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Synthetic, Thermochemical, and Catalytic Studies Involving Novel $R_2P(OR_f)$ [R = Alkyl or Aryl; R_f = $CH_2CH_2(CF_2)_5CF_3$] Ligands

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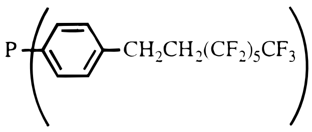
A series of mixed alkyl (or aryl) phosphinite compounds have been prepared from the alcohol $CF_3(CF_2)_5CH_2CH_2OH$ (R_fOH) and an appropriate $ClPR_2$ (R = OR_f, Ph, ^iPr, Cy) in the presence of base. A bidentate analog, $(R_fO)_2PCH_2CH_2P(OR_f)_2$, was synthesized in a similar manner. The ligands react with $[Rh(CO)_2Cl]_2$ yielding the complexes $RhCl(CO)(PR_3)_2$. The structure of $RhCl(CO)(PPh_2OR_f)_2$ (**6**) is reported. Infrared studies of the carbonyl complexes yield a relative ligand donor strength for this series. Solution calorimetry was performed on the rhodium reaction in order to quantify this donor strength scale. Both approaches lead to the same donor strength scale: $PCy_2OR_f > P^iPr_2OR_f > PPh_2OR_f > P(OR_f)_3$. These phosphinite ligands can be used as ancillary ligation in rhodium-mediated hydrogenation. A cationic rhodium complex of the chelating ligand displays selected solubility in fluorous media and biphasic catalysis can be performed.

Introduction

The use of phosphine ligands in organometallic chemistry and catalysis is widespead.[1] Recent developments in phosphine synthesis have allowed for catalysis to be carried out in nontraditional media, aqueous[2] and fluorous solvents,[3] as well as in supercritical carbon dioxide.[4,5] Horváth and Gladysz have developed and utilized a fluorinated ligand (eq 1) which allows for biphasic segregation of a catalyst from organic reactants and products.[6] Horváth has recently reported a detailed study of hydroformylation catalysts supported by this ancillary ligand.[7] Other researchers have also employed this strategy of attaching a fluorinated appendage to a phosphine ligand (**A** and **B**) in order to render transition metal catalysts (or precatalysts) soluble in fluorous or supercritical CO_2 media.[8,9] Hughes has employed this approach to solubilize cyclopentadienyl metal complexes.[10] Meyer and co-workers have recently taken advantage of the fluorous phase solubility of moieties bearing fluorinated appendages to develop a biphasic synthetic approach to organometallic complexes.[11]

$$PH_3 + 3CH_2CH(CF_2)_5CF_3 \xrightarrow{AIBN} P(CH_2CH_2(CF_2)_5CF_3)_3 \quad (1)$$



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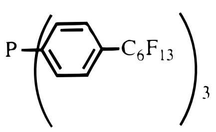

B

Following a collaboration with Horváth on the determination of stereoelectronic properties of the “ponytail” ligand $P(CH_2CH_2(CF_2)_5CF_3)_3$ using a rhodium system (eq 2),[12] we became interested in developing phosphine ligands with tunable stereoelectronic properties to carry

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Priciples and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Parshall, G. W.; Ittel, S. *Homogeneous Catalysis*; J. Wiley and Sons: New York, 1992. (c) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983.

(2) (a) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317−4325. (b) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627−1628.

(3) (a) Horváth, I. T.; Rábai, J. US Patent 5463082, 1995. (b) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72−75. (c) Vincent, J.-M.; Rabion, A.; Yachandra, V. K.; Fish, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2346−2349.

(4) Morgenstern, D. A.; LeLacheur, R. M.; Morita, D. K.; Borkowsky, S. L.; Feng, S.; Brown, G. H.; Luan, L.; Gross, M. F.; Burk, M. J.; Tumas, W. In *Green Chemistry*; Anastas, P. T., Williamson, T. C., Eds.; ACS Symposium Series 626; American Chemical Society: Washington, DC, 1996; pp 132−151.

(5) Fürstner, A.; Koch, D.; Langemann, K.; Leitner, W.; Six, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2466−2469.

(6) (a) Juliette, J. J. J.; Horváth, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1610−1612. (b) Guillevic, M.-A.; Arif, A. M.; Horváth, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1612−1615. (c) Guillevic, M.-A.; Rocaboy, C.; Arif, A. M.; Horváth, I. T.; Gladysz, J. A. *Organometallics* **1988**, *17*, 707−717.

(7) Horváth, I. T.; Kiss, G.; Cook, R. A.; Bond, J. E.; Stevens, P. A.; Rábai, J.; Mozeleski, E. J. *J. Am. Chem. Soc.* **1998**, *120*, 3133−3143.

(8) Kainz, S.; Koch, D.; Baumann, W.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628−1630.

(9) Betzemeir, B.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2623−2624.

(10) Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286−294.

(11) Spetseris, N.; Hadida, S.; Curran, D. P.; Meyer, T. Y. *Organometallics* **1998**, *17*, 1458−1459.

(12) Li, C.; Nolan, S. P.; Horváth, I. T. *Organometallics* **1998**, *17*, 452−456.

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

$$[Rh(CO)_2Cl]_{2(soln)} + 4L_{(soln)} \xrightarrow[30\ °C]{CH_2Cl_2} 2Rh(CO)(Cl)(L)_{2(soln)} + 2CO$$

L	complex	ν_{CO} (cm^{-1})	$-\Delta H_{(rxn)}$ [a,b]
$P(NC_4H_4)_3$	$Rh(CO)(Cl)(P[NC_4H_4]_3)_2$	2024	34.4 (0.2)
$P(NC_4H_4)_2(C_6H_5)$	$Rh(CO)(Cl)(P[NC_4H_4]_2[C_6H_5])_2$	2007	35.3 (0.2)
$P(OPh)_3$	$Rh(CO)(Cl)(P[OPh]_3)_2$	2016	42.6 (0.2)
$P(p\text{-}CF_3C_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}CF_3C_6H_4]_3)_2$	1990	43.8 (0.2)
$P(NC_4H_4)(C_6H_5)_2$	$Rh(CO)(Cl)(P[NC_4H_4][C_6H_5]_2)_2$	1993	44.8 (0.2)
$P(p\text{-}ClC_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}ClC_6H_4]_3)_2$	1984	47.8 (0.3)
$AsEt_3$	$Rh(CO)(Cl)(AsEt_3)_2$	1952	49.2 (0.3)
$P(p\text{-}FC_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}FC_6H_4]_3)_2$	1982	50.1 (0.3)
PPh_3	$Rh(CO)(Cl)(PPh_3)_2$	1978	51.7 (0.3)
$P(p\text{-}CH_3C_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}CH_3C_6H_4]_3)_2$	1975	56.1 (0.2)
$P(OR_f)_3$	$Rh(CO)(Cl)(P(OR_f)_3)_2$	2024	56.6 (0.5)[c,d]
$P(p\text{-}CH_3OC_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}CH_3OC_6H_4]_3)_2$	1973	58.7 (0.3)
PPh_2Me	$Rh(CO)(Cl)(PPh_2Me)_2$	1974	61.7 (0.3)
$P(OMe)_3$	$Rh(CO)(Cl)(P(OMe_3)_2$	2006	63.7 (0.2)
$PPh_2(OR_f)$	$Rh(CO)(Cl)(PPh_2(OR_f))_2$	1990	63.7 (0.4)[d]
$P^iPr_2(OR_f)$	$Rh(CO)(Cl)(P^iPr_2(OR_f))_2$	1966	64.9 (0.5)[d]
$PCy_2(OR_f)$	$Rh(CO)(Cl)(PCy_2)(OR_f))_2$	1963	68.4 (0.3)[d]
PR_{f3}	$Rh(CO)(Cl)(PR_{f3})_2$	1977	68.5 (0.2)[c]
$PPhMe_2$	$Rh(CO)(Cl)(PPhMe_2)_2$	1968	71.4 (0.3)
PEt_3	$Rh(CO)(Cl)(PEt_3)_2$	1956	77.2 (0.3)

[a] Enthalpy values are reported with 95% confidence limits. [b] Taken from refs 12 and 13a. [c] Work performed in THF. [d] This work.

out catalysis in nontraditional media. We now present

$$[Rh(CO)_2Cl]_2 + 4P(R_f)_3 \xrightarrow[30\ °C]{THF} 2Rh(CO)(Cl)(P(R_f)_3)_2 + 2CO \quad (2)$$

$$R_f = CH_2CH_2(CF_2)_5CF_3$$

the synthesis and catalytic application of an easily accessible, novel class of partially fluorinated "pigtail" ligands which allow regulation of phosphinite and metal center stereoelectronic properties. Elaborating on our earlier rhodium thermochemical studies,[13] we also report a solution calorimetric investigation of ligand substitution for a rhodium system.

Results and Discussion

Ligand Synthesis. The ligands synthesized in this study are prepared and isolated in a straightforward manner. Simple HCl elimination in the presence of a base affords the ligands in quantitative yields, as determined by NMR (eq 3). The $HNEt_3Cl$ is simply separated by cannula filtation. The filtrate is then dried under vacuum to yield the product in high purity. The

$$R_2PCl + R_fOH \xrightarrow[NEt_3]{THF} R_2POR_f + HNEt_3Cl \quad (3)$$

$$R = R_fO\ (\mathbf{1}),\ {}^iPr\ (\mathbf{2}),\ Ph\ (\mathbf{3}),\ Cy\ (\mathbf{4})$$

$$R_f = CH_2CH_2(CF_2)_5CF_3$$

chelating ligand **5** is prepared in a similar manner from $Cl_2PCH_2CH_2PCl_2$. This general procedure is very reminescent of the protocol employed by Moloy for the isolation of $P(NC_4H_4)_{3-x}Ph_x$ ($x = 0-2$) ligands (eq 4).[14]

$$Ph_2PCl + HNC_4H_4 \xrightarrow[NEt_3]{THF} Ph_2P(NC_4H_4) + HNEt_3Cl \quad (4)$$

All are soluble in THF, CH_2Cl_2, and pentane with the exception of $P(OR_f)_3$ and $(R_fO)_2PCH_2CH_2P(OR_f)_2$ which are soluble only in perfluoro(methylcyclohexane) and THF.

Organorhodium Complex Synthesis. All organorhodium complexes were prepared in a similar manner from $[Rh(CO)_2Cl]_2$ (eq 5). Addition of a CH_2Cl_2 or THF solution of the pigtail ligand to a solution of the rhodium precursor was accompanied by the vigorous evolution of CO gas and an immediate color change from yellow-orange to bright yellow. Complexes **7** and **8** are soluble in THF, CH_2Cl_2, and pentane, whereas **6** is only soluble in the polar solvents. In the case of complex **9**, the product immediately phase-separated from the mother liquor as a yellow-orange oil. In CH_2Cl_2, **9** was only slightly miscible; however, the compound could be dissolved in THF at elevated (~40 °C) temperature or in perfluoro(methylcyclohexane) at ambient temperature.

$$[Rh(CO)_2Cl]_2 + 4R_2POR_f \rightarrow 2RhCl(CO)(PR_2OR_f)_2 + 2CO \quad (5)$$

$$R = Ph\ (\mathbf{6}),\ {}^iPr\ (\mathbf{7}),\ Cy\ (\mathbf{8}),\ OR_f\ (\mathbf{9})$$

$$R_f = CH_2CH_2(CF_2)_5CF_3$$

Thermochemistry. A solution calorimetric investigation of the ligand substitution illustrated in eq 5 was carried out in order to gauge the enthalpic driving force behind the binding of these new ligands to rhodium. The enthalpies of reaction along with carbonyl stretching frequencies of these and previously studied complexes are reported in Table 1. When the pigtail ligand series (Ph, ^{i}Pr and Cy) is examined, the magnitude of the enthalpy of reaction trend follows the electronic donor property of the alkyl/aryl group as established by Tolman.[15] This is supported by the infrared stretching

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[13] (a) Serron, S. A.; Nolan, S. P.; Moloy, K. G. *Organometallics* **1996**, *15*, 4301−4306. (b) Huang, A.; Marcone, J. E.; Mason, K. L.; Marshall, W. J.; Moloy, K. G.; Serron, S. A.; Nolan, S. P. *Organometallics* **1997**, *16*, 4301−4306. (c) Serron, S. A.; Huang, J.; Nolan, S. P. *Organometallics* **1998**, *17*, 534−539.

[14] Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696−7710.

[15] Tolman, C. A. *Chem. Rev.* **1997**, *77*, 313−348.

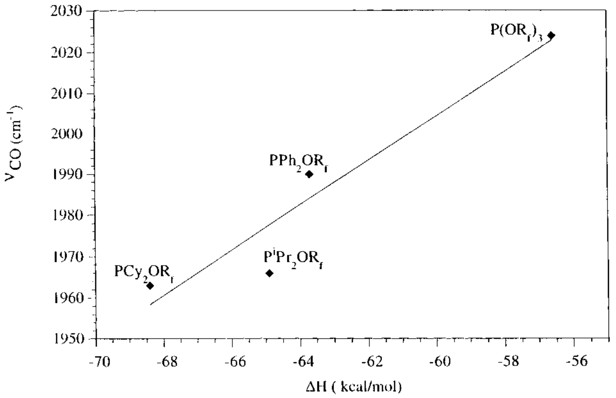

Figure 1. Carbonyl stretching frequency (cm^{-1}) vs enthalpy of reaction (kcal/mol) in the $RhCl(CO)(PR_2OR_f)_2$ system; slope = 5.47; $R = 0.96$.

frequency trend which illustrates the better donor property of Cy > ^{i}Pr > Ph > OR_f. A plot of the experimental carbonyl stretching frequency versus the enthalpy of reaction denotes a linear relationship between both observables (Figure 1). This is not entirely unexpected since such a relationship has previously been established in this rhodium system with tertiary phosphine ligands. We have previously noted that phosphite ligands comprise a unique ligand family in terms of bonding.[16] The pigtail ligands considered here appear to follow this distinct bonding pattern since they incorporate a mix of alkyl and alkoxy moieties. The relationship between IR and enthalpy data for all rhodium complexes, however, does not lead to a linear correlation. Side-by-side comparison between mixed and parent trialkyl- or triarylphosphines is informative.[17] In all cases the IR data of the rhodium carbonyl complexes bearing the pigtail ligands are higher by some 20 cm^{-1}. This alone would reflect the decreased donor capability of the phosphinite ligand. The difference is more dramatic when the PR_{f3} and $P(OR_f)_3$ data are compared (47 cm^{-1}), the effect being magnified by the number of alkoxy substituents.

When these two families are compared in terms of enthalpy trends, no clear picture emerges. For the $P^iPr_3/P^iPr_2OR_f$ and $PR_{f3}/P(OR_f)_3$ pairs, smaller enthalpies of reaction are measured when the OR_f group is present. This trend parallels the one previously observed for the $PPh_3/P(OPh)_3$ pair (see Table 1). The PCy_3/PCy_2OR_f and PPh_3/PPh_2OR_f pairs have opposite enthalpy trends: larger enthalpies of reaction are measured when the OR_f group is present.[18] The existence of geometric distortions from square planar geometry may explain the observed diverging trends. We are presently carrying out structural studies on this $Rh(CO)Cl(L)_2$ system in order to examine whether structural changes exist when sterically demanding phosphine ligands are present.[17]

Table 2. Crystal Data and Details of the Structure Determination of $Rh(CO)(Cl)(PPh_2OR_f)_2$ (6)

empirical formula	$C_{41}H_{28}ClF_{26}O_3P_2Rh$
fw	1262.93
temperature	295(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimensions	$a = 20.430(4)$ Å, $\alpha = 90°$ $b = 10.652(1)$ Å, $\beta = 113.24(1)°$ $c = 24.300(2)$ Å, $\gamma = 90°$
volume	4859.3 (10) Å^3
Z	4
density (calcd)	1.726 g/cm^3
abs. coeff	6.10 cm^{-1}
$F(000)$	2496
cryst size	0.20 × 0.20 × 0.30 mm
range for data collection	2.12 to 25.00°
index ranges	$0 \le h \le 22°$, $0 \le k \le 12°$, $-28 \le l \le 26°$
no. of reflcns collcd	8494
no. of indep reflcns	8243 ($R_{int} = 0.0265$)
refinement method	full-matrix least-squares on F^2
no. of data/restraints/ parameters	7161/14/ 667
goodness-of fit on F^2	1.049
final R indices [$I > 2\sigma(I)$]	R1 = 0.0625, wR2 = 0.1539
R indices (all data)	R1 = 0.1163, wR2 = 0.1874
largest diff peak and hole	0.731 and −0.561 e Å^{-3}

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Rh(CO)(Cl)(PPh_2OR_f)_2$ (6)

Bond Lengths			
Rh−C(1)	1.829(5)	Rh−P(1)	2.3000(13)
Rh−P(2)	2.3036(12)	Rh−Cl	2.3565(13)
P(1)−O(2)	1.624(3)	P(1)−C(2)	1.804(5)
P(1)−C(8)	1.821(5)	P(2)−O(3)	1.616(3)
P(2)−C(28)	1.814(4)	P(2)−C(22)	1.834(5)
O(1)−C(1)	1.123(6)	O(2)−C(14)	1.422(6)
O(3)−C(34)	1.436(5)		

Bond Angles			
C(1)−Rh−P	89.5(2)	C(1)−Rh−P(2)	88.1(2)
P(1)−Rh−P(2)	174.32(5)	C(1)−Rh−Cl	176.8(2)
P(1)−Rh−Cl	90.79(5)	P(2)−Rh−Cl	91.90(5)
O(1)−C(1)−Rh	177.3 (5)	O(2)−P(1)−C(8)	102.2(2)
O(2)−P(1)−C(2)	98.8(2)	O(2)−P(1)−Rh	115.57(12)
C(2)−P(1)−C(8)	106.4(2)	C(8)−P(1)−Rh	118.5(2)
C(2)−P(1)−Rh	113.0(2)	O(3)−P(2)−C(22)	100.2(2)
O(3)−P(2)−C(28)	104.5(2)	O(3)−P(2)−Rh	116.02(12)
C(28)−P(2)−C(22)	103.1(2)	C(22)−P(2)−Rh	113.9(2)
C(28)−P(2)−Rh	116.98(14)		

Structure Determination of *trans*-$Rh(CO)(Cl)(PPh_2OR_f)_2$ (6). While complexes **7**−**9** could only be isolated as oils, the crystallization of large, yellow blocks of **6** from CH_2Cl_2/pentane was unexpectedly straightforward. Results of single-crystal X-ray analysis of **6** are given in Table 2. Metrical parameters are given in Table 3, and an ORTEP plot of the structure appears in Figure 2. In its gross structural features, **6** is a typical square-planar Rh(I) complex, with *cis* L−Rh−L angles near 90° and summing to 360.3°. Akin to the previously reported $M(CO)Cl(P(R_f)_3)_2$ (M = Rh, Ir) system,[6c] the fluoroalkyl chains preferentially adopt a parallel configuration within each molecule of **6**, although there is no evidence in the packing diagrams that the chains exert any significant influence on the long-range ordering of the crystal lattice. Comparison with the former system, however, reveals several significant contrasts. The Rh−C(1) distance of 1.829(5) Å in **6** is 0.030 Å longer than in $Rh(CO)Cl(P(R_f)_3)_2$, while the C(1)−O(1) distance (1.123(6) Å) is shorter by 0.034

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[16] Serron, S. A.; Luo, L.; Stevens, E. D.; Nolan, S. P.; Jones, N. L.; Fagan, P. J. *Organometallics* **1996**, *15*, 5209−5215.

[17] Giering, W. P.; Fernandez, A. L.; Haar, C. M.; Nolan, S. P. Manuscript in preparation. IR and Δ*H* data for PCy_3 (1942 cm^{-1} and −66.4(0.4) kcal/mol) and P^iPr_3 (1947 cm^{-1} and −68.7(0.3) kcal/mol).

[18] In the end, the comparison discussed presents data for two different classes of ligands. The hybrid ligand series may well not conform to either of the parent series but follow a combination involving both.

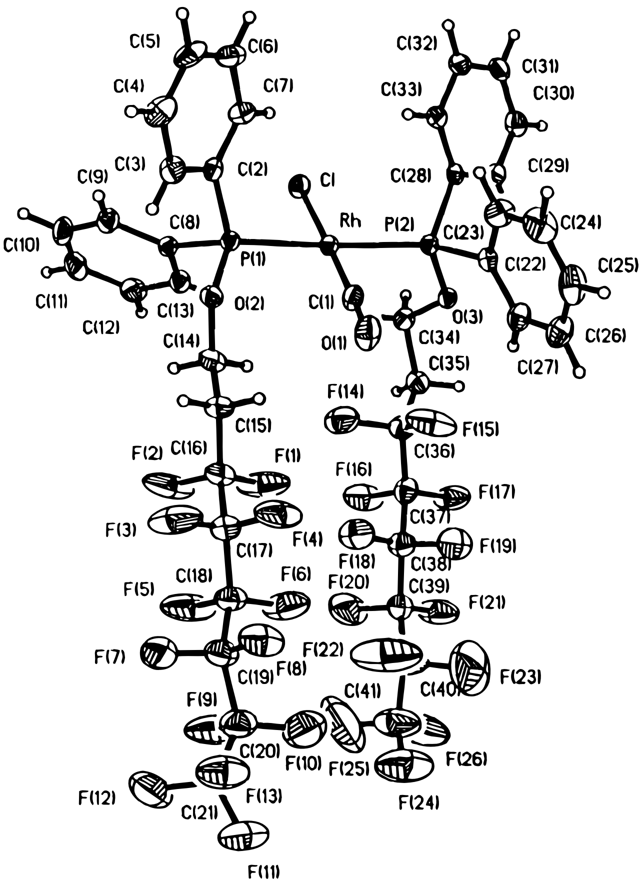

Figure 2. ORTEP of $Rh(CO)Cl[P(C_6H_5)_2OCH_2CH_2(CF_2)_5CF_3]_2$ (**6**). Ellipsoids are drawn in with 20% probability.

Å, consistent with a weaker Rh−CO interaction in **6**. This observation reflects the electron deficient/π-accepting nature of the diarylphosphinite **3** relative to the trialkyl ligand $P(R_f)_3$, and is consistent with the higher carbonyl stretching frequency in **6** (1990 vs 1979 cm^{-1} in $(Rh(CO)Cl(PR_f)_3)_2)$. The remaining Rh−P, and Rh−Cl distances in **6** are virtually indistinguishable from those in $M(CO)Cl(P(R_f)_3)_2$.

Comparison of the L−Rh−L angles in **6** with those in $M(CO)Cl(P(R_f)_3)_2$ reveals only very subtle differences. The P(1)−Rh−P(2) and C(1)−Rh−Cl angles (174.32(5) and 176.8(2)°) in **6** point to a slight tetrahedral distortion of the Rh coordination geometry. A similar distortion of the P−M−P angle was observed in $M(CO)Cl(P(R_f)_3)_2$ ($\angle P-M-P = 172°$); in the latter case, however, $\angle C-M-Cl = 179°$ was nearly linear. It is also interesting to note that while the Rh−P vectors in **6** are very slightly skewed toward CO (average $\angle C(1)-Rh-P = 88.8°$, average $\angle P-Rh-Cl = 91.4°$), in $M(CO)Cl(P(R_f)_3)_2$ they are bent in the opposite direction toward the Cl ligand (average $\angle C(1)-Rh-P = 93.9°$, average $\angle P-Rh-Cl = 86.1°$).

Comparison between **6** and $Rh(CO)Cl(PPh_3)_2$[19] helps us understand the enthalpy/IR trends. Complex **6** displays a shorter Rh−P bond distance (2.302(1) vs 2.323(1) Å for $Rh(CO)Cl(PPh_3)_2$), indicating increased donation from the phosphine ligand.

Fluorous Biphasic Hydrogenation of 1-Hexene. The reduction of 1-hexene by "$RhClL_3$", formed *in situ* from $[(COD)RhCl]_2$ and 6 equiv of either **1** or **3**, was undertaken 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). The resulting catalysts gave conversions of only 16 (**1**) and 40 (**3**) equiv per Rh over 24 h. In both cases, a small amount (<5%) of the initial terminal olefin appeared to have been isomerized to internal 2-hexene, as indicated by GC analysis and observed in the baseline of ^1H NMR spectra of the reaction mixtures upon termination of the catalytic runs. Apparently both steric and electronic properties of these ligands are unfavorable for the formation of active Wilkinson-type catalysts. This is not surprising, given their electron-poor nature as indicated by quite high ν_{CO} values in $Rh(CO)(Cl)(L)_2$ (2024 (**1**) and 1990 (**3**) cm^{-1}, cf. 2006 ($L = P(OMe)_3$) and 1978 ($L = PPh_3$) cm^{-1}) and their small calculated cone angles[15] of 109° (**1**) and 133° (**3**) (cf. PEt_3, $\theta = 132°$).

In the biphasic solvent system, only ligand **1** gave a Rh complex that was efficiently segregated into the fluorous phase. Apparently the level of fluorination in **3** was not sufficient to yield a fluorophilic species. The chelating ligand **5** was also examined as ancillary ligation for cationic Rh-catalyzed reduction of 1-hexene in a fluorous biphase system at 40 °C and 1 atm of H_2. Formation of $[(COD)Rh(dOR_fpe)]OTf$ *in situ* from $[(COD)_2Rh]OTf$ and **5** resulted in a catalyst capable of at least 1073 turnovers within 24 h. In addition, the Rh complex could be entirely segregated into the fluorous phase at any point in the reaction cycle by simply cooling the reaction mixture to slightly less than ambient temperature (~15 °C). As mentioned above, ^1H NMR analysis of the reaction mixture indicated the presence of a small amount of internal olefin after terminating the catalytic run.

Homogeneous Hydrogenation of 1-Hexene. Although the fluorous biphase hydrogenation trial with **3** indicated that the presence of only one fluoroalkoxy chain was insufficient to allow complete fluorous phase segregation of the catalyst, ligands **2** and **4** were screened in a homogeneous reaction medium to gauge the reactivity of catalysts derived therefrom. The reduction of neat 1-hexene by "$RhClL_3$", formed *in situ* from $[(COD)RhCl]_2$ and 6 equiv of either **2** or **4**, was undertaken at 40 °C and 1 atm of H_2. Not surprisingly, catalyst activities with both ligands were similar with 395 (**2**) and 441 (**4**) equivalents of olefin per Rh atom being converted to hexane in 24 h. In both cases, a small amount (≤5%) of the initial terminal olefin appeared to have been isomerized to internal hexene (2-hexene), as indicated by GC analysis of the reaction mixtures upon termination of the catalytic runs (see Experimental Section). On the basis of the carbonyl stretching frequencies of the $Rh(CO)(Cl)(L)_2$ complexes with these ligands, **2** and **4** are electronically quite similar to each other and even somewhat more electron rich than PPh_3 (see Table 1). Furthermore, their calculated cone angles[15] of 143° (**2**) and 150° (**4**) are quite close to that of PPh_3 (145°). It is therefore somewhat surprising that the Wilkinson-type catalysts derived from **2** and **4** should behave so differently from their archetype $RhCl(PPh_3)_3$, which is capable of 650 turnovers in 1 h.[20]

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[19] Chaloner, P. A.; Claver, C.; Hitchcok, P. B.; Masdeu, A. M.; Ruiz, A. *Acta Crystallogr.* **1991**, *C47*, 1307−1308.

Conclusion

The convenient synthesis of a series of fluorinated phosphinites and their complexes with rhodium has been presented. This approach affords exceptional control over the steric, electronic, and fluorous phase solubility properties of catalytic centers. Infrared and solution calorimetric studies establish a relative stability/donor scale for the phosphinite ligands in the series $Rh(CO)(Cl)(PR_2OR_f)_2$. Catalytic hydrogenation of 1-hexene can be carried out with $RhCl(PR_2OR_f)_3$; however, the most effective catalysts in this series did not demonstrate complete partitioning into fluorous versus organic phases in biphasic reaction media. In the case of $[(dOR_fpe)Rh(COD)]^+$, the chelating ligand **5** yielded an efficient catalyst which was completely partitioned to the fluorous phase. Since complete fluorination is not observed to be necessary to provide solubility in $scCO_2$, all of the new ligands are viable candidates for solubilization of catalysts in this solvent. Ongoing efforts are aimed at increasing the fluorous phase solubility of mixed phosphines and phosphinites, and testing of $scCO_2$ chemistry is ongoing with this and related phosphine ligand families.[21]

Experimental Section

General Considerations. All manipulations were performed under argon using standard high-vacuum or Schlenk tube techniques, or in a MBraun glovebox containing less than 1 ppm oxygen and water. The alcohol, R_fOH, was purchased from Lancaster and distilled under inert atmosphere prior to use. PPh_2Cl, P^iPr_2Cl, and PCl_3 (Aldrich) and $[(COD)RhCl]_2$, PCy_2Cl, and $Cl_2PCH_2CH_2PCl_2$ (Strem) were used as received. Triethylamine and solvents were dried and distilled under argon before use employing standard drying agents.[22] Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[23] or the enthalpy of solution of KCl in water.[24] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described[25] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

Synthesis. The compounds $[Rh(CO)_2Cl]_2$[26] and $[(COD)_2Rh]OTf$[27] were synthesized according to literature procedures. Experimental synthetic procedures leading to the isolation of previously unreported complexes are described below.

$P(OR_f)_3$ (1). A Schlenk flask equipped with a magnetic stirring bar was charged with HOR_f (5.0 mL, 8.4 g, 23 mmol), Et_3N (5 mL), and THF (50 mL). The solution was cooled to −78 °C, and PCl_3 (0.67 mL, 1.05 g, 7.7 mmol) was added, whereupon a copious amount of white precipitate formed. The reaction vessel was allowed to warm to room temperature and was then immersed in a 60 °C oil bath and allowed to stir for 1 day. After cooling, the reaction was filtered and the colorless solids washed with 2 × 20 mL of THF. Volatiles were removed *in vacuo*, and pentane (20 mL) was added. Although phase separation of the product occurred on standing, the pentane facilitated a final cannula filtration to remove the small amount of colorless solid which remained. The pentane was then removed *in vacuo*, affording the product as a light amber liquid in >95% purity, as determined by ^1H and ^{31}P NMR. Yield: 8.11 g (94%). ^1H NMR (THF-d_8): δ 2.57 (tt, 6H, CH_2CF_2), 4.16 (q, 6H, OCH_2). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 142.2.

$PPr^i_2OR_f$ (2) was prepared in a fashion similar to **1** from ClP^iPr_2 (2.15 g, 14.1 mmol) and HOR_f (3.1 mL, 5.2 g, 14.3 mmol). Yield: 6.48 g (96%). ^1H NMR (C_6D_6): δ 0.88−1.07 (m, 12H, $PCH(CH_3)_2$), 1.55 (septd, 2H, $PCH(CH_3)_2$), 2.04 (tt, 2H, CH_2CF_2), 3.77 (pseudo q, 2H, OCH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 156.8.

PPh_2OR_f (3) was prepared in a fashion similar to **1** from $ClPPh_2$ (2.02 g, 9.16 mmol) and HOR_f (2.0 mL, 3.4 g, 9.2 mmol). Yield: 4.1 g (82%). ^1H NMR (C_6D_6): δ 1.99 (tt, 2H, CH_2CF_2), 3.77 (pseudo q, 2H, OCH_2), 6.98−7.18 (m, 6H, phenyl), 7.48−7.58 (m, 4H, phenyl). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 116.7.

PCy_2OR_f (4) was prepared in a fashion similar to **1** from $ClPCy_2$ (2.04 g, 8.77 mmol) and HOR_f (1.9 mL, 3.2 g, 8.8 mmol). Yield: 3.9 g (80%). ^1H NMR (C_6D_6): δ 0.98−1.88 (m, 22H, Cy), 2.11 (tt, 2H, CH_2CF_2), 3.81 (pseudo q, 2H, OCH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 151.8.

$(R_fO)_2P(CH_2)_2P(OR_f)_2$ (dOR_fpe) (5). In the glovebox, a Schlenk flask equipped with a magnetic stirring bar was charged with $Cl_2P(CH_2)_2PCl_2$ (1.00 g, 4.31 mmol). The reaction vessel was removed from the glovebox and interfaced to a Schlenk line. Toluene (50 mL) and Et_3N (3 mL) were added, and then HOR_f (3.8 mL, 6.4 g, 18 mmol) was added dropwise *via* syringe to the rapidly stirring mixture. Heat was evolved along with the formation of a colorless precipitate. The reaction was allowed to stir at ambient temperature for ∼1 day, after which time ^{31}P NMR analysis of the crude mixture indicated complete conversion to product. The colorless solids were removed by filtration and washed 3 × 20 mL of THF. Volatiles were removed *in vacuo*, affording the product as colorless, waxy microcrystals, >95% pure by ^1H and ^{31}P NMR. Yield: 6.44 g (97%). ^1H NMR (THF-d_8): δ 1.64 ("t", 4H, $P(CH_2)_2P$), 2.53 (tt, 8H, CH_2CF_2), 4.15 (m, 8H, OCH_2). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 186.1. Anal. Calcd for $C_{34}H_{20}F_{52}O_4P_2$: C, 26.48; H, 1.31. Found: C, 26.29; H, 1.35.

***trans*-$Rh(CO)(Cl)(PPh_2OR_f)_2$ (6).** In the glovebox, a 25 mL Schlenk tube was charged with $[Rh(CO)_2Cl]_2$ (86.1 mg, 0.222 mmol) and CH_2Cl_2 (3 mL). A solution of PPh_2OR_f (486.3 mg, 0.887 mmol) in CH_2Cl_2 (3 mL) was then added, resulting in vigorous gas evolution and a clear, yellow solution. The reaction vessel was removed from the glovebox, interfaced to a vacuum line and allowed to stir for ∼1 h. The solvent volume was then reduced to ∼1 mL, and pentane (10 mL) was added. The solution volume was then reduced *in vacuo* until saturation, and then the solution was slowly cooled to −20 °C, yielding 0.50 g (89%) of the crude product as yellow microcrystals. Recrystallization of this material from CH_2Cl_2/pentane afforded the product as large, transparent, yellow blocks. Yield: 0.385 g (69%). IR (CH_2Cl_2) $\nu_{CO} = 1990\ cm^{-1}$. ^1H NMR (CD_2Cl_2): δ 2.62 (tt, 4H, CH_2CF_2), 4.51 (m, 4H, OCH_2), 7.47 (m, 12H, phenyl), 7.78 (m, 8H, phenyl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 121.3 ($^1J_{RhP} = 136$ Hz). Anal. Calcd for $C_{41}H_{28}ClF_{26}O_3P_2Rh$: C, 38.99; H, 2.23. Found: C, 39.06; H, 2.42.

***trans*-$Rh(CO)(Cl)(PPr^i_2OR_f)_2$ (7)** was prepared in a fashion similar to **6** from $[Rh(CO)_2Cl]_2$ (93.8 mg, 0.241 mmol) and $PPr^i_2OR_f$ (464.5 mg, 0.967 mmol) and isolated as a dark yellow oil. Yield: 0.50g (92%). IR (CH_2Cl_2) $\nu_{CO} = 1966\ cm^{-1}$. ^1H

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(20) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331−338 and references therein.

(21) Carter, C. A.; Baker, R. T.; Tumas, W.; Haar, C. M.; Nolan, S. P. Manuscript in preparation.

(22) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(23) Ojelund, G.; Wadsö, I. *Acta Chem. Scand.* **1968**, *22*, 1691−1699.

(24) Kilday, M. V. *J. Res. Natl. Bur. Stand. (U.S.)* **1980**, *85*, 467−481.

(25) (a) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357−362. (b) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 4446−4448.

(26) Colton, R.; Farthing, R. H.; Knapp, J. E. *Aust. J. Chem.* **1970**, 1351−1358.

(27) (a) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baket, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 88. (b) Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc., (A)* **1971**, 2334.

NMR (CD_2Cl_2): δ 1.26 (m, 24H, $PCH(CH_3)_2$), 2.48 (septd, 4H, $PCH(CH_3)_2$), 2.55 (tt, 4H, CH_2CF_2), 4.38 (m, 4H, OCH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 163.6 ($^1J_{RhP} = 132$ Hz). MS (EI) for $C_{29}H_{36}ClF_{26}O_3P_2Rh$: calcd *m/e* 1126, found *m/e* 1126.

***trans*-Rh(CO)(Cl)(PCy$_2$OR$_f$)$_2$ (8)** was prepared in a fashion similar to **6** from $[Rh(CO)_2Cl]_2$ (92.3 mg, 0.237 mmol) and PCy_2OR_f (464.5 mg, 0.955 mmol) and isolated as a dark yellow oil. Yield: 0.54 g (89%). IR (CH_2Cl_2) $\nu_{CO} = 1963$ cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.1−2.4 (m, 44H, Cy), 2.52 (tt, 4H, CH_2CF_2), 4.34 (m, 4H, OCH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 158.4 ($^1J_{RhP} =$ 129 Hz). MS (EI) for $C_{41}H_{52}ClF_{26}O_3P_2Rh$: calcd *m/e* 1286, found *m/e* 1286.

***trans*-Rh(CO)(Cl)(P(OR$_f$)$_3$)$_2$ (9)** was prepared in a fashion similar to **6** from $[Rh(CO)_2Cl]_2$ and $P(OR_f)_3$ and isolated as a dark yellow oil. IR (THF) $\nu_{CO} = 2024$ cm^{-1}. ^1H NMR (THF-d_8): δ 2.68 (tt, 12H, CH_2CF_2), 4.55 (m, 12H, OCH_2). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 129.8 ($^1J_{RhP} = 199$ Hz). MS (EI) for $C_{49}H_{24}ClF_{78}O_7P_2Rh$: calcd *m/e* 2406, found *m/e* 2406.

Solution Calorimetry. Infrared Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organorhodium complex was placed in a test tube fitted with a septum, and CH_2Cl_2 was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by infrared spectroscopy and the reactions were found to be rapid, clean and quantitative under experimental calorimetric (temperature and concentration), conditions necessary for accurate and meaningful calorimetric results. These conditions were satisfied for all organorhodium reactions investigated.

NMR Titrations. Prior to every set of calorimetric experiments involving a new phosphine ligand, an accurately weighed amount (±0.1 mg) of the organorhodium complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and CD_2Cl_2 or THF-d_8 was subsequently added. The solution was titrated with a solution of the phosphine of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^{31}P and ^1H NMR spectroscopy and were found to be rapid, clean, and quantitative. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organometallic reactions investigated.

Calorimetric Measurement of Reaction between [Rh(CO)$_2$Cl]$_2$ and PPh$_2$(OR$_f$). The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 10−15 mg sample of $[Rh(CO)_2Cl]_2$ was accurately weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A 4 mL volume of a stock solution of $PPh_2(OR_f)$ (510 mg) in CH_2Cl_2 (20 mL) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted into the calorimeter. The reference vesel was charged in an identical manner with the exception that no $[Rh(CO)_2Cl]_2$ was added. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h) the reaction was initiated by inverting the calorimeter. At the end of the reaction (1−2 h) the vessels were removed from the calorimeter and an IR spectrum was immediately recorded. Conversion to $RhCl(CO)(PPh_2(OR_f))_2$ was shown to be quantitative. The enthalpy of reaction, −55.1 ± 0.4 kcal/mol represents the average of five individual calorimetric determinations. The final enthalpy value listed in Table 1 (63.7 ± 0.4 kcal/mol) represents the enthalpy of reaction with all species in solution.[13a] This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study.

Structure Determination of Rh(CO)Cl[P(C$_6$H$_5$)$_2$OCH$_2$CH$_2$(CF$_2$)$_5$CF$_3$] (6). A crystalline fragment of $Rh(CO)Cl[P(C_6H_5)_2OCH_2CH_2(CF_2)_5CF_3]_2$ was sealed in a capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The reflections that were used for the unit cell determination were located and indexed by the automatic peak search routine XSCANS.[28] The corresponding lattice parameters and orientation matrix were provided from a nonlinear least-squares fit of the orientation angles of 40 centered reflections ($10 < 2\theta < 25°$) at 22 °C. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 2.

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and variable ω scans (4.0−10.0°/min). Background counts were measured at the beginning and the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections. Their combined intensity decreased by 2% during data collections. The data were corrected for Lorentz−polarization and the symmetry-equivalent reflections were averaged. No absorption correction was applied.

The initial coordinates for the non-hydrogen atoms were determined with a combination of direct methods and difference Fourier calculations performed with algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Idealized positions for the methylene and phenyl hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 times that of the adjacent carbon. Full-matrix least-squares refinement, based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$, with $w_i^{-1} = \sigma^2(F_o^2) + (0.0976P)^2 + 1.37P$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$,was performed with SHELXL-93.[29] After convergence, the final discrepancy indices were R1 = 0.0625 and wR2 = 0.1539 for 5045 reflections with $I > 2\sigma(I)$, and the overall GOF value was 1.049. Although the molecular structure of **6** is reasonably well-behaved, carbons C(40) and C(41) and fluorines F(22), F(23), F(24), F(25), and F(26) display large thermal displacements. However, attempts to refine this C_2F_5 fragment as a static two-site disorder were unsuccessful. Selected interatomic distances and angles are listed in Table 3. An ORTEP view of the complex is presented in Figure 2.

Homogeneous Catalytic Hydrogenation of 1-Hexene, Typical Procedure. In the glovebox, a 25 mL Schlenk tube was charged with $[(COD)RhCl]_2$ (4.4 mg, 8.9 μmol), 1-hexene (1.04 g, 12.4 mmol), and **2** (25.7 mg, 53.5 μmol). The reaction vessel was removed from the glovebox, interfaced to a Schlenk line, and freeze−pump−thaw degassed (3×). The vessel was then filled with H_2 (1 atm) and warmed in an oil bath to 40 °C with rapid stirring for 24 h. The reaction was then terminated by opening the reactor to air. An aliquot (∼100 μL) of the reaction mixture was then dissolved in toluene (∼3 mL), chromatographed on a 2 cm column of silica gel, and then subjected to GC analysis to determine the relative amounts of 1-hexene and hexane. In each reaction mixture, a small (≤5%) amount of isomerized alkene appeared in the gas chromatogram.

Biphasic Catalytic Hydrogenation of 1-Hexene. In the glovebox, a 25 mL Schlenk tube was charged with $[(COD)_2Rh]$-OTf (8.3 mg, 17.7 μmol) and 1-hexene (1.597 g, 18.98 mmol). A solution of **5** (27.3 mg, 17.7 μmol) in $CF_3C_6F_{11}$ (1.7 mL) was added to the stirred mixture, which became yellow in color. The reaction vessel was removed from the glovebox, interfaced to a Schlenk line, and freeze−pump−thaw degassed (3×). The vessel was then filled with H_2 (1 atm) and warmed in an oil bath to 40 °C with rapid stirring. After 24 h, the reaction was cooled to ∼15 °C, causing phase separation of the colorless, organic product layer (top) and the yellow, Rh-containing fluorous layer (bottom). The organic layer was removed by

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(28) XSCANS (version 2.0) is a diffractometer control system developed by Siemens Analytical X-ray Instruments, Madison, WI.

(29) SHELXL-93 is a FORTRAN-77 program (Professor G. Sheldrick, Institut für Anorganische Chemie, University of Göttingen, D-37077, Göttingen, Germany) for single-crystal X-ray structural analyses.

pipette. GC and ^{1}H NMR analysis indicated complete conversion of 1-hexene.

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Supporting Information Available: Tables of anisotropic thermal parameters, positional parameters, bond angles (degrees), and bond distances (Å) for $Rh(CO)Cl[P(C_6H_5)_2OCH_2CH_2(CF_2)_5CF_3]$ (**6**) (12 pages). Ordering information is given on any current masthead page.

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