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Synthetic, Thermochemical, and Catalytic Studies of Fluorinated Tertiary Phosphine Ligands R_2PR_f [R = Cy, Ph, ^iPr; $R_f = CH'_2CH_2(CF_2)_5CF_3$] in Rhodium Systems

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The fluoroalkylphosphine compounds PR_2R_f (R = Cy (**1**); ^iPr (**2**); $R_f = CH_2CH_2(CF_2)_5CF_3$) have been prepared from the reactions of the Grignard reagent $IMgR_f$ and appropriate $ClPR_2$ (R = Cy, ^iPr). The fluorinated phosphine ligands [PR_2R_f (R = Cy (**1**); ^iPr (**2**); Ph (**3**); $R_f = CH_2CH_2(CF_2)_5CF_3$] react with $[Rh(CO)_2Cl]_2$ to yield the corresponding $[Rh(CO)Cl(PR_2R_f)_2]$ (R = Cy (**4**); ^iPr (**5**); Ph (**6**)) complexes. Infrared studies on the carbonyl complexes and solution calorimetry studies of the reaction of $[Rh(CO)_2Cl]_2$ with PR_2R_f (R = Ph, ^iPr, Cy) have been used to quantify the relative ligand donor strength for the series: $PCy_2R_f \approx P^iPr_2R_f > PPh_2R_f$. The solid-state crystal structure of $[Rh(CO)Cl(PPh_2R_f)_2]$ (**6**) is reported. Additionally, these partially fluorinated phosphine ligands (**1** and **3**) can be used as supporting ligation in rhodium-mediated hydrogenation reactions.

Introduction

Phosphine ligands have and continue to play an important role in organometallic chemistry and homogeneous catalysis.[1−3] Recent developments in phosphine synthesis have allowed for innovative approaches to catalysis in nontraditional media such as supercritical CO_2,[4,5] aqueous,[6,7] and fluorinated solvents.[8−11] One strategy employed in fluorinated biphasic catalysis relies on ligand modification by attaching fluorinated substituents or tails, such as $(CH_2)_x(CF_2)_yCF_3$ to the ancillary ligand backbone.[8−10] Using this general technique a variety of fluorinated phase soluble ligands have been prepared, such as phosphines,[8−10,12,13] phosphites,[8−10] porphyrins,[14−16] and cyclopentadienes.[17] Thus, the synthesis of transition metal complexes bearing ancillary ligation containing fluorinated appendages has been utilized in order to render catalysts (or precatalysts) soluble in fluorinated or supercritical CO_2 media.[8−10] Examples of these fluorinated transition metal complexes include $HRh(CO)\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$,[8−10] $ClRh\{P[CH_2CH_2(CF_2)_5CF_3]_3\}_3$,[18] $ClM(CO)\{P[CH_2CH_2(CF_2)_5CF_3]\}_2$ (M = Ir, Rh),[19−21] fluorinated porphyrin complexes,[14−16] fluorinated cyclopentadienyl complexes,[17] as well as other complexes.[22] Importantly, Horváth and Gladysz have recently utilized a fluorinated phosphine ligand $P[CH_2CH_2(CF_2)_5CF_3]_3$ in biphasic catalytic hydrogenation and hydroboration which allows for segregation of the organometallic catalyst from the organic reactants and products.[10] Furthermore, Horváth has recently reported a detailed study of the ancillary ligand $P[CH_2CH_2(CF_2)_5CF_3]_3$ applied to hydroformylation.[23]

While probing the stereoelectronic properties of the "ponytail" ligand $P[CH_2CH_2(CF_2)_5CF_3]_3$ in a rhodium system,[24] we became interested in developing a series of fluorinated phosphine ligands with more tunable stereoelectronic properties. We have recently reported our initial efforts in this area which describe the examination of a series of easily synthesized, partially fluorinated, phosphinite ligands (R_2POR_f, R = Ph, ^iPr, Cy).[25] The steric and electronic properties of this ligand type are simply modulated by the steric and electronic properties of the aryl/alkyl group bound to the phosphorus atom. These variations

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were observed to affect the catalytic properties of rhodium centers bearing these ligands. We now report the synthesis of a new class of fluorophosphine ligands (R_2PR_f, R = Ph, ^iPr, Cy; $R_f = CH_2CH_2(CF_2)_5CF_3$), and their associated rhodium complexes and preliminary catalytic results of the novel rhodium complexes.

Results and Discussion

Ligand Syntheses. The PCy_2R_f (**1**) and $P^iPr_2R_f$ (**2**) ligands were prepared by reaction of an excess of the Grignard reagent[26] ($IMgR_f$) with the appropriate commercially available chloroalkylphosphine in Et_2O (eq 1). Upon workup, the phosphine ligands were obtained in high yields (80−85%).

$$R_2PCl + R_fMgI \xrightarrow{Et_2O} R_2PR_f + MgICl \qquad (1)$$

$$R = Cy\ (\mathbf{1}),\ {}^iPr\ (\mathbf{2});\quad R_f = CH_2CH_2(CF_2)_5CF_3$$

Attempts to prepare PPh_2R_f (**3**) using the same methodology proved unsuccessful. Compound **3** was prepared by modification of the previously reported methodology.[26] Ligands **1**, **2**, and **3** are soluble in a variety of solvents that include Et_2O, THF, CH_2Cl_2, $C_6H_5CF_3$, and pentane.

Organorhodium Syntheses. All organorhodium complexes were prepared in a similar manner from $[Rh(CO)_2Cl]_2$ and the appropriate phosphine ligands in CH_2Cl_2 at ambient temperature according to eq 2. In all cases, the reaction proceeded rapidly

$$[RhCl(CO)_2]_2 + 4R_2PR_f \xrightarrow{CH_2Cl_2} 2RhCl(CO)(R_2PR_f)_2 + 2CO \qquad (2)$$

$$R = Cy\ (\mathbf{4}),\ {}^iPr\ (\mathbf{5}),\ Ph\ (\mathbf{6});\quad R_f = CH_2CH_2(CF_2)_5CF_3$$

and was accompanied by the vigorous evolution of CO. Compounds **4** and **6** were isolated as yellow microcrystalline solids, while **5** was obtained as a yellow oil. Complexes **4**, **5**, and **6** are soluble in THF and CH_2Cl_2, while complexes **4** and **5** are also soluble in pentane.

Relationship between Thermochemical and Infrared Data. Solution calorimetric investigation of the ligand substitution of eq 2 was performed in CH_2Cl_2 to assess the binding affinity of the new ligands. The electronic properties of each ligand can be gauged by examining the position of the carbonyl stretching frequencies in the infrared spectrum. Enthalpies of reaction, carbonyl stretching frequencies of complexes **4**−**6**, and similar data for a selection of previously studied complexes are summarized in Table 1.

The enthalpy of reaction and carbonyl stretching frequency trends observed as a function of phosphine ligand in the PR_2R_f series follow the electronic donor properties of the alkyl/aryl groups as established by Tolman where the ligand donor ability is as follows: $PCy_2R_f \approx P^iPr_2R_f > PPh_2R_f$.[27] This is as expected but the thermochemical results offer a quantitative comparison of ligand donor properties.

Table 1. Enthalpies of Substitution (kcal/mol) in Reaction **2**

L	complex	ν_{CO} (cm^{-1})	$-\Delta H_{(rxn)}$[a]
PPh_2R_f	$Rh(CO)Cl(PPh_2R_f)_2$	1979	51.3 (0.3)[b]
PPh_3	$Rh(CO)Cl(PPh_3)_2$	1978	51.7 (0.3)[c]
$P(OR_f)_3$	$Rh(CO)Cl(P(OR_f)_3)_2$	2024	56.6 (0.5)[d]
PPh_2Me	$Rh(CO)Cl(PPh_2Me)_2$	1973	61.7 (0.3)[c]
$PPh_2(OR_f)$	$Rh(CO)Cl(PPh_2(OR_f))_2$	1990	63.7 (0.4)[d]
$P^iPr_2(OR_f)$	$Rh(CO)Cl(P^iPr_2(OR_f))_2$	1977	64.9 (0.3)[d]
PCy_3	$Rh(CO)Cl(PCy_3)_2$	1942	66.4 (0.4)[e]
PCy_2R_f	$Rh(CO)Cl(PCy_2R_f)_2$	1956	67.5 (0.3)[b]
$PCy_2(OR_f)$	$Rh(CO)Cl(PCy_2(OR_f))_2$	1963	68.5 (0.2)[d]
$P(R_f)_3$	$Rh(CO)Cl(P(R_f)_3)_2$	1977	68.5 (0.2)[f]
P^iPr_3	$Rh(CO)Cl(P^iPr_3)_2$	1947	68.7 (0.4)[e]
$P^iPr_2R_f$	$Rh(CO)Cl(P^iPr_2R_f)_2$	1960	68.7 (0.3)[b]
$PPhMe_2$	$Rh(CO)Cl(PPhMe_2)_2$	1968	71.4 (0.3)[c]

[a] Enthalpy data reported with 95% confidence limits. [b] This work. [c] Taken from ref 29. [d] Taken from ref 25. [e] Taken from ref 30. [f] Taken from ref 28.

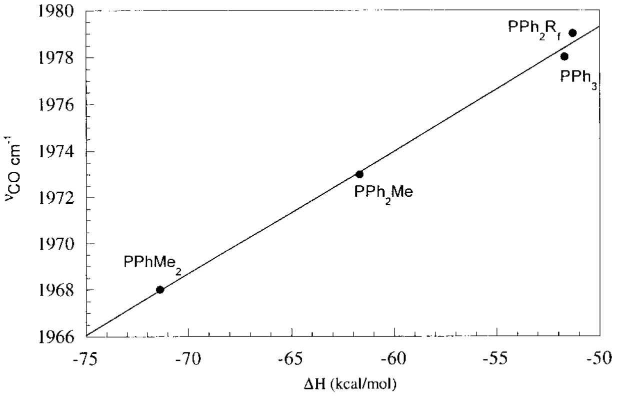

Figure 1. Carbonyl stretching frequency (cm^{-1}) versus enthalpy of reaction (kcal/mol) in the $RhCl(CO)(PR_2Ph)_2$ system; slope = 0.529; R = 0.998.

A comparison of the carbonyl stretching frequency and enthalpy of reaction data for a family of phenyl substituted ligands is shown in Figure 1. The observed relationship provides insight into the electronic parameters associated with the R_f subsituent. The excellent linear correlation between the carbonyl stretching frequency and enthalpy of reaction in Figure 1 suggests that the R_f moiety electronically behaves similarly to a phenyl group. Thus, the short methylene ($-CH_2CH_2-$) spacer does not effectively insulate the electron withdrawing properties of the fluorine containing moiety. A similar effect was observed in the determination of stereoelectronic properties of the ponytail ligand $P(R_f)_3$.[28] To compare the effect of the R_f fragment, carbonyl stretching frequency, and enthalpy of reaction data, pairs of cyclohexyl (Cy_2PR_f/PCy_3) and isopropyl ($^iPr_2PR_f/P^iPr_3$) substituted ligands can be compared. When these data are examined side by side, it can be concluded that the R_f group has a similar influence on the overall phosphine electronic effects. The carbonyl stretching frequency of the organorhodium complex moves to higher wavenumber, when either a cyclohexyl or isopropyl moiety is replaced by the R_f group. The R_f group is less donating than either Cy or ^iPr and thus leads to less electron density at the metal, which results in less back-donation into the CO π^* orbital resulting in higher carbonyl stretching frequencies. This trend suggests that the presence of the R_f group yields phosphines with weaker donor properties. The rhodium complexes bearing PPh_3 and **3** have similar carbonyl stretching frequencies which lead us to conclude that, electronically, the R_f behaves as a phenyl group within this series. Examination of the thermochemical data (in light of the conclusions drawn from infrared data) also provides useful information. The PPh_3[29]/**3** ligand pair have similar enthalpy data within experimental error. A similar trend follows for the $PiPr_3$/**2** ligand pair that have enthalpy data that are the same within experimental

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Table 2. Crystallographic Data for $Rh(CO)(Cl)(PPh_2R_f)_2$ (**6**)

chemical formula = $C_{41}H_{28}ClF_{26}OP_2Rh$	formula weight = 1230.93
$a = 12.1416(8)$ Å	space group = $P\bar{1}$
$b = 12.8890(9)$ Å	$T = 150(2)$ K
$c = 17.3455(13)$ Å	$\lambda = 0.71073$ Å
$\alpha = 84.180(2)$ deg	ρ(calcd) = 1.686 g/cm^3
$\beta = 80.976(2)$ deg	$\mu = 0.0606$ cm^{-1}
$\gamma = 64.847(2)$ deg	$R^a = 0.0766$
$V = 2424.8(3)$ Å^3	w$R^b = 0.1875$
$Z = 2$	

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$.

error. This is somewhat unexpected based on the measured infrared carbonyl stretching frequency difference. It should be kept in mind here that the enthalpy data does not reflect the variation in one single metal−ligand interaction but must also include reorganization energies after the initial ligand binding. This specific pair is a very clear example of the existence of reorganization energy. The differences between ligand pairs are relatively small and solvation effects may also play a role. The overall thermochemical effect of binding either P^iPr_3[30] or **2** is similar yet the infrared shows a significant rearrangement of the carbonyl C−O interaction. Also of importance in any comparison between this last ligand pair is the difference in phosphine steric property. This effect is more clearly exemplified in comparing the PCy_3/**1** ligand pair. The infrared data suggest PCy_3 is providing more electron density to rhodium than **1**. The thermochemical data suggest the ligand exchange (and reorganization energy) is more favorable (slightly if experimental error is considered) for **1**.

When the thermochemical and infrared data are examined for fluorinated phosphine and phosphinite ligands, no clear correlation emerges. For example, in the $^iPr_2PR_f/^iPr_2POR_f$ pair, a smaller reaction enthalpy is observed when the OR_f group is present while for the Cy_2PR_f/Cy_2POR_f pair the enthalpies are nearly identical. This contrasts with the Ph_2PR_f/Ph_2POR_f pair where a larger reaction enthalpy is measured when the OR_f group is present. The presence of an oxygen atom in the phosphonite ligand family makes this series unique and comparisons with phosphine families are not appropriate. We have previously observed such differing behavior between phosphine and phosphite ligand families. The existence of geometric distortions from square planar geometry cannot be excluded as a possible explanation of the observed diverging trends.[25]

Solid State Crystal Structure of *trans*-$Rh(CO)Cl(PPh_2R_f)_2$ (6). Suitable crystals of **6** where obtained from recrystallization from CH_2Cl_2/pentane to give large, yellow blocks. The data for the single-crystal X-ray analysis are given in Table 2. Selected bond lengths and angles are given in Table 3, and ORTEP depiction of the structure is given in Figure 2.

The structure of **6** is a typical square-planar rhodium(I) complex with trans P ligands. The fluoroalkyl chains in **6** preferentially adopt a parallel configuration. The X-ray structure of a similar complex, *trans*-$Rh(CO)Cl(PPh_2OR_f)_2$ (**7**), displaying similar fluorinated chain alignment, was presented in our previous report,[25] and the gross structural features of **7** are similar to **6**. While the Rh−C(1) bond distances of **6** and **7** are nearly identical, the C(1)−O(1) distance of **6** (1.144 Å) is 0.021 Å longer than the C(1)−O(1) in **7**, this is consistent with a weaker Rh−CO interaction in **6**. This observation reflects the electron deficient/π-accepting nature of **7** relative to **6** and is consistent with the higher carbonyl stretching frequency in **7** (1990 vs 1979 cm^{-1} in **6**). The observed difference makes chemical sense since it is reflected in the infrared measurement but statistically the two metrical parameters are nearly identical. Additionally, comparison of C(1)−O(1) and Rh−C(1) distances in **6** and *trans*-$Rh(CO)(Cl)/(PPh_3)_2$[31] (**8**) shows these distances to be nearly identical. It is then not surprising that the ν_{CO} for the complexes are similar (1978 cm^{-1} for **8** and 1977 cm^{-1} for **6**). The Rh−P and Rh−Cl bond lengths in **6**, **7**, and **8** are similar (±0.03 Å, see Table 4). These fluctuations in bond lengths can be attributed to differences in reorganization energy for these organorhodium complexes. Comparison of the L−Rh−L angles in **6** with those in **7** and **8** reveal only subtle differences, and point to a slight tetrahedral distortion of the P−Rh−P and C(1)−Rh−Cl angles in these complexes (see Table 4).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Rh(CO)(Cl)(PPh_2R_f)_2$ (**6**)

Bond Lengths			
Rh(1)−C(1)	1.828(13)	P(1)−C(2)	1.831(13)
Rh(1)−P(2)	2.312(4)	P(1)−C(10)	1.833(13)
Rh(1)−P(1)	2.319(4)	P(2)−C(36)	1.801(13)
Rh(1)−Cl(1)	2.341(3)	P(2)−C(22)	1.821(15)
O(1)−C(1)	1.144(14)	P(2)−C(30)	1.836(13)
P(1)−C(16)	1.789(14)		
Bond Angles			
C(1)−Rh(1)−P(2)	91.2(4)	C(16)−P(1)−C(10)	103.1(7)
C(1)−Rh(1)−P(1)	92.1(4)	C(2)−P(1)−C(10)	101.3(6)
P(2)−Rh(1)−P(1)	176.5(2)	C(16)−P(1)−Rh(1)	114.1(4)
C(1)−Rh(1)−Cl(1)	173.2(5)	C(2)−P(1)−Rh(1)	115.6(5)
P(2)−Rh(1)−Cl(1)	88.1(1)	C(10)−P(1)−Rh(1)	116.1(5)
P(1)−Rh(1)−Cl(1)	88.5(1)	O(1)−C(1)−Rh(1)	178.3(12)
C(16)−P(1)−C(2)	104.8(7)		

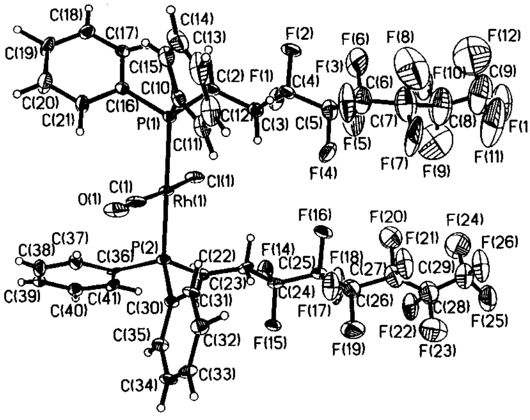

Figure 2. ORTEP of $Rh(CO)(Cl)(PPh_2R_f)_2$ (**6**). Ellipsoids are drawn at 50% probability.

Table 4. Selected Bond Lengths and Bond Angles for the Complexes $Rh(CO)(Cl)(PR)_2$ (R = PPh_2R_f, **6**; PPh_2OR_f, **7**; PPh_3, **8**)

complex	**6**	**7**	**8**[a]
	2.312(4)	2.3036(1)	2.333(1)
Rh−P, Å	2.319(4)	2.3000(13)	2.327(1)
Rh−C, Å	1.828(13)	1.829(5)	1.821(5)
Rh−Cl, Å	2.341(3)	2.3565(13)	2.395(1)
C−O, Å	1.144(14)	1.123(6)	1.141(6)
P(1)−Rh−P(2)	176.46(14)	174.32(5)	176.1(1)
C(1)−Rh−Cl	173.2(5)	176.8(2)	175.5(2)

[a] Taken from ref 31.

Fluorinated Biphasic Hydrogenation of 1-Hexene. The reduction of 1-hexene by $RClL_3$, formed in situ from [(COD)-

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RhCl]$_2$ and 6 equiv of **1** or **3** was performed at 40 °C and 1 atm of H_2 in a biphasic solvent system consisting of a ~1:2 volume ratio of 1-hexene/perfluoro(methylcyclohexane). These conditions are identical to the method employed in our previous report.[25] These transformations were carried out in order to directly compare the catalytic behavior of the phosphine ligands compared to the hybrid phosphonites previously synthesized. The resulting catalytic transformation gave turnovers of 75 for **1** and 202 for **3** in 24 h; no isomerized hexenes were detected in **1** while 30% of the initial 1-hexene was converted into internal olefins by **3**. The catalytic turnover numbers for the phosphine systems **1** and **3** are larger than the values determined for the phosphinite ligands PPh_2OR_f.[25] Apparently, both fluorinated phosphine and phosphinite ligands have electronic and steric properties that yield complexes that display lower reactivities in the hydrogenation catalysis compared to standard Wilkinson-type catalysts.[25] It should be mentioned that no obvious selective partitioning of the catalysts in the fluorinated phase was observed in the course of the catalytic reaction. The number of fluorinated appendages must be greater than what is used in the present system to afford catalyst selective solubilization in the fluorinated solvent.

Homogeneous Hydrogenation of 1-Hexene. Since no advantages are afforded by the use of fluorinated solvents, ligands **1** and **3** were screened using a similar protocol to the one mentioned above but in neat 1-hexene. The catalytic activities of both ligands were found to convert 275 (**1**) and 482 (**3**) equiv of olefin per Rh atom to hexane in 24 h. In both cases, some terminal olefins appeared to isomerize to internal hexenes, as indicated by GC analysis, 2% (**1**) and 23% (**3**), where the more active system **3** displayed a greater degree of isomerization. The catalytic turnovers for the phosphine system **1** are less active than the phosphinite ligand, PCy_2OR_f (441), while **3** displays a similar activity. These hydrogenation results remain significantly lower than the ones for $RhCl(PPh_3)_3$ which is capable of 650 turnovers in 1 h.[32]

Conclusion

The syntheses of a series of partially fluorinated phosphines and their rhodium complexes have been performed. This synthetic method allows control over steric and electronic properties of catalyst modifiers. Infrared and solution calorimetric studies establish a relative stability/donor scale for the phosphine ligands in the series $Rh(CO)(Cl)(PR_2R_f)_2$. Catalytic hydrogenation of 1-hexene can be carried out with $RhCl(PR_2R_f)_3$; however, the catalysts do not demonstrate complete partitioning into fluorinated versus organic phases in the biphasic reaction media. Ongoing efforts are aimed at increasing the fluorinated phase solubility of mixed phosphines and phosphinites ligands. Furthermore these ligand families are presently being tested in media which could benefit from partial fluorination.[33]

Experimental Section

General Considerations. All manipulations involving organometallic complexes were performed under an inert argon atmosphere using standard high-vacuum or Schlenk techniques or in a MBraun glovebox containing less than 1 ppm oxygen and water. All solvents were dried and distilled under argon before use employing standard drying agents.[34] Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Oxford 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[35] or the enthalpy of solution of KCl in water.[36] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described[37,38] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. GC analysis was performed on a HP 6890 series gas chromatograph. Elemental analyses were performed by Desert Analytical, Tucson, AZ. IR_f was distilled from Zenyol TELB (Dupont) while P^iPr_2Cl (Aldrich) and PCy_2Cl (Strem) were used as received. The compounds $[Rh(CO)_2Cl]_2$[39] and PPh_2R_f [17] were synthesized according to literature procedures. PPh_2R_f was purified by sublimation (50 °C at 10^{-5} Torr) instead of chromatography as reported in the literature. Experimental synthetic procedures leading to the isolation of previously unreported complexes are described below.

Synthesis of PCy_2R_f (1). A Schlenk flask was charged with 120 mL of 0.196 M Et_2O solution of $IMgR_f$ (15.7 mmol), and cooled to 0 °C. A 1.53 g portion of PCy_2Cl (6.56 mmol) dissolved in 20 mL of Et_2O was then added dropwise over 10 min and allowed to stir for 12 h at room temperature, after which time the solvent was removed in vacuo. The off-white residue was taken up in 100 mL of CH_2Cl_2 and extracted with degassed water (3 × 50 mL), and dried over $MgSO_4$ for 1 h. The suspension was filtered and the solvent was removed in vacuo. The resulting residue was recrystallized from absolute ethanol and yielded 3.045 g (85.3%) of **1**. ^1H NMR (399.95 MHz, C_6D_6, 23 °C): δ 1.00−1.90 (m, 24 H, Cy, $CH_2(CF_2)_5CF_3$); δ 2.00−2.35 (m, 2 H, P−CH_2). $^{31}P\{^1H\}$ NMR (161.90 MHz, C_6D_6, 23 °C): δ −0.71, (s).

Synthesis of $P^iPr_2R_f$ (2). A 250 mL Schlenk flask was charged with 1.80 g (11.8 mmol) of P^iPr_2Cl and 20 mL of Et_2O and cooled to 0 °C. Next, 75 mL of 0.147 M Et_2O solution of $IMgR_f$ (14.7 mmol) was added dropwise to the solution over 10 min. After stirring for 12 h, the solvent was removed in vacuo and the yellow-white oil was taken up in CH_2Cl_2 and extracted with degassed water (3 × 50 mL). The organic layer was separated and dried over $MgSO_4$ for 1 h, filtered, and the solvent was removed in vacuo to yield 4.38 g (80.3%) of **2**. ^1H NMR (399.95 MHz, C_6D_6, 23 °C): δ 0.80−1.20 (m, 16 H, ^iPr and $CH_2(CF_2)_5CF_3$); δ 2.00−2.35 (m, 2 H, P−CH_2). $^{31}P\{^1H\}$ NMR (161.90 MHz, C_6D_6, 23 °C): δ 5.16, (s).

Synthesis of *trans*-$RhCl(CO)(PCy_2R_f)_2$ (4). A 50 mL Schlenk flask was charged with 0.044 g (0.113 mmol) of $[RhCl(CO)_2]_2$, 0.298 g (0.547 mmol) of **1**, and 10 mL of CH_2Cl_2. After stirring for 4 h, the solvent was removed in vacuo and the yellow residue taken up with 30 mL of cold pentane (0 °C), and filtered. The filtrate was evaporated to dryness to give 0.248 g (75.6%) of **4** as a yellow solid. IR: $\nu_{CO} = 1956$ cm^{-1}. ^1H NMR (399.95 MHz, CD_2Cl_2, 23 °C) δ 1.9−2.4 (m, 4 H, $CH_2(CF_2)_5CF_3$ and 44 H, Cy); δ 2.8−3.2 (m, 4 H, P−CH_2). $^{31}P\{^1H\}$ NMR (161.90 MHz, CD_2Cl_2, 25 °C): δ 35.13, (d) ($^1J_{RhP} = 119.5$ Hz). Anal. Calcd for $C_{41}H_{52}ClF_{26}OP_2Rh$ (0.4 C_5H_{12}): C, 40.22; H, 4.42. Found: C, 40.07; H, 4.49.

Synthesis of *trans*-$RhCl(CO)(P^iPr_2R_f)_2$ (5). A 50 mL Schlenk flash was charged with 0.089 g (0.229 mmol) of $[RhCl(CO)_2]_2$, 0.470 g (1.012 mmol) of **2** and 10 mL of CH_2Cl_2. After stirring overnight, the solvent was removed in vacuo and the crude yellow oil was taken up in 30 mL of cold pentane (0 °C), and filtered. The filtrate was evaporated to dryness to yield 0.395 g (63.5%) of **5** as a yellow oil. IR: $\nu_{CO} = 1960$ cm^{-1}. ^1H NMR (399.95 MHz, 23 °C): δ 1.2−1.4 (m, 24 H, ^iPr); δ 2.1−2.8 (m, 12 H, P−CH_2; $CH_2(CF_2)_5$ CF_3); PCH). $^{31}P\{^1H\}$ NMR

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(161.90 MHz, CD_2Cl_2, 23 °C): δ 43.06, (s) ($^1J_{RhP} = 119.5$ Hz). MS (EI) calcd for $C_{29}H_{36}ClF_{26}OP_2Rh$: calcd *m*/*e* 1094, found *m*/*e* 1094.

Synthesis of *trans*-RhCl(CO)($PPh_2R_f)_2$ (6). A 50 mL Schlenk flask was charged with 0.045 g (0.116 mmol) of $[Rh(CO)_2Cl]_2$, 0.376 g (0.707 mmol) of **3**, and 10 mL of CH_2Cl_2. After stirring for 4 h, the solvent was removed in vacuo and the white-yellow residue was washed with 30 mL of cold pentane (0 °C). The residue was recrystallized from the pentane−CH_2Cl_2 mixture to yield 0.192 g (67.2%) of **6** as yellow plates. IR: $\nu_{CO} = 1979$ cm^{-1}. ^{1}H NMR (CD_2Cl_2, 23 °C): δ 2.20−2.65 (m, 4 H, P−CH_2); δ 2.85−3.00 (m, 4 H, $CH_2(CF_2)_5CF_3$); δ 7.15−7.95 (m, 20 H, Ph). ^{31}P{H} NMR (161.90 MHz, CD_2Cl_2, 23 °C): δ 25.27, (d) ($^1J_{RhP} = 126.5$ Hz). Anal. Calcd for $C_{41}H_{28}ClF_{26}OP_2Rh$: C, 40.01; H, 2.29. Found: C, 39.77; H, 2.17.

NMR and Infrared Titrations. Prior to every calorimetric experiment involving reactions of $[Rh(CO)_2Cl]_2$ with new phosphine ligands, NMR and IR spectroscopies were used to confirm the quantitative nature of the reaction. The general procedure is as follows: under an inert atmosphere, an accurately weighed amount (±0.1 mg) of the organorhodium complex was placed in a test tube with septum (or in a Wilmad screw top tube) and dry CH_2Cl_2 (or CD_2Cl_2) was subsequently added. To each tube the new ligand was added in ≈5-fold excess, followed by vigorous shaking. Spectra (IR and ^{1}H and ^{31}P) were then recorded. All reactions were found to be rapid, clean, and quantitative under experimental conditions. These conditions are necessary for accurate and meaningful calorimetric reactions and were satisfied for all reactions of the organorhodium complexes.

General Procedures for Solution Calorimetry. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 145 °C, and then taken into the glovebox. Typically, a 10−20 mg sample of sublimed $[Rh(CO)_2Cl]_2$ was accurately weighed into the lower vessel; it was capped and sealed with 1.5 mL of mercury; 4 mL of a stock solution of the phosphine ligand in CH_2Cl_2 (5-fold excess based on $[Rh(CO)_2Cl]_2$) was added; and the remainder of the cell was assembled, removed from the glovebox, and inserted into the calorimeter. The reference cell was loaded in an identical fashion with the exception that no organometallic complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (approximately 2 h), the reaction was initiated by inverting the calorimeter. At the end of each reaction (1−2 h), the mixing vessel was removed from the calorimeter and an infrared cell was immediately filled with the reaction solution. An IR spectrum was recorded for each calorimetric trial and conversion to the desired product was confirmed to be quantitative under the reactions conditions employed. The final enthalpy values listed in Table 1 represents the enthalpy of reaction with all species in solution.[40] This methodology represents a typical procedure involving all organometallic complexes and all reactions investigated in the present study.

Structure Determination for Rh(CO)Cl[$PPh_2R_f]_2$ (6). A single yellow needle of **6** having the dimensions of 0.65 × 0.10 × 0.005 mm was grown from slow cooling of a CH_2Cl_2−pentane mixture. The crystal was attached to a glass fiber, and mounted on a goniostat of an Enraf-Norinus CAD 4 automated X-ray diffractometer, and cooled to 150 K within a stream of N_2 gas. The reflections that were used for the unit cell determination were located and indexed by an automatic peak search routine. The corresponding lattice parameters and orientation matrix were provided from a nonlinear least-squares fit of the orientation angle obtained from centered reflections. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 2.

Intensity data were measured with graphite-monochromated Mo Kα ($\lambda = 0.7107$ Å) and variable ω scans. The data were corrected for Lorentz polarization, the symmetry-equivalent reflections were averaged, and an empirical absorption correction was applied. The initial coordinates for the nonhydrogen atoms were determined with a combination of direct methods and difference Fourier calculations performed with algorithms provided by the SHELXTL operating system on a PC workstation. Idealized positions of the methylene and phenyl hydrogens were included as fixed contributions using a riding model. Full-matrix least-squares refinement based upon the minimization of $\sum_i |F_o^2 - F_c^2|$ was performed by SHELXTL. After convergence, the final discrepancy indices were $R1 = 0.0766$ and $wR2 = 0.1875$ for 8331 reflections with $I > 2\sigma(I)$. Although the molecular structure of **6** is reasonable, the terminal CF_2CF_3 units (carbons C(40), C(41) and C(20), C(21) and their associated fluorines F(9), F(10), F(11), F(12), F(13) and F(22), F(23), F(24), F(25), F(26)) display large thermal displacements. Selected interatomic distances and angles are listed in Table 3, and an ORTEP depiction of the complex is presented in Figure 2.

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Supporting Information Available: X-ray crystallographic files in CIF format, for the structure determination of *trans*-RhCl(CO)-($PPh_2R_f)_2$ (**6**). This material is available free of charge via the Internet at http://pubs.acs.org.

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