMe_3; (3) α-F_B is close in space to PMe_3 and CH_3; (4) β-F_C and β-F_D are close in space to Cp* and PMe_3. The intensities of the cross-peaks for β-F_C and β-F_D clearly establish that β-F_C is in closer proximity to PMe_3 than is β-F_D, while β-F_D is closer to Cp* than is β-F_C. The only structure consistent with these observations is that observed in the solid state and shown in Figure 4. As usually found for this class of compounds, the R_F group (i.e. β-CF_2 and CF_3 in this case) is situated between Cp* and PMe_3.[41] An analogous $^{19}F\{^1H\}$ HOESY experiment provides the same conclusion regarding the solid-state and solution conformations of **1b**.

Conclusions

The original synthesis of complex **1a** (from the triflate complex **3** and CH_3Li) was found to be poorly reproducible, but treatment of the fluoroalkyl fluoride compounds **5** with 0.5 equiv of $Zn(CH_3)_2$ in toluene at −78 °C cleanly gave **1a** and a variety of primary and secondary fluoroalkyl analogues in high yields. Complexes **5** were themselves synthesized cleanly by treatment of the iodide precursors with AgF in methylene chloride in the dark or in toluene with ultrasound. With a reliable route to compounds **1** now in hand, detailed kinetic investigations of the C−F bond activation and methyl migration reactions of these compounds 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 Aquasorb, or in a Braun drybox. Methylene chloride, hexane, diethyl ether, and toluene were dried over an alumina column under nitrogen. Benzene was dried over sodium/benzophenone, distilled, and stored over 4 Å molecular sieves. AgF (Matrix) was used as received and handled in a drybox. NMR spectra were recorded on a Varian Unity Plus 300 or 500 MHz FT spectrometer. ^1H NMR spectra were referenced to the protio impurity in the solvent. ^{19}F NMR spectra were referenced to external $CFCl_3$ (0.00 ppm); for fluoride complexes **5** samples were run in the presence of dry CsF at 21 °C unless otherwise noted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Cp*Ir(PMe$_3$)(R$_F$)X (5, X = F; 4, X = I; 1, X = CH$_3$; R$_F$ = CF'$_2$CF$_2$CF$_3$ (a), CF$_2$CF$_3$ (b), CF(CF$_3$)$_2$ (c))

	5a	5b[a]		5d	4a[48]	4b[a,48]		4d[48]	1a	1b	1d[41]
Ir−X	2.070(2)	2.055(3)	2.060(4)	2.074(3)	2.7206(6)	2.7498(19)	2.8051(19)	2.7466(13)	2.145(4)	2.258(4)	2.22(2)
Ir−P	2.2858(11)	2.2801(17)	2.2719(18)	2.3029(18)	2.307(2)	2.283(4)	2.280(4)	2.333(4)	2.2568(11)	2.2870(14)	2.258(4)
Ir−C$_\alpha$	2.062(4)	2.072(6)	2.069(7)	2.125(5)	2.098(8)	2.12(3)	2.26(4)	2.19(2)	2.044(4)	2.074(5)	2.150(16)
Ir−Cp*(cen)	1.848(4)	1.843(6)	1.842(6)	1.853(5)	1.902(8)	1.914(16)	1.874(15)	1.90(2)	1.907(4)	1.931(5)	1.906(14)
C$_\alpha$−F$_A$	1.404(5)	1.398(7)	1.399(9)	1.393(5)	1.411(9)	1.23(3)	1.42(3)	1.46(2)	1.406(5)	1.424(5)	1.429(15)
C$_\alpha$−F$_B$	1.385(5)	1.407(7)	1.401(8)		1.395(9)	1.54(3)	1.59(4)		1.412(5)	1.434(6)	−
C$_\alpha$−Ir−P	94.20(12)	90.85(18)	90.6(2)	92.30(14)	92.7(2)	93.9(6)	94.2(6)	93.8(4)	93.90(12)	93.71(14)	94.1(4)
C$_\alpha$−Ir−X	84.79(14)	87.5(2)	89.9(2)	82.97(14)	88.0(2)	90.6(10)	91.9(11)	88.1(5)	84.72(19)	85.08(16)	87.9(7)
X−Ir−P	80.84(8)	83.16(12)	80.76(13)	80.11(10)	89.20(7)	88.73(15)	89.26(15)	86.97(13)	86.20(14)	86.26(11)	83.6(6)

[a] Two independent molecules.

Table 2. Crystal Data and Summary of X-ray Data Collection Details for Compounds 1 and 5

	1a	1b	5a	5b	5d
formula	$C_{17}H_{27}F_7IrP$	$C_{16}H_{27}F_5IrP$	$C_{16}H_{24}F_8IrP$	$C_{15}H_{24}F_6IrP$	$C_{16}H_{24}F_8IrP$
fw	587.56	537.55	591.52	541.51	591.52
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	8.6376(4)	8.739(4)	9.1540(7)	9.0365(19)	8.627(8)
b, Å	14.5419(6)	28.391(12)	13.0719(9)	17.816(4)	16.639(16)
c, Å	16.7255(7)	8.802(4)	16.7223(12)	22.964(5)	13.636(13)
α, deg	90	90	90	90	90
β, deg	104.3030(10)	117.028(5)	103.8990(10)	95.502(3)	104.583(12)
γ, deg	90	90	90	90	90
V, Å^3	2035.72(15)	1945.2(14)	1942.4(2)	3680.1(13)	1894(3)
Z, *Z*′	4, 1	4, 1	4, 1	8, 2	4, 2
cryst color, habit	yellow, block	colorless, plate	yellow, blades	yellow, rod	yellow, plate
D(calcd), g/cm^3	1.917	1.836	2.023	1.955	2.074
μ(Mo Kα), mm^{-1} (λ = 0.710 73 Å)	6.697	6.985	7.027	7.393	7.205
temp, K	100(2)	100(2)	120(2)	218(2)	100(2)
diffractometer			Bruker Smart Apex		
no. of indep rflns	4799 (R_{int} = 0.0234)	4288 (R_{int} = 0.0513)	4381 (R_{int} = 0.0220)	8058 (R_{int} = 0.0355)	4281 (R_{int} = 0.0307)
$R(F)$, %[a] ($I > 2\sigma(I)$)	3.04	3.47	2.77	3.72	2.99
$R_w(F^2)$, %[a] ($I > 2\sigma(I)$)	8.04	8.48	6.81	8.65	6.63

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

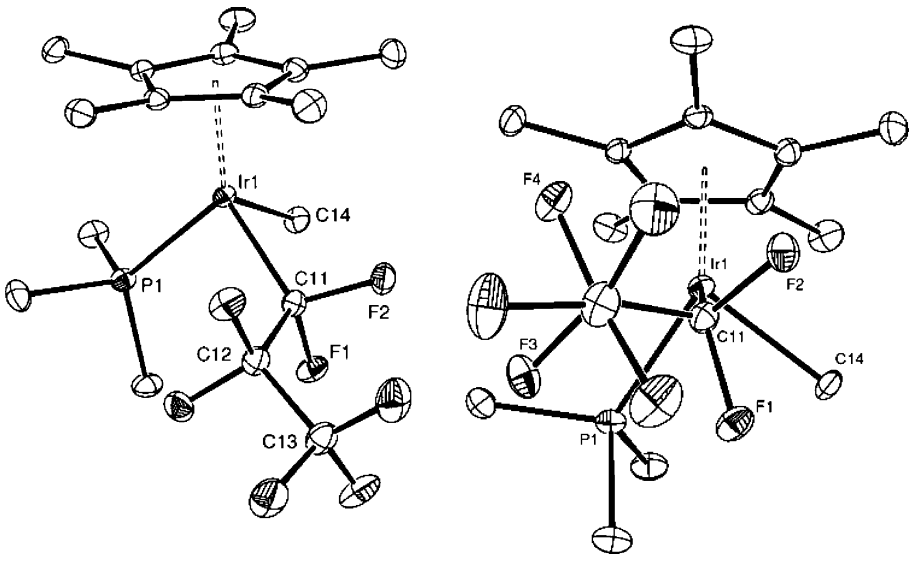


Figure 4. ORTEP diagrams of **1a** from two different perspectives with ellipsoids drawn at the 30% probability level. All hydrogen atoms are excluded. Selected bond lengths and angles are presented in Table 1.

$^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 (0.00 ppm). Microanalyses were performed by Schwartzkopf (New York). The characterizations of complexes Cp*Ir(PMe$_3$)(n-C$_3$F$_7$)-Me (**1a**),[40] Cp*Ir(PMe$_3$)(i-C$_3$F$_7$)Me (**1d**),[41] Cp*Ir(PMe$_3$)(n-C$_3$F$_7$)I (**4a**), Cp*Ir(PMe$_3$)(CF$_2$CF$_3$)I (**4b**), Cp*Ir(PMe$_3$)(i-C$_3$F$_7$)I (**4d**),[48] and Cp*Ir(PMe$_3$)(CF$_3$)I (**4c**)[49] have been previously reported.

Cp*Ir(PMe$_3$)(n-C$_3$F$_7$)F (5a). Cp*Ir(PMe$_3$)(n-C$_3$F$_7$)I (500 mg, 0.715 mmol) and AgF (272 mg, 2.14 mmol) were charged into a Schlenk flask. CH_2Cl_2 (30 mL) was added, and the mixture was stirred in the dark for 24 h, resulting in a dark precipitate of AgI. The yellow solution was filtered through Celite, and the solvent was removed to give the product as a yellow solid (yield 420 mg, 99%). Anal. Calcd for $C_{16}H_{24}F_8IrP$ (591.55): C, 32.49; H, 4.09. Found: C, 32.67; H, 4.26. ^1H NMR (C_6D_6): δ 1.33 (d, 15H, J_{PH} = 2 Hz, Cp*), 1.16 (d, 9H, J_{PH} = 11 Hz, PMe$_3$). ^{19}F NMR (C_6D_6):

(49) Hughes, R. P.; Laritchev, R. B.; Yuan, J.; Golen, J. A.; Rucker, A. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 15020−15021.

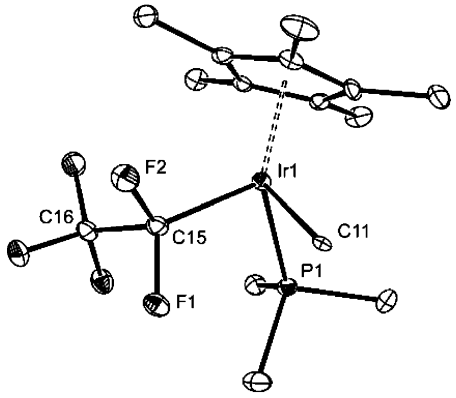


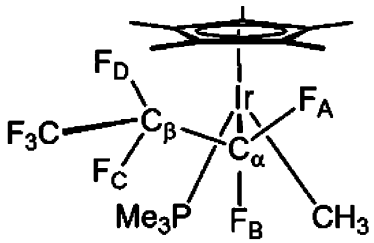
Figure 5. ORTEP diagram of **1b** with ellipsoids drawn at the 30% probability level. All hydrogen atoms are excluded. Selected bond lengths and angles are presented in Table 1.

δ −75.3 (dd, J_{AB} = 289 Hz, J_{PF} = 39 Hz, α-F), −79.3 (s, CF_3), −84.1 ppm (d, J_{AB} = 289 Hz, α-F), −116.4 (d, J_{AB} = 289 Hz, *β*-F), −118.8 ppm (d, J_{AB} = 289 Hz, *β*-F), −434 (br s, Ir−*F*). ^{19}F NMR (282.2 MHz, CD_2Cl_2): δ −81.7 (dddq, $^2J_{FF}$ = 280, $^3J_{FP}$ = 30, $^3J_{FF}$ = 13, $^4J_{FF}$ = 11 Hz, 1F, α-C−F), −80.6 (t, $^4J_{FF}$ = 11 Hz, 3F, CF_3), −88.2 (dq, $^2J_{FF}$ = 280, $^4J_{FF}$ = 11 Hz, 1F, α-C−F), −116.8 (d, $^2J_{FF}$ = 286 Hz, 1F, *β*-C−F), −119,5 (dddd, $^2J_{FF}$ = 286, $^3J_{FF}$ = 10, $^3J_{FF}$ = 10, $^4J_{FP}$ = 9 Hz, 1F, *β*-C−F), −446.1 (dd, $^2J_{PF}$ = 52, $^3J_{FF}$ = 13 Hz, 1F, Ir−F). ^{31}P{^{1}H} NMR (C_6D_6): δ −24.23 (ddd, $^2J_{PF}$ = 53 Hz, $^3J_{PF}$ = 39 Hz, $^4J_{PF}$ = 6 Hz). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2): δ −24.9 (ddd, $^2J_{PF}$ = 52, $^3J_{PF}$ = 30, $^4J_{PF}$ = 9 Hz, PMe_3).

Cp*Ir(PMe$_3$)(i-C$_3$F$_7$)F (5d). The complex Cp*Ir(PMe_3)(i-C_3F_7)F (**5d**) was synthesized from **4d** (500 mg, 0.715 mmol) and AgF (272 mg, 2.14 mmol) by an analogous procedure, affording a yellow solid (415 mg, 97%). Anal. Calcd for $C_{16}H_{24}F_8IrP$ (591.55): C, 32.49; H, 4.09. Found: C, 32.72; H, 4.17. ^{1}H NMR (C_6D_6): δ 1.10 (dd, J_{PH} = 11, J_{FH} = 1 Hz, 9H, PMe_3), 1.08 (s, 15H, Cp*). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.57 (dd, J_{PH} = 2 Hz, 15H, Cp*), 1.50 (dd, $^2J_{PH}$ = 11, J_{HF} = 2 Hz, 9H, PMe_3). ^{19}F NMR (C_6D_6): δ −66.9 (br s, 3F, CF_3), −68.7 (br s, 3F, CF_3), −171.3 (br s, 1F, α-F), −441 (br s, Ir−*F*). ^{31}P{^{1}H} NMR (C_6D_6): δ −28.24 (br s). ^{19}F NMR (CD_2Cl_2, 21 °C): δ −70.2 (dq, J = 17, $^4J_{FF}$ = 9 Hz, 3F, CF_3), −70.6 (br s, 3F, CF_3), −434.3 (br d, $^2J_{PF}$ = 50, 1F, Ir−F).

Cp*Ir(PMe$_3$)(CF$_2$CF$_3$)F (5b). Cp*Ir(PMe_3)(CF_2CF_3)I (190 mg, 0.292 mmol) and AgF (115 mg, 0.906 mmol) were charged into a Schlenk flask. Dry CH_2Cl_2 (30 mL) was added, and the mixture was stirred in the dark for 24 h at room temperature. The yellow solution was filtered, and the solvent was removed. The yellow oily residue was extracted with warm hexane (2 × 30 mL). Filtration and removal of the solvent afforded analytically pure product (146 mg) in 92% yield. Anal. Calcd for $C_{15}H_{24}F_6IrP$ (541.54): C, 33.27; H, 4.47. Found: C, 32.89; H, 4.50. ^{1}H NMR (500 MHz, C_6D_6): δ 1.37 (s, 15H, Cp*), 1.19 (d, $^2J_{PH}$ = 11 Hz, 9H, PMe_3). ^{19}F NMR (282.2 MHz, C_6D_6): δ −78.9 (dd, $^2J_{FF}$ = 278, $^3J_{FP}$ = 41 Hz, 1F, α-C−F), −80.5 (d, $^4J_{FF}$ = 15 Hz, 3F, CF_3), −82.8 (d, $^2J_{FF}$ = 278 Hz, 1F, α-C−F), −453.3 (br s, 1F, Ir−F). ^{19}F NMR (282.2 MHz, CD_2Cl_2): δ −80.5 (dd, $^2J_{FF}$ = 276, $^3J_{FP}$ = 34 Hz, 1F, α-C−F), −81.8 (d, $^4J_{FF}$ = 10 Hz, 3F, CF_3), −87.0 (d, $^2J_{FF}$ = 276 Hz, 1F, α-C−F), −446.8 (br dq, $^2J_{PF}$ = 50, $^4J_{FF}$ = 10 Hz, 1F, Ir−F). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ −24.2 (dd, $^2J_{PF}$ = 50, $^3J_{FP}$ = 41 Hz, PMe_3). ^{31}P{^{1}H} NMR (121.43 MHz, CD_2Cl_2): δ −24.2 (dd, $^2J_{PF}$ = 50, $^3J_{FP}$ = 34 Hz, PMe_3).

Cp*Ir(PMe$_3$)(CF$_3$)F (5c). Cp*Ir(PMe_3)(CF_3)I (50 mg, 0.083 mmol) and AgF (32 mg, 0.25 mmol) were charged into a Schlenk flask. Toluene (30 mL) was added and the mixture stirred in an ultrasound bath for 12 h, resulting in a dark precipitate of AgI. The yellow solution was filtered, and the solvent was removed to give a mixture of **5c** (70%) and **4c** (30%) as a yellow oily material



1a

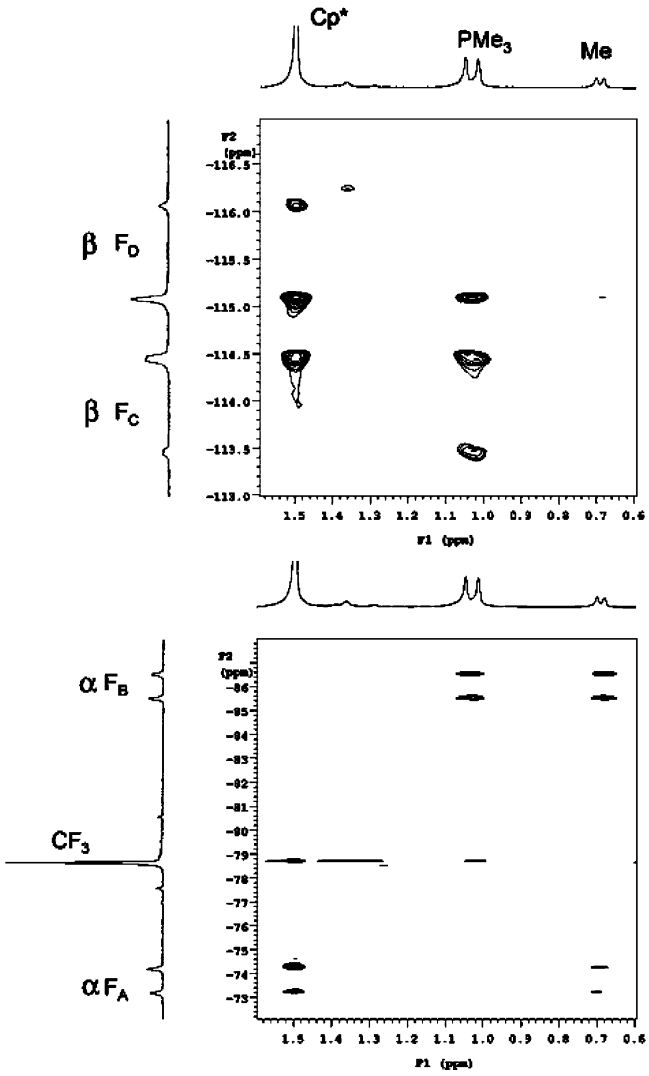


Figure 6. ^{19}F{^{1}H} HOESY spectrum for **1a** in C_6D_6 solution (mixing time 2.4 s).

(40 mg, 65% yield). This could not be separated and was used as a mixture for subsequent synthesis of **1c** (below). ^{1}H NMR (C_6D_6, 500 MHz, 21 °C): δ 1.21 (d, $^2J_{PH}$ = 10.8 Hz, 9H, PMe_3), 1.40 (dd, $^4J_{PH}$ = 1.5 Hz, $^4J_{FH}$ = 1.5 Hz, 15H, C_5Me_5). ^{19}F NMR (C_6D_6, 470.3 MHz, 21 °C): δ −17.30 (dd, $^3J_{FF}$ = 8.8 Hz, $^3J_{PF}$ = 5.1 Hz, 3F, CF_3), −442 (br m, 1F, IrF). ^{31}P{^{1}H} NMR (C_6D_6, 202.35 MHz, 21 °C): δ −25.26 (dq, $^2J_{PF}$ = 46 Hz, $^3J_{PF}$ = 5 Hz, 1P).

Cp*Ir(PMe$_3$)(s-C$_4$F$_9$)(F) (5e). Cp*Ir(PMe_3)(s-C_4F_9)(I) (0.207 g, 0.276 mmol) and silver fluoride (0.108 g, 0.851 mmol) were charged into a Schlenk flask, and methylene chloride (10 mL) was added. This mixture was stirred at room temperature in the dark (19 h). The orange solution was then filtered and the solvent removed to yield a yellow oily solid, which was recrystallized from methylene chloride/hexanes at −78 °C to give an analytically pure

yellow powder. The NMR spectra show the desired product as two diastereomers in a ratio of 2:1. Yield: 0.166 g (94%). Anal. Calcd for $C_{17}H_{24}F_{10}IrP$ (641.36): C, 31.83; H, 3.77. Found: C, 31.94; H, 3.75. A $^{19}F\{^1H\}$ HOESY experiment[41] (C_6D_6, 21 °C, mixing time 3 s) showed that the major diastereomer had the relative configurations (R_{Ir},S_C)(S_{Ir},R_C). Major diastereomer: ^1H NMR (C_6D_6) δ 1.21 (s, 15 H, C_5Me_5), 1.12 (dd, $^2J_{PH}$ = 11, $^3J_{HF}$ = 2 Hz, 9H, $P(CH_3)_3$); ^1H NMR (CD_2Cl_2, 300 MHz, 21 °C) δ 1.58 (d, J_{HP} = 2 Hz, 15H, Cp*), 1.49 (dd, $^2J_{PH}$ = 11, J_{HF} = 3 Hz, 15H, PMe_3); ^{19}F NMR (C_6D_6) δ −68.6 (s, 3F, CF_3^A), −79.8 (s, 3F, CF_3^B), −92.0 (dd, $^2J_{FF}$ = 280, $^3J_{FF}$ = 17 Hz, 1F, CF_2), −113.6 (dd, $^2J_{FF}$ = 282, $^3J_{FF}$ = 16 Hz, 1F, CF_2), −181.1 (s, 1F, CF), −442.1 (s, 1F, IrF); ^{19}F NMR (CD_2Cl_2, 282.2 MHz, 21 °C) δ −69.0 (s, 3F, CF_3), −80.6 (s, 3F, CF_3), −93.7 (dd, $^2J_{FF}$ = 270, $^3J_{FF}$ = 14 Hz, 1F, CF_2), −114.4 (dq, $^2J_{FF}$ = 270, $^3J_{FF}$ = 14 Hz, 1F, CF_2), −183.0 (s, 1F, α-C−F), −443.0 (br d, $^2J_{PF}$ = 52 Hz, 1F, Ir−F); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −23.8 (m, $P(CH_3)_3$). Minor diastereomer: ^1H NMR (C_6D_6) δ 1.21 (s, 15 H, C_5Me_5), 1.15 (dd, $^2J_{PH}$ = 11, $^3J_{HF}$ = 1.5 Hz, 9H, $P(CH_3)_3$); ^1H NMR (CD_2Cl_2, 300 MHz, 21 °C) δ 1.57 (d, J_{HP} = 2 Hz, 15H, Cp*), 1.50 (dd, $^2J_{PH}$ = 11, J_{HF} = 3 Hz, 9H, PMe_3); ^{19}F NMR (C_6D_6) δ −68.3 (br s, CF_3^A), −78.8 (s, 3F, CF_3^B), −97.0 (d, $^2J_{FF}$ = 292 Hz, 1F, CF_2), −110.6 (d, $^2J_{FF}$ = 292 Hz, 1F, CF_2), −184.5 (s, 1F, CF), −437.8 (s, 1F, IrF); ^{19}F NMR (CD_2Cl_2, 282.2 MHz, 21 °C) δ −69.0 (s, 3F, CF_3), −79.6 (s, 3F, CF_3), −97.4 (br d, $^2J_{FF}$ = 290 Hz, 1F, CF_2), −110.8 (br d, $^2J_{FF}$ = 290 Hz, 1F, CF_2), −185.4 (br s, 1F, α-C−F), −438.7 (br s, 1F, Ir−F); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −23.8 (m, $P(CH_3)_3$).

Cp*Ir(PMe$_3$)(n-C$_3$F$_7$)CH$_3$ (1a). To a solution of **5a** (100 mg, 0.169 mmol) in toluene (5 mL) at −78 °C was added a 2 M solution of $ZnMe_2$ (43 μL, 0.0845 mmol) in toluene by syringe. The mixture was stirred for 1 h at this temperature and then warmed slowly to room temperature. The yellow color lightened gradually as the reaction proceeded. A drop of EtOH was added to quench any remaining zinc alkyl, and then the solvent was removed in vacuo. The residue was extracted with hexane; the solution was filtered and then evaporated to afford the product as an off-white solid (yield 92 mg, 93%). Recrystallization from hexane at −70 °C affords a product pure by NMR and spectroscopically identical with that reported previously.[40]

Cp*Ir(PMe$_3$)(CF$_2$CF$_3$)CH$_3$ (1b) and Cp*Ir(PMe$_3$)(i-C$_3$F$_7$)CH$_3$ (1d) were prepared by an analogous procedure. Compound **1d** has been previously prepared and characterized by an alternative route.[41] **1b**: yield 88%. Anal. Calcd for $C_{16}H_{27}F_5IrP$ (537.58): C, 35.75; H, 5.06. Found: C, 36.14; H, 5.02. ^1H NMR (C_6D_6, 500 MHz, 21 °C): δ 0.71 (d, $^3J_{PH}$ = 5.8 Hz, 3H, $IrCH_3$), 1.02 (dd, $^2J_{PH}$ = 10.0 Hz, $^5J_{FH}$ = 1.0 Hz, 9H, PMe_3), 1.49 (d, $^4J_{PH}$ = 1.8 Hz, 15H, C_5Me_5). ^{19}F NMR (C_6D_6, 470.3 MHz, 21 °C): δ −77.30 (ddq, $^2J_{F(AB)}$ = 278, $^3J_{FP}$ = 7.4, $^3J_{FF}$ = 3.5 Hz, 1F, CF_2), −82.34 (ddd, $^3J_{FF}$ = 3.5, $^4J_{PF}$ = 3.5, $^3J_{FF}$ = 2.6 Hz, 3F, CF_3), −88.68 (dq decet, $^2J_{F(AB)}$ = 278, $^3J_{FF}$ = 2.6, $^5J_{FH}$ = 1.0 Hz, 1F, CF_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.35 MHz, 21 °C): δ −36.96 (dq, $^3J_{PF}$ = 7.4, $^4J_{PF}$ = 3.5 Hz, 1P).

Cp*Ir(PMe$_3$)(CF$_3$)CH$_3$ (1c). A mixture of **5c** and **4c** (vide supra) that proved to be inseparable by extraction was used for the reaction with $ZnMe_2$. Everything else was done according to the procedure described above to afford **1c** (81%). Anal. Calcd for $C_{15}H_{27}F_3IrP$ (487.58): C, 36.95; H, 5.58. Found: C, 37.12; H, 5.80. ^1H NMR (C_6D_6, 500 MHz, 21 °C): δ 0.69 (d, $^3J_{PH}$ = 5.8 Hz, 3H, $IrCH_3$), 1.09 (d, $^2J_{PH}$ = 10.2 Hz, 9H, PMe_3), 1.58 (d, $^4J_{PH}$ = 1.8 Hz, 15H, C_5Me_5). ^{19}F NMR (C_6D_6, 470.3 MHz, 21 °C): δ −9.70 (d, $^3J_{PF}$ = 3.9 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.35 MHz, 21 °C): δ −39.23 (q, $^3J_{PF}$ = 3.9 Hz, 1P).

Cp*Ir(PMe$_3$)(s-C$_4$F$_9$)CH$_3$ (1e). A clear yellow solution of Cp*Ir(PMe_3)(sC_4F_9)(F) (0.032 g, 0.050 mmol) in toluene (5 mL) was cooled to −78 °C. To this was added a solution of Me_2Zn (25 μL, 0.050 mmol, 2 M in toluene) dropwise. This mixture was stirred at −78 °C (30 min) and then slowly warmed to room temperature (1 h). The solution became a clear paler yellow. A drop of ethanol was added to destroy any unreacted Me_2Zn and the solvent removed to yield a yellow oily solid. Extraction in hexanes and removal of the solvent yielded a colorless solid, which was recrystallized from hexanes at −78 °C. Yield: 0.025 g (78%). NMR spectra showed the product to have a ∼1:1 diastereomer ratio, with properties identical with those previously prepared by another route.[41]

Acknowledgment. R.P.H. is grateful to the National Science Foundation for generous financial support.

Supporting Information Available: CIF files for compounds **1a**,**b** and **5a**,**b**,**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060267S