# Enthalpies of Reaction of Cp'Ru(COD)Cl ( $Cp' = C_5H_5$ , $C_5Me_5$ ; COD = Cyclooctadiene) with $P(p-XC_6H_4)_3$ (X = Cl, F, H, CH<sub>3</sub>, CF<sub>3</sub>, OCH<sub>3</sub>) Ligands: Ligand Steric vs **Electronic Contributions to the Enthalpy of Reaction**

Scafford A. Serron, Lubin Luo, Chunbang Li, Michèle E. Cucullu, Edwin D. Stevens, and Steven P. Nolan\*

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

Received June 20, 1995<sup>®</sup>

The enthalpies of reaction of Cp'Ru(COD)Cl (1; Cp' =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; COD = cyclooctadiene) with a series of para-substituted monodentate tertiary phosphine ligands, leading to the formation of  $Cp'Ru(PR_3)_2Cl$ , have been measured by anaerobic solution calorimetry in THF at 30.0 °C. These reactions are rapid and quantitative. Structural studies have been carried out on three complexes in this series. The relative importance of phosphine steric vs electronic ligand parameters is more closely examined in terms of the presented quantitative thermochemical and structural information. Comparisons with enthalpy data in this and related organometallic systems are also presented.

## Introduction

A fundamental question addressed by a number of recent kinetic and thermodynamic studies deals with the relative importance of ligand steric vs electronic effects.<sup>1-3</sup> One such class of ligands which researchers have attempted to characterize in this fashion is tertiary phosphines. This class of ligand, of fundamental importance in organometallic chemistry and catalysis, has been employed to fine-tune reactivity and selectivity.<sup>4-6</sup> A better understanding of the exact nature of ligand effects can help direct synthetic and catalytic research efforts. Our solution calorimetric investigations of organo-group 8 complexes, focusing on ligand substitution reactions, have contributed to a clarification of the exact partitioning of steric and electronic ligand contributions present in tertiary phosphine based systems.7,8

(2) (a) Huynh, M. H. V.; Bessel, C. A.; Takeuchi, K. J. Abstracts of Papers; 208th Annual Meeting of the American Chemical Society, Washington, DC, Aug 1994; American Chemical Society: Washington, DC, 1994; INOR 165. (b) Perez, W. J.; Bessel, C. A.; See, R. F.; Lake, C. H.; Churchill, M. R.; Takeuchi, K. J. In ref 2a, 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.
(3) Lorsbach, B. A.; Prock, A.; Giering, W. P. Organometallics 1995, 14, 1694-1699 and references cited therein.

(6) Noyori, R. Asymmetric Catalysis in Organic Synthesis; Wiley: New York, 1994 and references cited therein.

Thermochemical studies performed on organometallic systems have gained recognition as an area of research that can provide important insights into reactivity and bonding patterns.<sup>9-12</sup> Our recent contribution on the thermochemistry of ligand substitution in the (L)<sub>2</sub>Fe- $(CO)_3$  (L = PR<sub>3</sub>) system, where isosteric para-substituted triphenylphosphine ligands were employed as a diagnostic tool in the determination of the relative importance of ligand stereoelectronic factors, has clearly shown the importance of electronic contributions in this iron-based system.8c

Chemicals, 3rd ed.; Pergamon Press: New York, 1988.

0276-7333/95/2314-5290\$09.00/0

© 1995 American Chemical Society

<sup>\*</sup> Abstract published in Advance ACS Abstracts, October 15, 1995. (1) (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) Poe, A. J. Pure Appl. Chem. 1988, 60, 1209–1216 and references cited therein. (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. S.; Therei, M. J.; W. D. S.; Marker, M. J.; W. D. S.; Marker, M. J.; Chem. 1988, 27, 188–191. (c) 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. S.; Marker, M. J.; Krusic, P. J.; Therien, M. J.; Trogler, W. C. J. Am. Chem. Soc. 1988, 110, 8392–8412. (f) Rahman, M. S.; M. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. Organometallics 1987, 6, 650 - 658.

 <sup>(4) (</sup>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) Bennett, M. A.;
 Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 32.9.

<sup>(5) (</sup>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.

<sup>(7)</sup> 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, 3405-3411. (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 2004, 1000 (2004) 1994, 13, 3621-3627. (e) Cucullu, M. E.; Luo, L.; Nolan, S. P.; Fagan, P. J.; Jones, N. L.; Calabrese, J. C. Organometallics 1995, 14, 289–296. (f) Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P. Organometallics
 1995, 14, 1333–1338. (g) Serron, S. A.; Nolan, S. P. Organometallics, in press.

<sup>(8)</sup> For organoiron system see: (a) Luo, L.; Nolan, S. P. Organome-tallics 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.

<sup>(9)</sup> For leading references in this area, see: (a) Nolan, S. P. Bonding Energetics of Organometallic Compounds. In Encyclopedia of Inorganic Chemistry; Wiley: 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 7; Elsevier: Oxford, U.K., 1988. (10) See for example: (a) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.;

Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. G. J. Am. Chem. Soc. **1987**, 109, 3143-3145 and references therein. (b) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. Organometallics **1986**, 5. 2529-2537.

 <sup>(11) (</sup>a) Nolan, S. P.; Porchia, M.; Marks, T. J. Organometallics 1991,
 10, 1450-1457. (b) Nolan, S. P.; Stern, D.; Marks, T. J. J. Am Chem. Soc. 1989, 111, 7844-7854.

<sup>(12) (</sup>a) Nolan, S. P.; Stern, D.; Hedden, D.; Marks, T. J. In ref 1d, J. J. Am. Chem. Soc. 1988, 110, 7701-7715.
 (13) Perrin, D. D.; Armarego, W. L. F. Purification of Laboratory

#### Ligand Effects in Organoruthenium Systems

In the present study, we report on the application of this approach in determining the relative importance of such ligand effects in two related organoruthenium systems. Furthermore, structural investigations were carried out on three complexes in the present series, allowing for a wider sampling of bond length variation with change in ancillary ligation.

### **Experimental Section**

General Considerations. All manipulations involving organoruthenium 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 less than 1 ppm of oxygen and water. Ligands were purchased from Strem Chemicals or Aldrich and used as received. Solvents were dried and distilled under dinitrogen before use by employing standard drying agents.<sup>13</sup> Only materials of high purity, as indicated by IR and 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<sup>14</sup> or the enthalpy of solution of KCl in water.<sup>15</sup> The experimental enthalpies for these two standard reactions compare very closely to literature values. This calorimeter has been previously described,<sup>16</sup> 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.

**Synthesis.** The compounds CpRu(COD)Cl<sup>17</sup> and Cp\*Ru-(COD)Cl<sup>18</sup> were synthesized according to literature procedures. The identities of the organoruthenium products Cp\*Ru(PPh<sub>3</sub>)<sub>2</sub>-Cl,<sup>7b</sup> CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl,<sup>19</sup> CpRu(P(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>Cl,<sup>20</sup> CpRu(P(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>Cl,<sup>21</sup> and CpRu(P(*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>Cl<sup>22</sup> were ascertained by comparison with literature NMR spectroscopic data. Experimental synthetic procedures, leading to isolation of crystalline materials, for previously unreported complexes are described below.

**CpRu**(**P**(*p*-**CF**<sub>3</sub>**C**<sub>6</sub>**H**<sub>4</sub>)<sub>3</sub>)<sub>2</sub>**Cl.** A 25 mL flask was charged with 108 mg (0.35 mmol) of CpRu(COD)Cl, 10 mL of dried THF, and 328 mg (0.70 mmol) of P(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. After it was stirred overnight, the solution was placed under vacuum to remove volatiles. Five milliliters of hexane was then added to the solid residue, and the mixture was stirred for about 20 min. The suspension was then filtered, and the remaining microcrystalline solid was washed with a small amount of hexanes. Solvent was removed, and the yellow/orange powder was dried under vacuum, giving a 340 mg (86%) yield. <sup>1</sup>H NMR (300 MHz, THF-*d*<sub>8</sub>, 25 °C):  $\delta$  4.34 (s, 5 H, Cp), 7.50 (d, 12H, Ph), 7.69 (m, 12 H, Ph). Anal. Calcd for RuClP<sub>2</sub>F<sub>18</sub>-C<sub>47</sub>H<sub>24</sub>: C, 49.73; H, 2.58. Found: C, 49.70; H, 2.55.

(18) (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.
 (10) Bruce, M. L. Harreitter, C. Swinzer, A. C. Wollie, P. C. Lawretter, S. C. 1987, 111, 1698-1719.

(19) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. Inorg.
Synth. 1982, 21, 78-84.
(20) Hartwig, J. F.; Bhandari, S.; Rablen, P. R. J. Am. Chem. Soc.

(21) Bruce, M. I.; Windsor, N. J. Aust. J. Chem. **1977**, 30, 1601–

(21) Endler, M. I., Windson, N. S. Aust. S. Chem. 1911, 50, 1001 1604. (22) Fielder, D. Braden, R. Buding, H. Gar, Offen, DE 3 337 294

(22) Fiedler, P.; Braden, R.; Buding, H. Ger. Offen. DE 3 337 294, 1985.

**CpRu**(**P**(*p*-**ClC**<sub>6</sub>**H**<sub>4</sub>)<sub>3</sub>)<sub>2</sub>**Cl.** A 25 mL flask was charged with 100 mg (0.32 mmol) of CpRu(COD)Cl and 236 mg (0.64 mmol) of P(*p*-ClC<sub>6</sub>**H**<sub>4</sub>)<sub>3</sub>. Then, 30 mL of dry THF was vacuum-transferred into this flask and the solution was stirred overnight. The solution was filtered, and the solvent was removed under vacuum until dryness. A 30 mL portion of hexane was then vacuum-transferred onto the residue and the mixture stirred for 20 min, after which time the suspension was filtered and the remaining orange solid was washed with a small amount (ca. 2 mL) of hexane. The solvent was removed and the powder was dried under vacuum, giving a 230 mg (77%) yield. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  4.19 (s, 5 H, Cp), 7.18–7.41 (m, 24 H, Ph). Anal. Calcd for RuCl<sub>7</sub>P<sub>2</sub>C<sub>41</sub>H<sub>29</sub>: C, 52.79; H, 3.13. Found: C, 52.69; H, 3.10.

**Cp\*Ru**(**P**(*p*-**CF**<sub>3</sub>**C**<sub>6</sub>**H**<sub>4</sub>)<sub>3</sub>)<sub>2</sub>**Cl.** A 25 mL flask was charged with 90 mg (0.24 mmol) of Cp\*Ru(COD)Cl, 10 mL of dried THF, and 220 mg (0.48 mmol) of P(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. After it was stirred overnight, the solution was placed under vacuum to remove volatiles. Five milliliters of hexane was then added to the solid residue, and the mixture was stirred for about 20 min. The suspension was then filtered, and the remaining microcrystalline solid was washed with a small amount of hexanes. Solvent was removed, and the yellow powder was dried under vacuum, giving a 260 mg (90%) yield. <sup>1</sup>H NMR (300 MHz, THF-*d*<sub>8</sub>, 25 °C):  $\delta$  1.08 (s, 15 H, Cp\*), 7.46, 7.69 (br, 24 H, Ph). Anal. Calcd for RuClP<sub>2</sub>F<sub>18</sub>C<sub>52</sub>H<sub>39</sub>: C, 51.86; H, 3.26. Found: C, 51.57; H, 2.95.

 $Cp*Ru(P(p-ClC_6H_4)_3)_2Cl.$  A 25 mL flask was charged with 200 mg (0.53 mmol) of Cp\*Ru(COD)Cl and 423 mg (1.06 mmol) of  $P(p-ClC_6H_4)_3$ . Then, 20 mL of dry THF was vacuumtransferred into this flask and it was stirred overnight. The solution was filtered, and solvent was removed under vacuum until dryness. About 16 mL of a solvent mixture of hexane and THF (3:1) was vacuum-transferred into the cooled (-78)°C) flask containing the residue. This mixture was warmed to room temperature with stirring. After filtration, the solution was slowly cooled to -78 °C and kept at this temperature overnight. Cold filtration afforded orange-red crystals, which were washed with a small amount of hexane and dried under vacuum, giving a 451 mg (85%) yield. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>, 25 °C): δ 1.06 (s, 15 H, Cp\*), 7.15, 7.42 (br, 24 H, Ph). Anal. Calcd for  $RuCl_7P_2C_{46}H_{39}$ : C, 55.09; H, 3.92. Found: C, 54.80; H, 4.17.

**Cp\*Ru**(**P**(*p*-**CH<sub>3</sub><b>OC**<sub>6</sub>**H**<sub>4</sub>)<sub>3</sub>)<sub>2</sub>**Cl.** A 25 mL flask was charged with 100 mg (0.26 mmol) of Cp\*Ru(COD)Cl, 20 mL of dried THF, and 183 mg (0.52 mmol) of P(*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. After it was stirred overnight, the solution was put under vacuum to remove volatiles. A 5 mL solvent mixture of THF and hexane (1:4) was then added to the solid, and the mixture was stirred for about 20 min. The suspension was then filtered, and the remaining solid was washed with a small amount of hexane. Solvent was removed, and the yellow powder was dried under vacuum, giving a 220 mg (87%) yield. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  1.05 (s, 15 H, Cp\*), 3.73 (s, 18 H, CH<sub>3</sub>), 7.46, 7.69 (br, 24 H, Ph). Anal. Calcd for RuClP<sub>2</sub>O<sub>6</sub>C<sub>52</sub>H<sub>57</sub>: C, 63.96; H, 5.88. Found: C, 63.78; H, 5.68.

**Cp\*Ru(P(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>Cl.** A 25 mL flask was charged with 200 mg (0.53 mmol) of Cp\*Ru(COD)Cl and 350 mg (1.06 mmol) of P(p-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. Then, 20 mL of dried THF was vacuum-transferred into this flask and the solution was stirred overnight. The solution was filtered and solvent was removed under vacuum until dry. About 16 mL of a solvent mixture of hexane and THF (3:1) was vacuum-transferred to the cooled (-78 °C) residue. This mixture was warmed to room temperature and stirred. After filtration, the solution was slowly cooled to -78 °C and kept at this temperature overnight. Cold filtration afforded orange-red crystals which were washed with a small amount of hexane and dried under vacuum, giving a 380 mg (80%) yield. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  1.05 (s, 15 H, Cp\*), 6.87, 7.48 (br, 24 H, Ph). Anal. Calcd for RuClP<sub>2</sub>F<sub>6</sub>C<sub>46</sub>H<sub>39</sub>: C, 61.10; H, 4.35. Found: C, 61.37; H, 4.41.

 <sup>(14)</sup> Ojelund, G.; Wadsö, I. Acta Chem. Scand. 1968, 22, 1691–1699.
 (15) Kilday, M. V. J. Res. Natl. Bur. Stand. (U.S.) 1980, 85, 467–481.

 <sup>(16) (</sup>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.

C. D. Inorg. Chem. **1986**, 25, 4446-4448. (17) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. Organometallics **1986**, 5, 2199-2205.

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

 $Cp'Ru(COD)Cl(soln) + 2L(soln) \xrightarrow{THF} Cp'Ru(L)_2Cl(soln) + COD(soln)$ 

 $Cp' = Cp, Cp^*$ 

| L                    | complex                         | $-\Delta H_{\text{reacn}}(Cp^*)^a$ | $-\Delta H_{\rm reacn}({\rm Cp})^a$ |
|----------------------|---------------------------------|------------------------------------|-------------------------------------|
| $(C_6H_5)_3P$        | $Cp'Ru[P(C_6H_5)_3]_2Cl$        | 18.1 (0.2)                         | 22.9 (0.3)                          |
| $(p-CH_3C_6H_4)_3P$  | $Cp'Ru[P(p-CH_3C_6H_4)_3]_2Cl$  |                                    | 23.7 (0.3)                          |
| $(p-CF_3C_6H_4)_3P$  | $Cp'Ru[[P(p-CF_3C_6H_4)_3]_2Cl$ | 20.7 (0.3)                         | 24.4(0.2)                           |
| $(p-CH_3OC_6H_4)_3P$ | $Cp'Ru[P(p-CH_3OC_6H_4)_3]_2Cl$ | 21.8 (0.4)                         | 24.6 (0.3)                          |
| $(p-ClC_6H_4)_3P$    | $Cp'Rup[P(p-ClC_6H_4)_3]_2Cl$   | 21.7(0.4)                          | 24.0(0.2)                           |
| $(p-FC_6H_4)_3P$     | $Cp'Ru[P(p-FC_6H_4)_3]_2Cl$     | 22.0 (0.5)                         | 24.2(0.2)                           |

| <sup>a</sup> Enthalpy | values | are repo         | rted with          | 95%             | confider | ce limits. |
|-----------------------|--------|------------------|--------------------|-----------------|----------|------------|
| Table 2.              | Sumn   | nary of<br>Co*Ru | Crysta<br>(CaH12)( | llogr<br>Cl (1) | aphic ]  | Data for   |

| - F -                              |                                      |
|------------------------------------|--------------------------------------|
| empirical formula                  | C <sub>18</sub> H <sub>27</sub> ClRu |
| space group                        | Pbca                                 |
| unit cell dimens                   |                                      |
| a, Å                               | 14.222(3)                            |
| b, Å                               | 13.876(3)                            |
| $c, \mathrm{\AA}$                  | 16.473(3)                            |
| α, deg                             | 90                                   |
| $\beta$ , deg                      | 90                                   |
| $\gamma$ , deg                     | 90                                   |
| V, Å <sup>3</sup>                  | 3251 (2)                             |
| Z, molecule/cell                   | 8                                    |
| density (calcd), g/cm <sup>3</sup> | 1.552                                |
| $\mu(Mo), cm^{-1}$                 | 11.01                                |
| wavelength, Å                      | 0.710 73                             |
| monochromator                      | highly ordered graphite crystal      |
| temp, K                            | 100(2)                               |
| abs cor                            | empirical ( $\psi$ -scan method)     |
| diffractometer                     | Enraf-Nonius CAD 4                   |
| scan type                          | $\theta - 2\theta$                   |
| data collected                     | $0 \le h \le 16, 0 \le k \le 16,$    |
|                                    | $0 \le l \le 18$                     |
| 2	heta range, deg                  | 4.0 - 50.0                           |
| no. of collected rfins             | 2824                                 |
| no. of obsd rflns                  | 1903                                 |
| $R_F$ (obsd data), %               | 3.2                                  |
| $R_{\mathrm{w}F},$ %               | 4.8                                  |
| goodness of fit                    | 1.76                                 |
| no. of variables                   | 279                                  |
| residual density, e/Å <sup>3</sup> |                                      |
| max                                | 0.56(5)                              |
| min                                | -0.86(5)                             |

<sup>1</sup>H NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount ( $\pm 0.1 \text{ mg}$ ) of the organoruthenium 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 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 <sup>1</sup>H NMR 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 organoruthenium reactions investigated.

Solution Calorimetry. Calorimetric Measurement of Reaction between CpRu(COD)Cl (1) and P(p-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>. 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 30-40 mg sample of recrystallized CpRu(COD)-Cl was accurately weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of P(p-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (1 g of P(p-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub> in 25 mL of THF) 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 organoruthenium complex was added to the lower vessel. After the calorimeter had

| Table | 3. | Sele | cted | Bone  | l Di            | istanc | es           | (Å) | and   | Bond |
|-------|----|------|------|-------|-----------------|--------|--------------|-----|-------|------|
|       | An | gles | (deg | ) for | Cp <sup>4</sup> | Ru(C   | 8 <b>H</b> 1 | 2)C | l (1) |      |

| Bond Lengths <sup><math>a</math></sup> |          |                         |          |  |  |  |  |
|--|----------|-------------------------|----------|--|--|--|--|
| Ru-Cl(1)                               | 2.472(2) | $\tilde{R}u(1) - C(15)$ | 2.225(4) |  |  |  |  |
| Ru-C(1)                                | 2.235(4) | Ru-C(16)                | 2.236(5) |  |  |  |  |
| Ru-C(2)                                | 2.247(5) | C(11) - C(12)           | 1.385(7) |  |  |  |  |
| Ru-C(3)                                | 2.242(4) | C(11) - C(18)           | 1.495(8) |  |  |  |  |
| Ru-C(4)                                | 2.209(4) | C(15) - C(16)           | 1.391(8) |  |  |  |  |
| Ru-C(5)                                | 2.274(4) | C(14) - C(15)           | 1.507(7) |  |  |  |  |
| Ru-C(11)                               | 2.200(4) | Ru-C(12)                | 2.190(4) |  |  |  |  |
| Ru-Cp(cen)                             | 1.885(2) | Ru-C(Cp av)             | 2.241(2) |  |  |  |  |
|  | Bond     | Angles <sup>a</sup>     |          |  |  |  |  |
| Cl-Ru-C(1)                             | 86.3(1)  | C(11) - Ru - C(12)      | 36.8(2)  |  |  |  |  |
| Cl-Ru-C(2)                             | 84.3(2)  | C(11) - Ru - C(15)      | 92.5(2)  |  |  |  |  |
| Cl-Ru-C(3)                             | 116.2(1) | C(11) - Ru - C(16)      | 79.7(2)  |  |  |  |  |
| Cl-Ru-C(4)                             | 145.4(2) | C(12) - Ru - C(15)      | 78.2(2)  |  |  |  |  |
| Cl-Ru-C(5)                             | 119.6(2) | C(12)-Ru-C(16)          | 88.0(2)  |  |  |  |  |
| Cl-Ru-C(11)                            | 80.5(1)  | C(15)-Ru-C(16)          | 36.3(2)  |  |  |  |  |
| Cl-Ru-C(12)                            | 117.4(1) | C(11)-Ru-Cp(cen)        | 137.4(2) |  |  |  |  |
| Cl-Ru-C(15)                            | 113.9(1) | C(12)-Ru-Cp(cen)        | 115.6(2) |  |  |  |  |
| Cl-Ru-C(16)                            | 78.3(1)  | C(15)-Ru- $Cp(cen)$     | 115.7(2) |  |  |  |  |
| Cl-Ru-Cp(cen)                          | 112.2(1) | C(16)-Ru-Cp(cen)        | 141.5(2) |  |  |  |  |

 $^{\boldsymbol{\alpha}}$  Numbers in parentheses are the estimated standard deviations.

reached thermal equilibrium at 30.0 °C (about 2 h), the calorimeter was inverted, thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h), the vessels were removed from the calorimeter. Conversion to  $CpRu(P(p-MeOC_6H_4)_3)_2Cl$  was found to be quantitative under these reaction conditions. Control reactions with Hg and no phosphine show no reaction. The enthalpy of reaction,  $-20.7 \pm 0.2$  kcal/mol, represents the average of five individual calorimetric determinations. The final enthalpy value listed in Table 1 (-24.6  $\pm$  0.3 kcal/mol) represents the enthalpy of ligand substitution with all species in solution. The enthalpy of solution of 1  $(3.9 \pm 0.1 \text{ kcal/mol})$  has therefore been subtracted from the -20.7 kcal/mol value. This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study.

Structure Determination of Cp\*Ru(COD)Cl (1). An orange needle, grown from a saturated THF solution, having approximate dimensions  $0.22 \times 0.25 \times 0.40$  mm was selected and mounted on the end of a glass fiber in a random orientation. This selected crystal was mounted on an Enraf-Nonius CAD4 diffractometer, and data were collected using Mo K $\alpha$  radiation at 100 K under a stream of cold nitrogen gas. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with  $30^{\circ} < 2\theta$  $< 46^{\circ}$ . The structure was solved using direct methods (MUL-TAN80) and refined by full-matrix least-squares techniques. Crystal data for 1 are summarized in Table 2, and selected bond distances and angles are listed in Table 3. Positional and equivalent isotropic thermal parameters are presented in Table 4. Figure 1 gives an ORTEP drawing of this molecule.

Structure Determination of  $Cp*Ru(P(p-CF_3C_6H_4)_2Cl$ (2). An orange needle, grown from slow evaporation of a saturated solution of anhydrous ethanol, having approximate

Table 4. Fractional Coordinates ( $\times 10\ 000$ ) and Isotropic Thermal Parameters for  $Cp^*Ru(C_0H_{12})Cl\ (1)^a$ 

| atom                  | x          | у          | z          | B (Å <sup>2</sup> ) |  |  |  |
|-----------------------|------------|------------|------------|---------------------|--|--|--|
| Ru                    | 0.88416(3) | 0.17875(3) | 0.70944(2) | 1.140(7)            |  |  |  |
| <b>C</b> ( <b>l</b> ) | 0.8995(1)  | 0.00138(9) | 0.71441(8) | 2.15(3)             |  |  |  |
| C(1)                  | 0.9551(4)  | 0.1700(4)  | 0.5887(3)  | 1.5(1)              |  |  |  |
| C(2)                  | 0.8550(4)  | 0.1548(4)  | 0.5769(3)  | 1.5(1)              |  |  |  |
| C(3)                  | 0.8069(4)  | 0.2391(4)  | 0.6023(3)  | 1.7(1)              |  |  |  |
| C(4)                  | 0.8769(4)  | 0.3065(3)  | 0.6297(3)  | 1.6(1)              |  |  |  |
| C(5)                  | 0.9671(4)  | 0.2640(3)  | 0.6158(3)  | 1.23(9)             |  |  |  |
| C(6)                  | 1.0306(4)  | 0.1002(4)  | 0.5656(3)  | 1.9(1)              |  |  |  |
| C(7)                  | 0.8106(4)  | 0.0666(4)  | 0.5405(3)  | 2.0(1)              |  |  |  |
| C(8)                  | 0.7039(4)  | 0.2586(5)  | 0.5922(4)  | 2.4(1)              |  |  |  |
| C(9)                  | 0.8608(4)  | 0.4097(4)  | 0.6492(4)  | 2.5(1)              |  |  |  |
| C(10)                 | 1.0599(4)  | 0.3155(4)  | 0.6230(3)  | 1.8(1)              |  |  |  |
| C(11)                 | 0.7730(4)  | 0.1459(4)  | 0.7980(3)  | 2.1(1)              |  |  |  |
| C(12)                 | 0.7759(4)  | 0.2447(4)  | 0.7860(3)  | 2.0(1)              |  |  |  |
| C(13)                 | 0.8120(5)  | 0.3149(5)  | 0.8493(4)  | 3.5(1)              |  |  |  |
| C(14)                 | 0.9161(5)  | 0.3311(4)  | 0.8479(4)  | 2.7(1)              |  |  |  |
| C(15)                 | 0.9703(4)  | 0.2556(5)  | 0.8017(3)  | 2.0(1)              |  |  |  |
| C(16)                 | 0.9706(4)  | 0.1581(4)  | 0.8215(3)  | 2.4(1)              |  |  |  |
| C(17)                 | 0.9120(5)  | 0.1179(5)  | 0.8920(4)  | 3.3(1)              |  |  |  |
| C(18)                 | 0.8101(5)  | 0.0974(5)  | 0.8724(4)  | 3.9(2)              |  |  |  |
|                       |            |            |            |                     |  |  |  |

 $^{a}$  Numbers in parentheses are the estimated standard deviations.



Figure 1. ORTEP of  $Cp^{\ast}Ru(C_{8}H_{12})Cl\ (1)$  with ellipsoids drawn in at the 50% probability level.

dimensions  $0.06 \times 0.06 \times 0.44$  mm was selected and mounted on the end of a glass fiber in a random orientation. This selected crystal was mounted on an Enraf-Nonius CAD4 diffractometer, and data were collected using Mo Ka radiation at 100 K under a stream of cold nitrogen gas. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with  $25^{\circ} < 2\theta < 38^{\circ}$ . The structure was solved by using the heavy-atom method and refined by full-matrix least-squares techniques. Crystal data for **2** are summarized in Table 5, and selected bond distances and angles are listed in Table 6. Positional and equivalent isotropic thermal parameters are presented in Table 7. Figure 2 gives an ORTEP drawing of this molecule.

Structure Determination of CpRu(p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Cl (3). A rectangular orange plate, grown by slow evaporation of a saturated THF solution, having approximate dimensions 0.46  $\times$  0.40  $\times$  0.22 mm was selected and mounted on the end of a glass fiber in a random orientation. This selected crystal was mounted on an Enraf-Nonius CAD4 diffractometer, and data were collected using Mo K $\alpha$  radiation at 100 K under a stream of cold nitrogen gas. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with 42° < 2 $\theta$  < 55°. The structure was solved using direct methods (MULTAN80) and refined by full-matrix

Table 5. Summary of Crystallographic Data for  $Cp^*Ru(P(p-CF_3C_6H_4)_3)_2Cl\cdot 0.5C_2H_5OH(2)$ 

| 1 1 0 0                            |  |
|------------------------------------|--|
| empirical formula                  | $C_{52}H_{39}ClF_{18}P_{2}Ru {\boldsymbol{\cdot}} 0.5C_{2}H_{5}OH$ |
| space group                        | 14   |
| unit cell dimens                   |  |
| a, Å                               | <b>26.333</b> (14)   |
| c, Å                               | 17.337(9)  |
| $V, \dot{A}^3$                     | 12022 (18)   |
| Z, molecule/cell                   | 8  |
| density (calcd), g/cm <sup>3</sup> | 1.360  |
| $\mu$ (Mo), cm <sup>-1</sup>       | 4.38   |
| wavelength, Å                      | 0.710 73   |
| monochromator                      | highly ordered graphite crystal                                    |
| temp, K                            | 100(2)   |
| abs cor                            | empirical ( $\psi$ -scan method)                                   |
| diffractometer                     | Enraf-Nonius CAD 4   |
| scan type                          | $\theta - 2\theta$   |
| data collected                     | $0 \le h \le 25, 0 \le k \le 25,$                                  |
|                                    | $0 \leq l \leq 16$   |
| $2\theta$ range, deg               | 4.0-40.0   |
| no. of collected rfins             | 3097   |
| no. of obsd rflns                  | 3074   |
| $R_F$ (obsd data), %               | 7.9  |
| $R_{\mathrm{w}F}, \%$              | 10.2   |
| goodness of fit                    | 3.25   |
| no. of variables                   | 650  |
| residual density, e/Å <sup>3</sup> |  |
| max                                | 1.01(5)  |
| min                                | -1.20(5)   |
|                                    |  |

## Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for Cp\*Ru(P(p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>Cl (2)

| Bond Lengths <sup>a</sup> |                 |                               |                 |  |  |  |
|---------------------------|-----------------|-------------------------------|-----------------|--|--|--|
| Ru-Cl                     | 2.439(5)        | $\mathbf{Ru} - \mathbf{C}(4)$ | 2.20(2)         |  |  |  |
| Ru-P(1)                   | 2.315(6)        | Ru-C(5)                       | 2.17(2)         |  |  |  |
| Ru-P(2)                   | 2.334(5)        | P(1) - C(11)                  | 1.82(2)         |  |  |  |
| Ru-C(1)                   | 2.21(2)         | P(1) - C(17)                  | 1.86(2)         |  |  |  |
| Ru-C(2)                   | 2.19(3)         | P(1) - C(23)                  | 1.79(2)         |  |  |  |
| Ru-C(3)                   | 2.27(2)         | P(2) - C(29)                  | 1.83(2)         |  |  |  |
| Ru-Cp(cen)                | 1.890(11)       | P(2) - C(35)                  | 1.80(2)         |  |  |  |
| Cp C - C(av)              | 1.35 (2)        | P(2) - C(41)                  | 1.70(2)         |  |  |  |
|                           | Bond            | $Angles^a$                    |                 |  |  |  |
| Cl-Ru-P(1)                | 92.3(2)         | P(2)-Ru-C(2)                  | 112.6(7)        |  |  |  |
| Cl-Ru-P(2)                | 91.3(2)         | P(2) - Ru - C(3)              | 144.9(6)        |  |  |  |
| Cl-Ru-C(1)                | 127.9(11)       | P(2) - Ru - C(4)              | 150.6(5)        |  |  |  |
| Cl-Ru-C(2)                | 148.1(6)        | P(2) - Ru - C(5)              | 111.5(5)        |  |  |  |
| Cl-Ru-C(3)                | 120.7(6)        | C(11) - P(1) - C(23)          | <b>93.9(9</b> ) |  |  |  |
| Cl-Ru-C(4)                | 88.8(5)         | C(11) - P(1) - C(17)          | 105.8(9)        |  |  |  |
| Cl-Ru-C(5)                | 90.7(5)         | C(23) - P(1) - C(17)          | 102.6(9)        |  |  |  |
| P(1) - Ru - P(2)          | <b>93.8</b> (2) | C(29) - P(2) - C(35)          | 102.7(10)       |  |  |  |
| P(1) - Ru - C(1)          | 138.0(12)       | C(29) - P(2) - C(41)          | 101.9(10)       |  |  |  |
| P(1) - Ru - C(2)          | 106.3(5)        | C(35) - P(2) - C(41)          | <b>96.7(9</b> ) |  |  |  |
| P(1)-Ru-C(3)              | <b>98.5</b> (5) | Cl-Ru-Cp(cen)                 | 117.5(3)        |  |  |  |
| P(1) - Ru - C(4)          | 115.6(5)        | P(1)-Ru-Cp(cen)               | 125.6(3)        |  |  |  |
| P(1) - Ru - C(5)          | 115.6(5)        | P(2)-Ru-Cp(cen)               | 125.8(3)        |  |  |  |
| P(2) - Ru - C(1)          | 96.7(7)         | _                             |                 |  |  |  |

 $^{\boldsymbol{a}}$  Numbers in parentheses are the estimated standard deviations.

least-squares techniques. Crystal data for 3 are summarized in Table 8, and selected bond distances and angles are listed in Table 9. Positional and equivalent isotropic thermal parameters are presented in Table 10. Figure 3 gives an ORTEP drawing of this molecule.

### Results

A facile entryway into the thermochemistry of CpRu-(PR<sub>3</sub>)<sub>2</sub>Cl complexes is made possible by the rapid and quantitative reaction of CpRu(COD)Cl (1) with a variety of phosphine ligands.<sup>7e</sup>

This type of phosphine binding reaction appears to be general and was found to be rapid and quantitative for all ligands calorimetrically investigated at 30.0 °C in tetrahydrofuran. A similar trend has previously been

Table 7. Fractional Coordinates ( $\times 10\ 000$ ) and Isotropic Thermal Parameters for Cp\*Ru(P(p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>Cl (2)<sup>a</sup>

|                 |            |            | <b>_</b>   | 1 0                 | 0 I.G.A |           |           |           |                     |
|-----------------|------------|------------|------------|---------------------|---------|-----------|-----------|-----------|---------------------|
| atom            | x          | у          | z          | B (Å <sup>2</sup> ) | atom    | x         | у         | z         | B (Å <sup>2</sup> ) |
| Ru              | 0.33946(9) | 0.29444(8) | 0.2206(1)  | 1.80(4)             | C(18)   | 0.3326(9) | 0.4499(8) | 0.259(2)  | 2.2(7)              |
| Cl              | 0.2850(3)  | 0.2355(3)  | 0.1503(4)  | 2.8(2)              | C(19)   | 0.338(1)  | 0.485(1)  | 0.316(2)  | 3.9(8)              |
| P(1)            | 0.2850(3)  | 0.3618(3)  | 0.1982(4)  | 2.5(2)              | C(20)   | 0.303(1)  | 0.489(1)  | 0.376(2)  | 4.7(8)              |
| P(2)            | 0.3012(3)  | 0.2726(3)  | 0.3374(4)  | 1.9(2)              | C(21)   | 0.263(1)  | 0.457(1)  | 0.378(2)  | 2.5(7)              |
| $\mathbf{F}(1)$ | 0.3464(9)  | 0.4570(8)  | -0.152(1)  | 8.0(6)              | C(22)   | 0.2575(9) | 0.4222(9) | 0.324(2)  | 1.7(6)              |
| F(2)            | 0.2915(9)  | 0.4057(6)  | -0.1855(9) | 5.8(5)              | C(23)   | 0.2172(9) | 0.358(1)  | 0.190(1)  | 1.8(6)              |
| F(3)            | 0.273(1)   | 0.4744(9)  | -0.149(1)  | 11.0(9)             | C(24)   | 0.187(1)  | 0.314(1)  | 0.180(2)  | 3.4(8)              |
| <b>F</b> (4)    | 0.2946(9)  | 0.5786(8)  | 0.408(2)   | 9.2(7)              | C(25)   | 0.135(1)  | 0.318(1)  | 0.171(1)  | 2.7(7)              |
| F(5)            | 0.361(1)   | 0.5396(8)  | 0.458(1)   | 10.9(7)             | C(26)   | 0.1075(8) | 0.362(1)  | 0.171(2)  | 4.3(8)              |
| F(6)            | 0.284(1)   | 0.5258(9)  | 0.494(1)   | <b>15.1(9</b> )     | C(27)   | 0.138(1)  | 0.410(1)  | 0.180(2)  | 4.5(8)              |
| $\mathbf{F}(7)$ | 0.0344(8)  | 0.406(1)   | 0.141(2)   | 12(1)               | C(28)   | 0.187(1)  | 0.404(1)  | 0.187(2)  | 3.9(8)              |
| F(8)            | 0.0309(8)  | 0.359(1)   | 0.226(2)   | <b>16</b> (1)       | C(29)   | 0.3131(9) | 0.3124(8) | 0.421(2)  | 2.9(7)              |
| <b>F</b> (9)    | 0.0377(8)  | 0.333(1)   | 0.114(2)   | 14(1)               | C(30)   | 0.2888(9) | 0.304(1)  | 0.496(2)  | 1.5(6)              |
| F(10)           | 0.378(1)   | 0.4502(8)  | 0.594(1)   | 8.7(7)              | C(31)   | 0.295(1)  | 0.334(1)  | 0.554(2)  | 4.0(8)              |
| F(11)           | 0.3036(9)  | 0.4312(9)  | 0.638(1)   | 9.7(7)              | C(32)   | 0.332(1)  | 0.373(1)  | 0.545(2)  | <b>4.9</b> (8)      |
| F(12)           | 0.3658(9)  | 0.3872(7)  | 0.669(1)   | 7.5(6)              | C(33)   | 0.356(1)  | 0.386(1)  | 0.475(2)  | 5.4(8)              |
| F(13)           | 0.402(1)   | 0.0564(7)  | 0.485(2)   | 11.0(8)             | C(34)   | 0.344(1)  | 0.350(1)  | 0.413(2)  | 4.0(8)              |
| F(14)           | 0.370(1)   | 0.0231(8)  | 0.385(1)   | 9.7(7)              | C(35    | 0.318(1)  | 0.2104(9) | 0.371(1)  | 2.5(6)              |
| F(15)           | 0.332(1)   | 0.0335(9)  | 0.477(2)   | <b>13.1(9</b> )     | C(36    | 0.319(1)  | 0.1687(9) | 0.319(2)  | 1.9(6)              |
| F(16)           | 0.0579(6)  | 0.2008(7)  | 0.374(1)   | 5.9(5)              | C(37    | 0.334(1)  | 0.121(1)  | 0.337(2)  | 2.7(7)              |
| F(17)           | 0.0511(6)  | 0.2427(9)  | 0.274(1)   | 7.9(6)              | C(38    | 0.349(1)  | 0.111(1)  | 0.414(2)  | 3.6(8)              |
| F(18)           | 0.0462(8)  | 0.278(1)   | 0.381(1)   | 8.5(7)              | C(39    | 0.347(1)  | 0.159(2)  | 0.462(2)  | 9(1)                |
| C(1)            | 0.4188(9)  | 0.283(2)   | 0.258(1)   | 7(1)                | C(40)   | 0.331(1)  | 0.200(1)  | 0.434(2)  | 5.3(9)              |
| C(2)            | 0.415(1)   | 0.3274(9)  | 0.236(1)   | 3.4(7)              | C(41)   | 0.237(1)  | 0.2644(9) | 0.342(2)  | 3.0(7)              |
| C(3)            | 0.410(1)   | 0.3270(9)  | 0.165(2)   | <b>2.4</b> (6)      | C(42)   | 0.210(1)  | 0.224(1)  | 0.307(2)  | 3.9(8)              |
| C(4)            | 0.398(1)   | 0.2825(8)  | 0.133(2)   | 2.1(7)              | C(43)   | 0.157(1)  | 0.220(1)  | 0.305(1)  | 2.5(6)              |
| C(5)            | 0.405(1)   | 0.247(1)   | 0.197(1)   | 2.8(7)              | C(44)   | 0.1287(8) | 0.252(1)  | 0.341(1)  | 2.9(7)              |
| C(6)            | 0.434(1)   | 0.257(1)   | 0.323(2)   | 9.9(9)              | C(45)   | 0.151(1)  | 0.2942(9) | 0.376(1)  | 3.3(8)              |
| C(7)            | 0.443(1)   | 0.366(1)   | 0.284(2)   | 4.5(7)              | C(46)   | 0.203(1)  | 0.301(1)  | 0.371(2)  | 3.5(8)              |
| C(8)            | 0.413(1)   | 0.378(1)   | 0.108(2)   | <b>4.9(9</b> )      | C(47)   | 0.301(1)  | 0.436(1)  | -0.131(2) | 3.7(8)              |
| C(9)            | 0.391(1)   | 0.269(1)   | 0.050(3)   | 10(1)               | C(48)   | 0.308(2)  | 0.537(1)  | 0.433(3)  | 7(1)                |
| C(10)           | 0.406(1)   | 0.189(1)   | 0.187(2)   | 3.9(8)              | C(49)   | 0.061(2)  | 0.367(2)  | 0.171(3)  | 7(1)                |
| C(11)           | 0.293(1)   | 0.387(1)   | 0.101(1)   | 2.1(6)              | C(50)   | 0.343(1)  | 0.410(1)  | 0.607(2)  | 3.1(7)              |
| C(12)           | 0.287(1)   | 0.3514(9)  | 0.042(1)   | 1.7(6)              | C(51)   | 0.362(1)  | 0.054(1)  | 0.436(2)  | <b>4.9(9</b> )      |
| C(13)           | 0.292(1)   | 0.371(1)   | -0.032(2)  | 3.1(7)              | C(52)   | 0.083(2)  | 0.248(2)  | 0.342(3)  | 10(2)               |
| C(14)           | 0.298(1)   | 0.423(1)   | -0.052(2)  | 3.2(7)              | C(201)  | 0.137(3)  | 0.418(3)  | 0.458(4)  | 9(2)*               |
| C(15)           | 0.302(1)   | 0.4535(9)  | 0.005(2)   | 2.8(7)              | C(202)  | 0.158(1)  | 0.410(1)  | 0.509(2)  | $1.7(8)^*$          |
| C(16)           | 0.298(1)   | 0.4401(9)  | 0.086(2)   | 2.3(7)              | C(203)  | 0.1426    | 0.4262    | 0.5747    | 4(1)                |
| C(17)           | 0.294(1)   | 0.417(1)   | 0.265(2)   | 3.0(7)              |         |           |           |           | • •                 |

<sup>a</sup> Numbers in parentheses are the estimated standard deviations. <sup>b</sup> Starred values denote atoms refined isotropically.

observed for the Cp\*Ru(COD)Cl complex.<sup>7b</sup> A compilation of phosphine ligands with their respective enthalpies of reaction where all species are in solution is presented in Table 1.

Single-crystal structural studies were carried out on the three new complexes Cp\*Ru(COD)Cl(1),  $Cp*Ru(P(p-CF_3C_6H_4)_2Cl(2)$ , and  $CpRu(p-CF_3C_6H_4)_2Cl(3)$ . Tables 2-10 give crystallographic data and important bond distances and angles as well as positional parameters. ORTEP drawings of the three complexes are presented in Figures 1-3.

#### Discussion

The relative importance of steric vs electronic ligand effects has been the subject of numerous studies, and it has not been until fairly recently that clear stereoelectronic pictures have emerged from organometallic studies. We have taken the approach of gauging the relative importance of such effects based on ligand properties and metal-ligand reaction enthalpies. We judged this approach useful in view of a "common sense" understanding that strong metal-ligand interactions will result from strong electron donation from the ligand and minimal steric interaction (repulsion) with metalancillary ligation. This approach has been used in an iron-based system to clearly illustrate the overwhelming importance of electronic ligand effects. Enthalpies of



**Figure 2.** ORTEP of  $Cp*Ru(P(p-CF_3C_6H_4)_3)_2Cl$  (2) with ellipsoids drawn in at the 50% probability level.

reaction span some 8 kcal/mol in the iron system and correlate very well with electronic parameter variation.<sup>8c</sup>

The present study clearly indicates an important lack of sensitivity associated with the enthalpies of ligand substitution reactions as a function of electronic variation (note here that the experimental approach and ligand selection maintain the phosphine cone angle constant at 145°). The measured enthalpies of reaction listed in Table 1 are fairly constant; some are the same within experimental error. This trend is valid for both systems (Cp' = Cp and Cp\*) investigated. We take

| Table 8.                  | Summary of   | f Crystal               | lographic   | Data for |
|---------------------------|--|-------------------------|-------------|----------|
| $\mathbf{C}_{\mathbf{I}}$ | $\mathbf{pRu}(\mathbf{P}(\mathbf{p} \cdot \mathbf{CF}_3))$ | $C_{6}H_{4})_{3})_{2}C$ | 21·0.5THF ( | (3)      |

| empirical formula                  | $C_{47}H_{29}F_{18}P_2ClRu \cdot 0.5 C_4H_8O$ |
|------------------------------------|---|
| space group                        | $P2_1/n$                                      |
| unit cell dimens                   |   |
| a, Å                               | 13.613(2)                                     |
| b, Å                               | 16.895(4)                                     |
| c, Å                               | 21.997(2)                                     |
| α, deg                             | 90  |
| $\beta$ , deg                      | 101.96 (2)                                    |
| $\gamma$ , deg                     | 90  |
| V, Å <sup>3</sup>                  | 4949 (3)                                      |
| Z, molecule/cell                   | 4   |
| density (calcd), g/cm <sup>3</sup> | 1.570   |
| $\mu(Mo), cm^{-1}$                 | 5.281   |
| wavelength, Å                      | 0.710 73                                      |
| monochromator                      | highly ordered graphite cryst                 |
| temp, K                            | 100(2)  |
| abs cor                            | empirical ( $\psi$ -scan method)              |
| diffractometer                     | Enraf-Nonius CAD 4                            |
| scan type                          | $\theta - 2\theta$                            |
| data collected                     | $0 \le h \le 16, 0 \le k \le 20,$             |
|                                    | $-26 \leq l \leq 25$                          |
| $2\theta$ range, deg               | 4.0 - 50.0                                    |
| no. of collected rflns             | 9041  |
| no. of obsd rfins                  | 7376  |
| $R_F$ (obsd data), %               | 5.8   |
| $R_{wF}, \%$                       | 9.4   |
| goodness of fit                    | 3.84  |
| no. of variables                   | 642   |
| residual density, e/Å <sup>3</sup> |   |
| max                                | 0.52(5)                                       |
| min                                | -0.99(5)                                      |
|                                    |   |

these similar trends to indicate that electronic ligand effects only play a minor role in dictating the magnitude of the reaction enthalpy.<sup>23</sup> We have previously explained relative stability trends for monodentate and bidentate ligands in both these systems as being primarily directed by ligand steric effects. The present study and observed trends clearly demonstrate that steric factors must be the overwhelming component influencing the magnitude of the reaction enthalpy. If a relationship is established between phosphine cone angle (steric factor) and enthalpy of reaction, good linear correlations are established for both systems investigated (Figures 4 and 5).

These relationships are surprisingly good, considering that they only account for the influence of one of the two ligand factors. Similar correlation can be established, with poorer correlation coefficients (R = 0.95 for Cp\* data and R = 0.90 for Cp data; treatment included all phosphine ligands but excluded phosphites), between enthalpy of reaction data and Brown's steric  $E_R$  parameter values.<sup>2e</sup> Brown points out that these  $E_R$  values are system-dependent and this might account for the poor fit of the ruthenium data to the corresponding steric parameters.<sup>2e</sup>

Enthalpy data within a system (Table 1) are essentially constant. When the Cp and Cp\* values are now compared, a variation in reaction enthalpy favoring the Cp-based system is observed. This has also been observed in our previous studies, and a graphical representation is given in Figure 6, which includes all ligands investigated thus far.

The only notable variation in Table 1 is observed in the  $PPh_3$  cases, where the enthalpies of reaction indicate

| Table 9. | Selected  | Bond | Distances               | (Å) and  | Bond  |
|----------|-----------|------|-------------------------|----------|-------|
| Angles   | (deg) for | CpRı | ı(P(p-CF <sub>3</sub> C | 6H4)3)2C | l (3) |

| Bond Lengths <sup>a</sup> |                 |                        |           |  |  |  |
|---------------------------|-----------------|------------------------|-----------|--|--|--|
| Ru-Cl                     | 2.4294(6)       | P(1) - C(15)           | 1.844(3)  |  |  |  |
| Ru-P(1)                   | 2.3087(7)       | P(2) - C(21)           | 1.847(3)  |  |  |  |
| Ru-P(2)                   | 2.3102(6)       | P(2) - C(23)           | 1.840(3)  |  |  |  |
| P(2) - C(25)              | 1.845(6)        | C(11) - C(12)          | 1.524(6)  |  |  |  |
| C(13) - C(14)             | 1.529(4)        | C(15) - C(16)          | 1.515(5)  |  |  |  |
| C(21)-C(22)               | 1.515(5)        | P(1) - C(11)           | 1.848(4)  |  |  |  |
| C(23) - C(24)             | 1.524(5)        | P(1) - C(13)           | 1.839(3)  |  |  |  |
| C(25) - C(26)             | 1.522(5)        | Ru-Cp(cen)             | 1.890(2)  |  |  |  |
| Dand Angles(              |                 |                        |           |  |  |  |
| $C_{1}$ $D_{11}$ $D_{11}$ | 00 49(9)        | $D(0)$ $D_{10}$ $C(4)$ | 100 4(1)  |  |  |  |
| $O_{I} = R_{I} = P(1)$    | 90.43(3)        | F(2) = Ru = C(4)       | 120.4(1)  |  |  |  |
| CI-Ru-P(2)                | 90.50(3)        | P(2) - Ru - C(5)       | 158.6(1)  |  |  |  |
| P(1)-Ru-P(2)              | 94.71(3)        | Ru - P(1) - C(11)      | 120.5(1)  |  |  |  |
| Ru - P(1) - C(13)         | 117.6(1)        | Ru - P(1) - C(15)      | 111.8(1)  |  |  |  |
| Ru - P(2) - C(21)         | 120.9(1)        | Ru - P(2) - C(23)      | 118.1(1)  |  |  |  |
| Ru - P(2) - C(25)         | 112.2(1)        | C(11) - P(1) - C(13)   | 100.8(2)  |  |  |  |
| C(11) - P(1) - C(15)      | 100.3(2)        | P(1)-C(11)-C(12)       | 116.5(3)  |  |  |  |
| C(13) - P(1) - C(15)      | 103.2(2)        | P(1)-C(13)-C(14)       | 117.6(2)  |  |  |  |
| C(21) - P(2) - C(23)      | 100.9(2)        | P(1) - C(15) - C(16)   | 115.4(3)  |  |  |  |
| C(21) - P(2) - C(25)      | <b>99.5</b> (2) | P(2)-C(21)-C(22)       | 115.5(3)  |  |  |  |
| C(23) - P(2) - C(25)      | 102.2(2)        | P(2)-C(23)-C(24)       | 117.3(3)  |  |  |  |
| P(2) - C(25) - C(26)      | 114.6(2)        | P(1)-Ru-Cp(cen)        | 125.00(5) |  |  |  |
| P(2)-Ru-Cp(cen)           | 124.59(5)       | Cl-Ru-Cp(cen)          | 115.98(5) |  |  |  |
| -                         |                 | -                      |           |  |  |  |

 $^{\alpha}$  Numbers in parentheses are the estimated standard deviations.

a weaker  $Ru-PPh_3$  bond energy. These measurements have been repeated a number of times, and the reported enthalpy data represent a real difference from the isosteric relatives. The exact reason for this lower  $Ru-PR_3$  BDE for PPh<sub>3</sub> is currently under investigation. Since Cp is less electron donating than Cp<sup>\*</sup>,<sup>4a</sup> the Cp system will be able to accommodate greater electron density from the incoming two-electron donor (higher electrophilicity), therefore leading to more exothermic enthalpies of ligand substitution.

A difference between enthalpies of reaction between the two reactions  $(2.3 \pm 0.3 \text{ kcal/mol})$  is reminiscent of our earlier work comparing these two systems.<sup>7e</sup> This difference in electronic properties at the metal center gauges a change in metal basicity. Sowa and Angelici have investigated a series of iridium complexes and have observed a difference in enthalpies of protonation of 5.7 kcal/mol between CpIr(COD) and Cp\*Ir(COD) complexes.<sup>24</sup> In these experiments,  $H^+$  proved to be more strongly bound to  $M-Cp^*$  by ca. 5 kcal/mol. This is in view of the increased electron density imparted by the better Cp\* donor. In the present ruthenium systems electron-donating phosphine groups are more strongly bound in the CpRu system. Both sets of experiments, although using different approaches, relate information concerning the same fundamental characteristics, namely metal basicity. Hoff and co-workers have first demonstrated this difference in metal basicity between Cp and Cp\* in their thermochemical investigations of organomolybdenum complexes.<sup>16</sup>

The enthalpy difference between ligand substitution reactions, -2.3 kcal/mol, reflects the difference in metal basicity accompanying a change of the ancillary ligation. This difference is of the same order of magnitude as Angelici's enthalpies of protonation and the average difference in enthalpy of ligand substitution in the Cp versus Cp\* organoruthenium systems.

A single-crystal diffraction study was carried out on the synthetic precursor to the  $Cp*Ru(PR_3)_2Cl$  complexes.

<sup>(23)</sup> Another possible explanation, which cannot be discounted at this point, is the involvement of phosphine  $\pi$ -acid character, which could also explain for the lack of enthalpy variation associated with electronic variations observed to be significant in the L<sub>2</sub>Fe(CO)<sub>3</sub> system.<sup>3c</sup>

<sup>(24) (</sup>a) Sowa, J. R., Jr.; Angelici, R. J. J. Am. Chem. Soc. **1991**, 113, 2537–2544. (b) Rottink, M. K.; Angelici, R. J. J. Am. Chem. Soc. **1993**, 115, 7267–7274.

Table 10. Fractional Coordinates (×10 000) and Isotropic Thermal Parameters for CpRu(P(p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sub>2</sub>Cl

| (3)*          |            |            |            |                     |       |           |            |            |                     |
|---------------|------------|------------|------------|---------------------|-------|-----------|------------|------------|---------------------|
| atom          | x          | У          | z          | B (Å <sup>2</sup> ) | atom  | x         | у          | z          | B (Å <sup>2</sup> ) |
| Ru            | 0.93656(3) | 0.36846(2) | 0.30539(2) | 1.784(7)            | C(15) | 1.0534(4) | 0.0298(3)  | 0.2718(3)  | 3.2(1)              |
| Cl            | 0.77860(8) | 0.43950(7) | 0.29374(5) | 2.50(2)             | C(16) | 1.0958(4) | 0.1031(3)  | 0.2873(3)  | 3.0(1)              |
| P(1)          | 0.94966(9) | 0.38086(7) | 0.20285(5) | 2.04(2)             | C(17) | 1.0360(3) | 0.1678(3)  | 0.2923(2)  | 2.34(9)             |
| P(2)          | 0.85659(8) | 0.24714(6) | 0.29306(5) | 1.74(2)             | C(18) | 0.8053(3) | 0.2174(3)  | 0.3608(2)  | 2.12(8)             |
| <b>F</b> (1)  | 0.4594(3)  | 0.1496(2)  | 0.0662(2)  | 4.64(8)             | C(19) | 0.8072(4) | 0.1399(3)  | 0.3827(3)  | 3.8(1)              |
| <b>F</b> (2)  | 0.5132(3)  | 0.2520(3)  | 0.0265(2)  | 6.8(1)              | C(20) | 0.7614(5) | 0.1206(3)  | 0.4314(3)  | 4.2(1)              |
| F(3)          | 0.4111(3)  | 0.2636(2)  | 0.0881(2)  | <b>6.6(1</b> )      | C(21) | 0.7132(4) | 0.1754(3)  | 0.4593(2)  | 3.0(1)              |
| <b>F</b> (4)  | 1.2094(3)  | -0.0273(2) | 0.2701(4)  | 11.6(2)             | C(22) | 0.7121(5) | 0.2538(3)  | 0.4393(2)  | 3.7(1)              |
| <b>F</b> (5)  | 1.1128(4)  | -0.0933(3) | 0.3111(3)  | 11.7(2)             | C(23) | 0.7588(4) | 0.2734(3)  | 0.3909(2)  | 3.2(1)              |
| <b>F</b> (6)  | 1.0858(4)  | -0.0847(3) | 0.2194(3)  | 14.3(2)             | C(24) | 1.0373(4) | 0.3088(3)  | 0.1813(2)  | 2.55(9)             |
| F(7)          | 0.6012(3)  | 0.0912(3)  | 0.4951(2)  | 7.5(1)              | C(25) | 1.0031(4) | 0.2415(3)  | 0.1477(3)  | 3.3(1)              |
| F(8)          | 0.7269(4)  | 0.1298(3)  | 0.5610(2)  | 7.8(1)              | C(26) | 1.0706(5) | 0.1836(3)  | 0.1372(3)  | 4.1(1)              |
| <b>F</b> (9)  | 0.6084(3)  | 0.2085(3)  | 0.5284(2)  | 7.2(1)              | C(27) | 1.1731(4) | 0.1938(3)  | 0.1609(3)  | 4.6(1)              |
| <b>F</b> (10) | 1.3362(4)  | 0.1405(3)  | 0.1788(2)  | 10.1(1)             | C(28) | 1.2070(4) | 0.2594(3)  | 0.1942(3)  | 4.0(1)              |
| <b>F</b> (11) | 1.2500(3)  | 0.1298(3)  | 0.0880(2)  | 7.1(1)              | C(29) | 1.1396(4) | 0.3166(3)  | 0.2041(3)  | 3.3(1)              |
| F(12)         | 1.2123(4)  | 0.0592(3)  | 0.1554(3)  | 16.2(2)             | C(30) | 0.8451(4) | 0.3814(3)  | 0.1341(2)  | 2.34(9)             |
| <b>F</b> (13) | 0.6074(6)  | 0.3524(3)  | -0.0665(2) | 11.6(2)             | C(31) | 0.7477(4) | 0.3978(3)  | 0.1406(2)  | 2.6(1)              |
| F(14)         | 0.6267(5)  | 0.4765(3)  | -0.0576(2) | 10.1(1)             | C(32) | 0.6706(5) | 0.4080(3)  | 0.0890(3)  | 3.7(1)              |
| F(15)         | 0.5191(4)  | 0.4182(3)  | -0.0154(2) | 10.6(1)             | C(33) | 0.6907(6) | 0.4001(3)  | 0.0307(3)  | 4.7(1)              |
| F(16)         | 1.0538(4)  | 0.7650(2)  | 0.1644(3)  | 10.7(1)             | C(34) | 0.7876(7) | 0.3822(4)  | 0.0228(3)  | 5.8(2)              |
| F(17)         | 1.0671(5)  | 0.7224(2)  | 0.0800(2)  | 10.4(2)             | C(35) | 0.8655(5) | 0.3752(4)  | 0.0747(3)  | 4.4(1)              |
| F(18)         | 1.1880(3)  | 0.7180(2)  | 0.1524(3)  | 9.7(2)              | C(36) | 1.0005(3) | 0.4779(3)  | 0.1857(2)  | 2.39(9)             |
| O(1)          | 0.3518(5)  | 0.3900(4)  | 0.5669(3)  | 3.0(1)*             | C(37) | 0.9618(4) | 0.5449(3)  | 0.2074(2)  | 2.7(1)              |
| C(1)          | 1.0773(4)  | 0.4381(3)  | 0.3407(3)  | 3.5(1)              | C(38) | 0.9907(4) | 0.6200(3)  | 0.1921(2)  | 2.9(1)              |
| C(2)          | 1.0961(4)  | 0.3561(3)  | 0.3516(3)  | 3.4(1)              | C(39) | 1.0589(4) | 0.6271(3)  | 0.1550(3)  | 3.4(1)              |
| C(3)          | 1.0351(4)  | 0.3319(3)  | 0.3934(3)  | 3.5(1)              | C(40) | 1.0998(4) | 0.5618(3)  | 0.1336(3)  | <b>4.9</b> (1)      |
| C(4)          | 0.9758(5)  | 0.3968(4)  | 0.4052(2)  | 3.8(1)              | C(41) | 1.0690(4) | 0.4869(3)  | 0.1469(3)  | 3.8(1)              |
| C(5)          | 1.0028(5)  | 0.4625(3)  | 0.3721(3)  | 3.8(1)              | C(42) | 0.4902(4) | 0.2241(3)  | 0.0791(3)  | <b>3.9</b> (1)      |
| C(6)          | 0.7438(3)  | 0.2352(2)  | 0.2304(2)  | 1.90(8)             | C(43) | 1.1164(5) | -0.0423(3) | 0.2658(4)  | 6.0(2)              |
| C(7)          | 0.6531(3)  | 0.2671(3)  | 0.2361(2)  | <b>2.19(9</b> )     | C(44) | 0.6631(5) | 0.1512(4)  | 0.5100(2)  | 4.1(1)              |
| C(8)          | 0.5708(3)  | 0.2647(3)  | 0.1885(2)  | 2.6(1)              | C(45) | 1.2437(6) | 0.1292(4)  | 0.1467(4)  | 6.7(2)              |
| C(9)          | 0.5784(4)  | 0.2281(3)  | 0.1327(2)  | 2.8(1)              | C(46) | 0.6108(8) | 0.4118(4)  | -0.0268(3) | 8.3(2)              |
| C(10)         | 0.6693(4)  | 0.1953(3)  | 0.1262(2)  | 2.9(1)              | C(47) | 1.0925(5) | 0.7077(3)  | 0.1392(3)  | 4.3(1)              |
| C(11)         | 0.7501(4)  | 0.1997(3)  | 0.1751(2)  | 2.7(1)              | C(48) | 0.338(1)  | 0.3768(9)  | 0.5059(7)  | 5.5(3)*             |
| C(12)         | 0.9320(3)  | 0.1599(3)  | 0.2816(2)  | 2.08(8)             | C(49) | 0.294(2)  | 0.441(2)   | 0.486(1)   | $14.7(11)^*$        |
| C(13)         | 0.8885(4)  | 0.0868(3)  | 0.2651(3)  | 2.8(1)              | C(50) | 0.276(2)  | 0.492(2)   | 0.526(1)   | $11.3(7)^*$         |
| C(14)         | 0.9494(4)  | 0.0217(3)  | 0.2596(3)  | 3.4(1)              | C(51) | 0.338(1)  | 0.4711(9)  | 0.5731(6)  | 5.1(3)*             |

<sup>a</sup> Numbers in parentheses are the estimated standard deviations. <sup>b</sup> Starred values denote atoms refined isotropically.



Figure 3. ORTEP of  $CpRu(P(p-CF_3C_6H_4)_3)_2Cl$  (3) with ellipsoids drawn in at the 50% probability level.

The ORTEP of complex 1 (Figure 1) shows Cp\*Ru-(COD)Cl to have the cyclooctadiene ligand in a boat conformation, characteristic of other metal-COD complexes.<sup>4</sup> Important bond distances in 1 are listed in Table 3 and include Ru-Cp\*(centroid) = 2.241(2) Å and Ru-Cl = 2.472(2) Å.

In an effort to structurally compare the Cp and Cp<sup>\*</sup> systems, single crystals of two complexes bearing the same phosphine ligands were grown. Complexes 2 and 3 were investigated by single-crystal diffraction studies, results of which are presented in Tables 5–10. Complexes 2 and 3 have the same Ru-Cp(centroid) bond distance (1.890 Å), and their respective Ru-Cl bond distances are 2.439(5) and 2.4294(9) Å, a difference of



**Figure 4.** Phosphine cone angle vs enthalpy of reaction for a series of tertiary phosphine ligands in the Cp\*Ru- $(PR_3)_2Cl$  system (slope -2.11; R = 0.96).

0.01 Å. The most important difference between the two structures resides in the Ru-P bond distances; for 2, Ru-P distances are 2.315(6) and 2.334 (5) Å, respectively. These values can be compared to the Ru-P distances in 3, 2.3087(7) and 2.3102(6) Å. The average Ru-P distance is 0.015 Å shorter in 2 than in 3. The observed shortening of bonds in structure 3 supports the previously mentioned assumption that stronger bonds should exist in the CpRu(PR<sub>3</sub>)<sub>2</sub>Cl system in comparison to those in their Cp\* analogs.<sup>7e</sup>

Furthermore, a single-crystal diffraction study of 3 was undertaken in order to add to the number of known



Figure 5. Phosphine cone angle vs enthalpy of reaction for a series of tertiary phosphine ligands in the CpRu(PR<sub>3</sub>)<sub>2</sub>-Cl system (slope -1.80; R = 0.95).



Figure 6. Enthalpies of reaction for CpRu(PR<sub>3</sub>)<sub>2</sub>Cl and  $Cp*Ru(PR_3)_2Cl$  systems as a function of phosphine ligand.

Cp-based metal-ligand bond distances. These fundamental data enable us to examine whether there in fact exists a bond strength/bond length relationship in this system. Five other  $CpRu(ER_3)_2Cl$  (ER<sub>3</sub> = AsEt<sub>3</sub>, PEt<sub>3</sub>,  $PMe_3$ ,  $P(OMe)_3$  and  $PPh_3$ ) complexes have previously been structurally characterized.<sup>25,26</sup> A comparison involving all six complexes in terms of bond distances (Table 11) suggests a linear relationship between bond enthalpy data and ruthenium-phosphine-arsine bond length information.<sup>27</sup> A graphic representation of the relationship is presented in Figure 7 and shows a good correlation (R = 0.89) to exist in this system.

Further structural studies are in progress in order to examine to what extent this relationship remains valid within these ruthenium systems.<sup>28</sup>

## Conclusion

The labile nature of the COD ligand in CpRu(COD)-Cl and Cp\*Ru(COD)Cl was used to gain access into the

Table 11. Selected Bond Distances (Å) and Enthalpies of Ligand Substitution (kcal/mol) for CpRu(ER<sub>3</sub>)<sub>2</sub>Cl Complexes

| $ER_3$                   | M-ER <sub>3</sub> | $-\Delta H$ |  |  |  |
|--------------------------|-------------------|-------------|--|--|--|
| P(OMe)3 <sup>a</sup>     | 2.217(3)          | 41.8(0.2)   |  |  |  |
| $\mathbf{PMe_{3}}^{b,c}$ | 2.28(1)           | 38.4(0.4)   |  |  |  |
| $\operatorname{PEt_3}^d$ | 2.304(1)          | 34.5(0.2)   |  |  |  |
| $P(p-CF_3C_6H_5)_3^e$    | 2.309(1)          | 24.4(0.2)   |  |  |  |
| $PPh_{3}^{b}$            | 2.336(1)          | 22.9(0.4)   |  |  |  |
| $\mathrm{AsEt}_{3^d}$    | 2.414(1)          | 19.4(0.2)   |  |  |  |
|                          |                   |             |  |  |  |

<sup>a</sup> See ref 25b. <sup>b</sup> See ref 24c. <sup>c</sup> Two independent molecules are found in this unit cell. <sup>d</sup> See ref 7e. <sup>e</sup> This work.



Figure 7. Average Ru-E bond distance vs enthalpy of ligand substitution reaction in the  $CpRu(PR_3)_2Cl$  complexes (E = As, P) (slope -0.006; R = 0.89).

thermochemistry of ligand substitution for para-substituted triphenylphosphine ligands. The enthalpy trend can be explained in terms of overwhelming steric contribution to the enthalpy of reaction. The increased exothermicity displayed by the CpRu(PR<sub>3</sub>)<sub>2</sub>Cl system over its Cp\* parent is taken as a gauge of the increased metal basicity on going from Cp to Cp\*. A quantitative relationship is established between structural and thermodynamic parameters and displays a good correlation. Three structural determinations have been carried out and show interesting metal-ligand bond length modulations with respect to ancillary ligand variation. Further thermochemical, kinetic, mechanistic, and catalytic investigations focusing on this and related systems are presently underway.

Acknowledgment. The Board of Regents of the Louisiana Education Quality Support Fund (Grant No. LEQSF(RF/1993-96)-RD-A-47) and the National Science Foundation (Grant No. CHE-9305492) are gratefully acknowledged for support of this research. M.E.C. acknowledges Du Pont for partial support through an Educational Aid Grant. We are also indebted to Aesar/ Johnson-Matthey for the generous loan of ruthenium salts.

Supporting Information Available: Tables of hydrogen atomic coordinates, selected bond distances and angles, and anisotropic thermal displacement parameters for 1-3 (42) pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

OM9504765

<sup>(25) (</sup>a) Treichel, P. M.; Komar, D. A. Synth. React. Inorg. Met.-Org. (20) (a) Ireichel, P. M.; Romar, D. A. Synth. React. thorg. Met.-Org.
Chem. 1980, 10, 205-210. (b) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. J. Chem. Soc., Dalton Trans. 1981, 1398-1405. (c)
Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. J. Chem. Soc., Dalton Trans. 1982, 2203-2207.
(26) (a) Treichel, P. M.; Komar, D. A. Synth. React. Inorg. Met.-Org.
Chem. 1984, 14, 383-400. (b) Bruce, M. I.; Cifuentes, M. P.; Snow, M. R.; Tiekink, R. T. J. Organomet. Chem. 1983, 379-399.
(27) Such a correlation in correct difference in program.

<sup>(27)</sup> Such a correlation is expected if no important variation in Ru- $L_n$  ( $L_n$  = ancillary ligand) bond distance or  $\hat{L}_n$ -Ru- $L_n$  bond angle is present in these complexes. Studies aimed at probing the extent and reasons for such a correlation to exist in the present system are currently underway.

<sup>(28)</sup> Luo, L.; Li, C.; Cucullu, M. E.; Mahler, C. H.; Fagan, P. J.; Jones, N.; Calabrese, J. C.; Nolan, S. P. Manuscript in preparation.