452 *Organometallics* **1998,** *17,* 452−456

Solution Thermochemical Study of a Fluorous Tertiary Phosphine Ligand in Rhodium and Ruthenium Systems

Chunbang Li and Steven P. Nolan*,†

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

István T. Horváth

Corporate Research Laboratories, Exxon Research and Engineering Company,
Clinton Township, Route 22 East, Annandale, New Jersey 08801

Received September 11, 1997

The enthalpies of reaction of a fluorous tertiary phosphine, $P(CH_2CH_2(CF_2)_5CF_3)_3$ (PR_{f3}) with $[Rh(CO)_2Cl]_2$ (**1**) and Cp′Ru(COD)Cl (Cp′ = η^5-C_5H_5 (**2**), η^5-C_5Me_5 (**3**)), leading to the formation of $RhCl(CO)(PR_{f3})_2$ and $Cp'Ru(PR_{f3})_2Cl$ complexes have been measured by anaerobic solution calorimetry in THF at 30.0 °C. These reactions are rapid and quantitative. The measured reaction enthalpies allow for a quantitative determination of characteristic phosphine steric and electronic parameters associated with this novel tertiary phosphine ligand. Sterically, the $P(CH_2CH_2(CF_2)_5CF_3)_3$ ligand appears identical to PEt_3.

Introduction

The industrial utilization of homogeneous rhodium−phosphine catalysts for the hydroformylation of lower molecular weight olefins (C2−8) is well established.[1−4] The application of triphenylphosphine-modified rhodium

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{Rh catalysts}} RCH_2CH_2C(O)H + R(CH_3)CHC(O)H \quad (1)$$

catalysts for the hydroformylation of higher olefins is limited by catalyst degradation during the separation of the aldehyde from the catalysts.[5] While water-soluble catalysts could provide easy separation for heavy aldehydes,[6] the low solubility of the higher olefins in water limits the application of aqueous catalysts.[7] One of us has recently provided a novel and environmentally benign alternative to these hydroformylation catalyst systems.[8a] The use of a partially fluorinated phosphine ligand in a fluorous biphasic system has proven to be an effective way to separate catalyst from product.[8]

Researchers have been involved in recent years in describing metal−ligand systems in terms of stereoelectronic contributions, using a variety of methods.[9−11] We have been interested in clarifying the exact partitioning of steric and electronic ligand contributions present in tertiary phosphine-based systems by means of solution calorimetry.[12−15] We have achieved this in part for iron-[13] and ruthenium-[12] based organometallic systems.

$$Cp^*Ru(COD)Cl_{(soln)} + 2PR_{3(soln)} \xrightarrow[30\ °C]{THF} Cp^*Ru(PR_3)_2Cl_{(soln)} + COD_{(soln)} \quad (2)$$

$$CpRu(COD)Cl_{(soln)} + 2PR_{3(soln)} \xrightarrow[30\ °C]{THF} CpRu(PR_3)_2Cl_{(soln)} + COD_{(soln)} \quad (3)$$

$$(BDA)Fe(CO)_{3(soln)} + 2PR_{3(soln)} \xrightarrow[50\ °C]{THF} \mathit{trans}\text{-}(PR_3)_2Fe(CO)_{3(soln)} + BDA_{(soln)} \quad (4)$$

$$Cp = C_5H_5;\ Cp^* = C_5Me_5;$$
$$BDA = PhCH{=}CHCOMe;\ PR_3 = \text{tertiary phosphine}$$

Most recently we have examined a number of rhodium[14] systems.

---

† E-mail: spncm@uno.edu.

§ E-mail: ithorva@erenj.com.

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science: Mill Valley, CA 1987. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, Wiley Interscience: New York, 1992.

(2) (a) Falbe, J. *Carbon Monoxide in Organic Synthesis*; Springer-Verlag: Berlin, 1980. (b) van Rooy, A.; de Bruijn, J. N. H.; Roobek, K. F.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1996**, *507*, 69−73 and references cited.

(3) (a) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 35. (b) Sharp, P. R. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 8, Chapter 2.

(4) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348. (b) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983.

(5) Jamerson, J. D.; Pruett, R. L.; Billig, E.; Fiato, R. A. *J. Organomet. Chem.* **1980**, *193*, C43−46.

(6) (a) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570−574. (b) Wiebus, E.; Cornils, B. *Chem. Ing. Technol.* **1994**, *66*, 916−923.

(7) Horváth, I. T. *Catal. Lett.* **1990**, *6*, 43−48.

(8) (a) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72−75. (b) Juliette, J. J. J.; Horváth, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1610−1612. (c) Guillevic, M.-A.; Arif, A. M.; Horváth, I. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1612−1615.

(9) (a) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1−7. (b) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Inorg. Chem.* **1989**, *28*, 1759−1763. (c) Poë, A. J. *Pure Appl. Chem.* **1988**, *60*, 1209−1216 and references cited. (d) Gao, Y.-C; Shi, Q.-Z; Kersher, D. L.; Basolo, F. *Inorg. Chem.* **1988**, *27*, 188−191. (e) Baker, R. T.; Calabrese, J. C.; Krusic, P. J.; Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 8392−8412. (f) Rahman, M. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650−658.

S0276-7333(97)00805-4 CCC: \$15.00

$$[RhCl(CO)_2]_2 + 4ER_3 \rightarrow 2RhCl(CO)(ER_3)_2 + 2CO \tag{5}$$

$$ER_3 = \text{phosphine, phosphite, arsine}$$

$$Rh(acac)(CO)_2 + PR_3 \rightarrow Rh(acac)(CO)(PR_3) + CO \tag{6}$$

$$PR_3 = \text{phosphine, phosphite}$$

With the assistance of our previously determined enthalpy versus steric and electronic factor trends, we present in this report a determination of the stereoelectronic parameters associated with the fluorous phosphine ligand $P(CH_2CH_2(CF_2)_5CF_3)_3$ (PR_{f3}).

Experimental Section

General Considerations. All manipulations involving organometallic complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in a Vacuum/Atmospheres glovebox containing <1 ppm oxygen and water. Solvents including deuterated solvents for NMR analysis were dried and distilled under dinitrogen before use by employing the standard drying agents.[16] Only materials of high purity as indicated by IR and NMR spectroscopies were used in the calorimetric experiments. Infrared spectra were recorded using a Perkin-Elmer FTIR model 2000 spectrometer in 0.1-mm NaCl cells. NMR spectra were recorded using a Varian Gemini 300 or Oxford 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[17] or the enthalpy of solution of KCl in water.[18] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[19] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. The organometallic complexes ($[Rh(CO)_2Cl]_2$[20] (**1**), CpRu(COD)Cl[21] (Cp = η^5-C_5H_5, COD = C_8H_{12}) (**2**), and Cp*Ru(COD)Cl[22] (Cp* = η^5-C_5H_5, COD = C_8H_{12}) (**3**)) and the phosphine ligand $P(CH_2CH_2(CF_2)_5CF_3)_3$[8] were synthesized using literature procedures.

IR Titration. Prior to calorimetric experiments involving reaction of the $[Rh(CO)_2Cl]_2$ complex with a phosphine ligand, IR spectroscopy was used to confirm the quantitative nature of the reaction. The general procedure is as follows: in the inert atmosphere glovebox, an accurately weighed amount (±0.1 mg) of the organorhodium complex was placed in a test tube with a septum, and dry THF was subsequently added. The ligand was subsequently added in a 10-fold excess, followed by vigorous shaking. The reaction was monitored by IR spectroscopy. The reaction was found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all reactions of organorhodium complexes.

NMR Titrations. Prior to every set of calorimetric experiments involving the Cp′Ru(COD)Cl complexes, **2** and **3**, an accurately weighed amount (±0.1 mg) of the organometallic complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF-*d*$_8$ was subsequently added. The solution was titrated with a solution of phosphine ligand by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^{1}H NMR spectroscopy and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions were satisfied for all organoruthenium reactions investigated.

Solution Calorimetry. (a) Calorimetric Measurement for Reaction of $[Rh(CO)_2Cl]_2$ (1) with PR_{f3}. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. The vessels consist of an inner and outer compartments in order to accommodate the solution of the two starting materials. Two stock solutions were prepared in volumetric flasks before being loaded in the vessels. One solution is made of 150 mg of **1** in 15 mL of THF, the other of 1.654 g of phosphine in 15 mL of THF corresponding to a 1:1 ratio of ligand to metal complex. Then, 2 mL of each stock solution were added respectively to the inner and outer compartments and the remainder of the vessel was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no rhodium complex 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

---

(10) (a) Huynh, M. H. V.; Bessel, C. A.; Takeuchi, K. J. Presented at the 208th National Meeting of the American Chemical Society, Washington, DC, Aug 21−26, 1994, Paper INOR 165. (b) Perez, W. J.; Bessel, C. A.; See, R. F.; Lake, C. H.; Churchill, M. R.; Takeuchi, K. J. Presented at the 208th National Meeting of the American Chemical Society, Washington, DC, Aug 21−26, 1994, Paper INOR 166. (c) Ching, S.; Shriver, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 3238−3243. (d) Lee, K.-W.; Brown, T. L. *Inorg. Chem.* **1987**, *26*, 1852−1856. (e) Brown, T. L.; Lee, K. J. *Coord. Chem. Rev.* **1993**, *128*, 89−116.

(11) Lorsbach, B. A.; Prock, A.; Giering, W. P. *Organometallics* **1995**, *14*, 1694−1699 and references cited.

(12) For organoruthenium systems, see: (a) Nolan, S. P.; Martin, K. L.; Stevens, E. D.; Fagan, P. J. *Organometallics* **1992**, *11*, 3947−3953. (b) Luo, L.; Fagan, P. J.; Nolan, S. P., *Organometallics* **1993**, *12*, 4305−4311. (c) Luo, L.; Zhu, N.; Zhu, N.-J.; Stevens, E. D.; Nolan, S. P.; Fagan, P. J. *Organometallics***1994**, *13*, 669−675. (d) Li, C.; Cucullu, M. E.; McIntyre, R. A.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1994**, *13*, 3621−3627. (e) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781−4786. (f) Cucullu, M. E.; Luo, L.; Nolan, S. P.; Fagan, P. J.; Jones, N. L.; Calabrese, J. C. *Organometallics* **1995**, *14*, 289−296. (g) Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P. *Organometallics* **1995**, *14*, 1333−1338. (h) Serron, S. A.; Nolan, S. P. *Organometallics* **1995**, *14*, 4611−4616. (i) Serron, S. A.; Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P. *Organometallics* **1995**, *14*, 5290−5297. (j) Li, C.; Serron, S. A.; Nolan, S. P.; Petersen, J. L.*Organometallics* **1996**, *15*, 4020−4029. (k) Li, C.; Ogasawa, M.; Nolan, S. P.; Caulton, K. G..*Organometallics* **1996**, *15*, 4900−4903.

(13) For the organoiron system, see: (a) Luo, L; Nolan, S. P. *Organometallics* **1992**, *11*, 3483−3486. (b) Luo, L.; Nolan, S. P. *Inorg. Chem.* **1993**, *32*, 2410−2415. (c) Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 1327−1332. (d) Li, C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1995**, *14*, 3791−3797. (e) Serron, S. A.; Nolan, S. P. *Inorg. Chim. Acta* **1996**, *252*, 107−113.

(14) For organorhodium system, see: (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*, 3377−3380. (c) Serron, S. A.; Huang, J.; Nolan, S. P. *Organometallics*, in press.

(15) For leading references in this area, see: (a) Nolan, S. P. *Bonding Energetics of Organometallic Compounds*. In *Encyclopedia of Inorganic Chemistry*; J. Wiley and Sons: New York, 1994. (b) Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40*, 503−561. (c) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629−688. (d) Marks, T. J., Ed. *Bonding Energetics In Organometallic Compounds*; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990. (e) Marks, T. J., Ed. *Metal−Ligand Bonding Energetics in Organotransition Metal Compounds*; Polyhedron Symposium-in-Print, **1988**, *7*.

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

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

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

(19) (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.

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

(21) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199−2205.

(22) (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am.Chem.Soc.* **1988**, *110*, 2981−2983. (b) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698−1719 and references therein. (c) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843−1852.

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

$$[Rh(CO)_2Cl]_{2(soln)} + 4PR_{3(soln)} \xrightarrow[30\ °C]{CH_2Cl_2} 2Rh(CO)(Cl)(PR_3)_{2(soln)} + 2CO$$

L	complex	ν_{CO} (cm^{-1})	$-\Delta H_{(rxn)}$[a,b]
PPh_3	$Rh(CO)(Cl)(PPh_3)_2$	1978	51.7 (0.3)
P(*p*-$CH_3C_6H_5)_3$	Rh(CO)(Cl)(P[p-$CH_3C_6H_4]_3)_2$	1975	56.1 (0.2)
P(*p*-$CH_3OC_6H_5)_3$	Rh(CO)(Cl)(P[p-$CH_3OC_6H_4]_3)_2$	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)
$P((CH_2)_2(CF_2)_5CF_3)_3$	$Rh(CO)(Cl)(PR_{f3})_2$	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 ref 14a. [c] This work in THF.

h), the vessels were removed from the calorimeter and taken into the glovebox, where an infrared cell was filled with the reaction solution under inert atmosphere. An infrared spectrum was recorded after each calorimetric run using this procedure. Conversion to the desired product was confirmed to be quantitative under these reaction conditions. The enthalpy of reaction, −68.5 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations.

Calorimetric Measurement for Reactions of Cp′Ru(COD)Cl (Cp′ = η^5-C_5H_5, Cp (2), η^5-C_5Me_5, Cp* (3)) with PR_{f3}. 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 20−30-mg sample of recrystallized **2** was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury; 4 mL of a stock solution of the phosphine ligand in THF (10-fold excess based on **2**) was added; and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel 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 (about 2 h), the reaction was initiated by inverting the calorimeter. At the end of the reaction (1−2 h), reaching thermal equilibrium again, the enthalpy of the reaction was calculated. Conversion to the desired products was confirmed to be quantitative under these reaction conditions by ^{1}H NMR spectroscopy prior the calorimetry experiments. The enthalpy of reaction in Table 2 represents the average of five individual calorimetric determinations.

Synthesis. $CpRu(PR_{f3})_2Cl$ (4). A 50-mL flask of a swivel frit assembly was charged with 27.2 mg (0.088 mmol) of **2**, 188.2 mg (0.175 mmol) of PR_{f3}, and 10 mL of THF. After stirring for 8 h at room temperature, the solvent was removed in vacuum. The residue was rinsed with pentane and filtered, and the volatiles were removed in vacuo, yielding 175 mg (85%) of an orange oil. ^{1}H NMR (THF-d_8, 25 °C): δ 4.75 (s, 5H, Cp); 2.52 (m, 18H, CH_2); 2.10 ppm (m, 6H, CH_2). ^{31}P NMR (THF-d_8, 25 °C): δ 31.3, (s) EI-MS (M^+ ion): calcd for $C_{53}H_{29}ClF_{78}P_2Ru$, 2346.2; found, 2346. Anal. Calcd for $C_{53}H_{29}ClF_{78}P_2Ru$: C, 27.13; H, 1.24. Found: C, 27.27; H, 1.36.

Cp*$Ru(PR_{f3})_2Cl$ (5). In a fashion analogous to that for **4**, complex **5** was isolated as an orange oil in 85% yield. ^{1}H NMR (THF-d_8, 25 °C): δ 2.62 (m, 6H, CH_2); 2.33 (m, 18H, CH_2); 1.66 ppm (s, 15H, Cp*). ^{31}P NMR (THF-d_8, 25 °C): δ 42.6 (s) EI-MS (M^+ ion): calcd for $C_{58}H_{39}ClF_{78}P_2Ru$, 2416.3; found, 2416. Anal.Calcd for $C_{58}H_{39}ClF_{78}P_2Ru$: C, 28.83; H, 1.63. Found: C, 29.20; H, 1.76.

$Rh(PR_{f3})_2(CO)Cl$ (6).[23] In a manner analogous to that for **4**, **6** was isolated from **1** and the phosphine as a yellow microcrystalline solid in 90% yield. ^{31}P NMR (THF-d_8, 25 °C): δ 23.54 (d, J_{Rh-P} = 121 Hz). IR (THF): ν_{CO} 1977 cm^{-1}. EI-MS (M^+ ion): calcd for $C_{49}H_{24}OClF_{78}P_2Rh$, 2309.9; found, 2310. Anal. Calcd for $C_{49}H_{24}OClF_{78}P_2Rh$: C, 25.47; H, 1.05. Found: C, 25.77; H, 1.45.

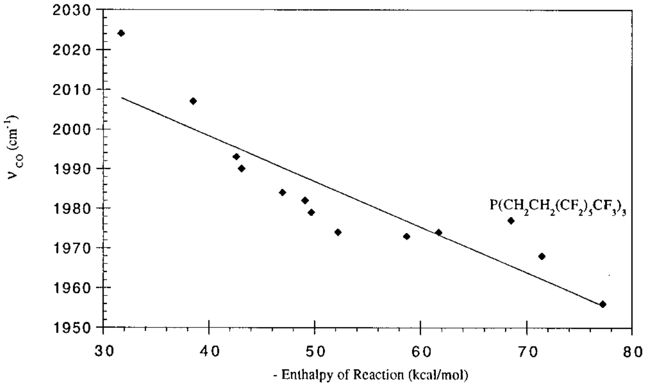

Figure 1. Carbonyl stretching frequency (cm^{-1}) vs enthalpies of reaction (kcal/mol) for the $RhCl(CO)(PR_3)_2$ system: slope, −1.15; R = 0.89.

Results and Discussion

The use of **1** as a versatile synthetic precursor has been reported.[3] Direct entry into the thermochemistry of $RhCl(CO)(PR_3)_2$ complexes is made possible by the rapid and quantitative reaction of $[RhCl(CO)_2]_2$ with stoichiometric amounts of phosphine ligands.[3]

$$[RhCl(CO)_2]_2 + 4ER_3 \rightarrow 2RhCl(CO)(ER_3)_2 + 2CO \tag{7}$$

$$ER_3 = \text{phosphine, phosphite, arsine}$$

This type of phosphine binding reaction appears general and was found to be rapid and quantitative for the fluorous phosphine ligand, PR_{f3}, which was calorimetrically investigated at 30.0 °C in tetrahydrofuran.

$$[Rh(CO)_2Cl]_2 + 4PR_{f3} \xrightarrow[30\ °C]{THF} 2Rh(PR_{f3})_2(CO)Cl + 2CO \tag{8}$$

$$\Delta H = -687.5\ (0.1)\ \text{kcal/mol}$$

The ^{31}P NMR spectrum is very diagnostic of the quantitative nature of the substitution reaction. The $[P(CH_2CH_2(CF_2)_5CF_3)_3]_2Rh(CO)Cl$ product exhibits a doublet at δ 23.54 ppm (J_{Rh-P} = 121 Hz). The related $[P(CH_2CH_2(CF_2)_7CF_3)_3]_2Rh(CO)Cl$ complex exhibits a doublet at δ 21.98 ppm (J_{Rh-P} = 119.9 Hz) in $CF_3C_6F_{11}$

---

[23] The X-ray structure of $Rh(PR_{f3})_2(CO)Cl$ has recently been published: Fawcett, J.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Russel, D. R.; Stuart, A. M.; Cole-Hamilton, D. J.; Pane, M. *J. Chem. Commun.* **1997**, 1127−1128.

Table 2. Selected Enthalpies of Substitution (kcal/mol) in the Reaction

$$Cp'Ru(COD)Cl_{(soln)} + 2L_{(soln)} \xrightarrow[30\ °C]{THF} Cp'Ru(L)_2Cl_{(soln)} + COD_{(soln)}$$

$$Cp' = Cp, Cp^*$$

L	complex	$-\Delta H_{rxn}{}^{a,b}$ (Cp)	$-\Delta H_{rxn}{}^{a,c}$ (Cp*)
PPh_3	$Cp'Ru(PPh_3)_2Cl$	22.9 (0.4)	18.1 (0.2)
PPh_2Me	$Cp'Ru(PPh_2Me)_2Cl$	32.8 (0.2)	29.4 (0.2)
$P(OPh)_3$	$Cp'Ru(P(OPh)_3)_2Cl$	34.1 (0.4)	31.2 (0.2)
PEt_3	$Cp'Ru(PEt_3)_2Cl$	34.5 (0.2)	27.2 (0.2)
$P((CH_2)_2(CF_2)_5CF_3)_3$	$Cp'Ru(PR_{f3})Cl$	34.7 (0.3)[d]	26.1 (0.3)[d]
P^nBu_3	$Cp'Ru(P^nBu_3)_2Cl$	35.4 (0.2)	26.0 (0.2)
$PPhMe_2$	$Cp'Ru(PPhMe_2)_2Cl$	35.9 (0.2)	31.8 (0.3)
PMe_3	$Cp'Ru(PMe_3)_2Cl$	38.4 (0.4)	32.2 (0.4)
$P(OMe)_3$	$Cp'Ru(P(OMe)_3)_2Cl$	41.8 (0.2)	37.5 (0.4)

[a] Enthalpy values are reported with 95% confidence limits. [b] Taken from ref 12f. [c] Taken from ref 12b. [d] This work.

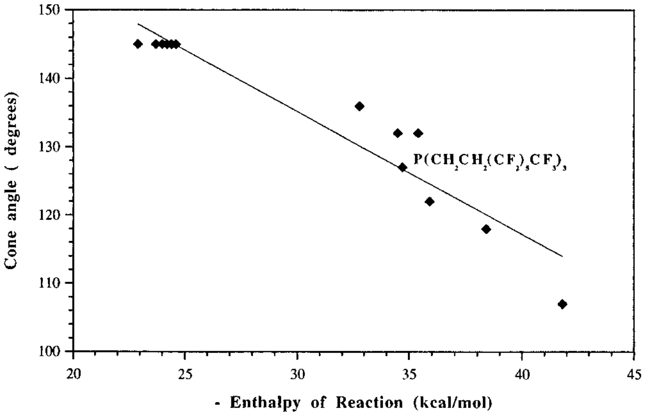

Figure 2. Phosphine cone angle (deg) vs enthalpies of reaction (kcal/mol) for the $CpRu(PR_3)_2Cl$ system: slope, −1.80; $R = 0.95$.

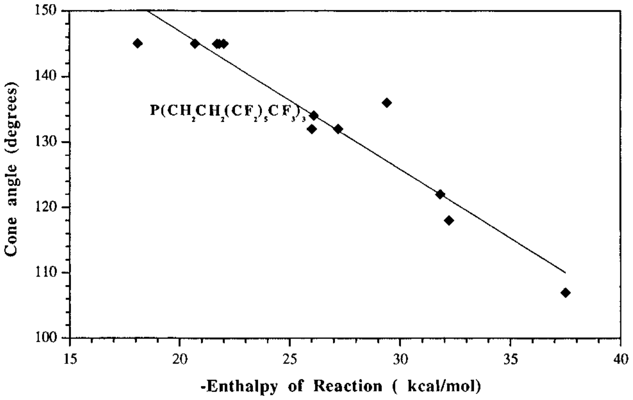

Figure 3. Phosphine cone angle (deg) vs enthalpies of reaction (kcal/mol) for the $Cp^*Ru(PR_3)_2Cl$ system: slope, −2.10; $R = 0.96$.

solvent.[24] This enthalpy result and a selection of previously measured enthalpies of reaction for other phosphine ligands are presented in Table 1. These enthalpy values are reported on the basis of 1 mol of the rhodium dimer **1** and consider all species in solution. A direct comparison of this enthalpy measurement in THF with previously performed work in CH_2Cl_2 is possible since enthalpy of ligand substitution values in both solvents are identical.[25]

We have previously shown that in view of the mutually trans arrangement of phosphine ligands in $RhCl(CO)(PR_3)_2$ complexes, the predominant factor dictating the magnitude of the enthalpy of ligand substitution is associated with phosphine donor ability, or the electronic factor of the phosphine.[14] In the present case, such a value for the fluorous tertiary phosphine has not yet been obtained. With the help of the existing trend, such a value can be determined. A simple one-component relationship shows a fair linear relationship existing between the enthalpy of reaction and the experimentally recorded carbonyl stretching frequency of each phosphine complex. This relationship is illustrated in Figure 1, where enthalpy data are taken from our previous report on this system.[14]

From the onset, the synthetic strategy leading to the fluorous ligand assumed the shielding effect of the two methylene units.[8] The role of these two methylene units between the phosphorus and the perfluorohexyl moieties was to shield the phosphorus atom from the electron-withdrawing effects of the perfluoroalkyl groups (or fluorous ponytails). With this in mind, the electronic factor displayed by complex **6** should be near that of the PEt_3 complex (a good model for two methylene units). According to Figure 1, the electronic parameter versus enthalpy value relationship is near that displayed by the $PPhMe_2$ complex. Electronically, the fluorous ligand is a poorer donor than PEt_3, the shielding effect of the two methylene units being somewhat efficient but not completely insulating.

The determination of the steric parameter associated with PR_{f3} requires an observable which is uniquely (or principally) dependent on this factor. We have already mentioned our work on the $Cp'Ru(PR_3)_2Cl$ systems which, in view of the mutual cis arrangement of phosphines in these complexes, exhibit a marked dependence on steric parameters.[12] In order to establish such a relationship, reaction enthalpies for ligand substitution involving the fluorous PR_{f3} ligand and both **2** and **3** were measured and are illustrated in eq 9. A listing of

$$Cp'Ru(CO)ECl + 2PR_{f3} \xrightarrow[30\ °C]{THF} Cp'Ru(PR_{f3})_2Cl + COD \quad (9)$$

$$\Delta H = -34.7(0.3)\ \text{kcal/mol},\ Cp' = Cp$$

$$\Delta H = -26.1(0.3)\ \text{kcal/mol},\ Cp' = Cp^*$$

enthalpy data for these and related complexes can be found in Table 2. By simple interpolation, the enthalpy

---

(24) Bernatis, P.; Gladysz, J. A.; Horváth, I. T., unpublished results.
(25) Li, C.; Nolan, S. P., unpublished results.

of reaction value of the fluorous ligand can be inserted into the simple one-component relationships illustrated in Figures 2 and 3. The steric factor associated with this fluorous tertiary phosphine can thereby be quantified. Respective values of 134 (from the Cp* data) and 127° (from the Cp data) are obtained for the Tolman steric parameter θ.[4a] We therefore use the average of the two values, 130°, to represent a measure of the steric parameter associated with this phosphine ligand. This value of 130 ± 4° is within experimental error of the PEt_3 value of 132° reported by Tolman.[4a] This can be easily explained in terms of the F ionic radius and normal C−F bond lengths, which are similar to their H analogues.[26] Sterically, the $P(CH_2CH_2(CF_2)_5CF_3)_3$ ligand appears identical to PEt_3.

Conclusion

The solution calorimetric investigation of a ligand substitution reaction involving the $P(CH_2CH_2(CF_2)_5CF_3)_3$ ligand in three organometallic systems has been performed in order to extract the steric and electronic parameters characterizing this ligand. From the rhodium system, where the electronic character of the ligand principally dictates the magnitude of the reaction enthalpies, an electronic parameter similar to PMe_2Ph is observed and best characterizes the fluorous phosphine ligand. From two ruthenium systems, where ligand sterics dominate, a cone angle of 130 ± 4° is estimated from two enthalpy versus steric parameter correlations.

Acknowledgment. The National Science Foundation (Grant CHE-963116) is gratefully acknowledged for support of this research.

OM970805O

---

[26] Patai, R., Ed. *The Chemistry of the Carbon−Halogen Bond*; Wiley: New York, 1973; Part 1, pp 49−62.