

Enthalpies of Reaction of Cp'Ru(COD)Cl (Cp' = C₅H₅, C₅Me₅; COD = Cyclooctadiene) with π -Acceptor Chelating Phosphine Ligands

Jinyu Shen, Edwin D. Stevens, and Steven P. Nolan^{*,†}

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

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The enthalpies of reaction of Cp'Ru(COD)Cl (Cp' = C₅H₅, C₅Me₅; COD = 1,5-cyclooctadiene) with a series of π -acceptor bidentate phosphines, leading to the formation of Cp'Ru(PP)Cl complexes, have been measured by anaerobic calorimetry in THF at 30 °C. These reactions are rapid and quantitative. Structural studies have been carried out on two complexes in this series. The overall relative order of stability established for these complexes in both Cp and Cp* systems is (PhO)₂PNMeNMeP(OPh)₂ > Ph₂PNMeNMeP Ph₂ \approx (C₄H₄N)₂PCH₂-CH₂P(NC₄H₄)₂ > ((EtO₂C)₂C₄H₂N)₂PCH₂CH₂P(NC₄H₂(CO₂ Et)₂)₂. Present thermochemical data are discussed in terms of the nature of the bonding involved in the present complexes.

Introduction

Chelating diphosphine ligands have been widely used in organometallic chemistry. Kinetic, catalytic, and structural studies have been performed on organometallic systems incorporating this type of ligand.¹ One dramatic example of the use of diphosphine ligands is illustrated in the different linear to branched product ratios obtained when monodentate versus bidentate phosphine ligands are bound to metals used to mediate the oxo process.² Recently, diphosphine compounds with weak σ -donor and strong π -acceptor character, e.g., fluoroalkylphosphine chelate (C₃F₇)₂PCH₂CH₂P(C₃F₇)₂,³ bisphosphanyl hydrazides R₂PN(Me)N(Me)PR₂,⁴ and *N*-pyrrolyl-substituted diphosphines,^{5,6} have attracted some attention, largely because of their potential use as ligands. Furthermore, it has been revealed that

higher selectivity is obtained in some catalytic systems modified with stronger π -acceptor and weak σ -donor ligands.⁷ With the development of the coordination chemistry of π -acceptor chelates, a study focusing on their binding to transition metals would improve the understanding of the reactivity and selectivity imparted by these ancillary ligands.

Solution calorimetric studies have been useful in providing insight into bonding and reactivity patterns^{8–10} and in directing the design of new metal-catalyzed transformations.¹¹ We have been involved in mapping out the thermochemical surface of organometallic systems bearing phosphine ligands. Researchers have been involved in describing metal–ligand systems in terms of steric and electronic contributions using a variety of methods. We have been interested in clarifying the exact partitioning of these effects in tertiary phosphine-based systems by means of solution calorimetry.^{12,13} We have already achieved this in part for some ruthenium-based organometallic systems (eqs 1 and 2).¹³

[†] E-mail: spncm@uno.edu.

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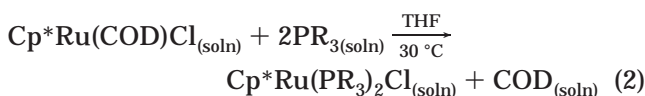
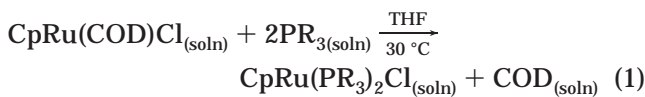
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Cp = C₅H₅; Cp* = C₅Me₅; PR₃ = tertiary phosphine

Recently, we have also studied the solution thermochemistry of reactions involving CpRu(COD)Cl and Cp*Ru(COD)Cl with some bidentate phosphine ligands.^{12c,13d} We now wish to expand on our solution thermochemical studies of organoruthenium complexes by focusing on quantitatively addressing the binding ability of a series of interesting π -acceptor diphosphine ligands to the CpRuCl and Cp*RuCl fragments and examine how these ligands compare to more classical chelating diphosphines.

Experimental Section

General Consideration. All manipulations involving organoruthenium complexes were performed under an inert atmosphere of argon or nitrogen using standard high-vacuum or Schlenk-tube techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. Tetrahydrofuran was stored over sodium wire, distilled from sodium benzophenone ketyl, stored over Na/K alloy, and vacuum transferred into flame-dried glassware prior to use. NMR spectra were recorded using either a Varian Gemini 300 or 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80), which was periodically calibrated using the TRIS reaction¹⁴ or the enthalpy of solution of KCl in water.¹⁵ The experimental enthalpies for these two standard reactions compare very closely to literature values. This calorimeter has been previously described,¹⁶ and typical procedures are described below. Only materials of high purity, as indicated by NMR spectroscopy, were used in the calorimetric experiments. Experimental enthalpy data are reported with 95% confidence limits. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

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Synthesis. CpRu(COD)Cl (**1**),¹⁷ Cp*Ru(COD)Cl (**2**),¹⁸ and all chelating diphosphines^{4,5d,6} were synthesized according to literature procedures. All new complexes synthesized were isolated using the procedure described for complex **3**.

CpRu(Ph₂PNMeNMePPh₂)Cl (3**).** A 50 mL Schlenk tube was charged with 62 mg (0.20 mmol) of CpRu(COD)Cl, 85 mg (0.20 mmol) of Ph₂PNMeNMePPh₂, and 2 mL of dry THF. After the mixture was stirred for 2 h at room temperature, the resulting yellow precipitate was collected on a glass frit, washed with hexane several times, and dried in a vacuum, giving a yield of 51 mg (40%). ¹H NMR (CD₂Cl₂): 2.75 (t, 6H, J_{HP} = 4.0 Hz, NMe), 4.37 (s, 5H, Cp), 7.05 (m, 4H, Ph), 7.18 (m, 8H, Ph), 7.34 (m, 4H, Ph), 7.87 (m, 4H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): 138.1. Anal. Calcd for C₃₁H₃₁ClN₂P₂Ru: C, 59.10; H, 4.96; N, 4.45. Found: C, 59.23; H, 4.87; N, 4.35.

CpRu(PhO)₂PNMeNMeP(OPh)₂Cl (4**).** **4** was isolated as a yellow microcrystalline solid in 82% yield. ¹H NMR (CD₂Cl₂): 3.09 (t, 6H, J_{HP} = 3.9 Hz, NMe), 4.25 (t, 5H, J_{HP} = 1.2 Hz, Cp), 7.15–7.45 (m, 20H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): 171.2. Anal. Calcd for C₃₁H₃₁ClN₂O₄P₂Ru: C, 53.65; H, 4.50; N, 4.04. Found: C, 53.28; H, 4.77; N, 3.95.

CpRu((C₄H₄N)₂PCH₂CH₂P(NC₄H₄)₂)Cl (5**).** **5** was isolated as a yellow microcrystalline solid in 75% yield. ¹H NMR (CD₂Cl₂): 2.90 (m, 4H, CH₂CH₂), 4.92 (s, 5H, Cp), 6.29 (s, 4H, NC₄H₄), 6.41 (s, 8H, NC₄H₄), 7.37 (s, 4H, NC₄H₄). ³¹P{¹H} NMR (CD₂Cl₂): 152.2. Anal. Calcd for C₂₃H₂₅ClN₄P₂Ru: C, 49.69; H, 4.53; N, 10.08. Found: C, 49.29; H, 4.58; N, 9.91.

CpRu((EtO)₂C)₂C₄H₂N)₂PCH₂CH₂P(NC₄H₂(CO₂Et)₂)Cl (6**).** **6** was isolated as a yellow microcrystalline solid in 67% yield. ¹H NMR (CD₂Cl₂): 1.23 (m, 24H, OCH₂CH₃), 2.96 (m, 4H, CH₂CH₂), 4.19 (m, 16H, OCH₂CH₃), 5.09 (s, 5H, Cp), 6.87 (s, 4H, NC₄H₂), 7.62 (s, 4H, NC₄H₂). ³¹P{¹H} NMR (CD₂Cl₂): 158.9. Anal. Calcd for C₄₇H₅₇ClN₄O₁₆P₂Ru: C, 49.85; H, 5.07; N, 4.95. Found: C, 50.18; H, 5.34; N, 4.91.

Cp*Ru(Ph₂PNMeNMePPh₂)Cl (7**).** **7** was isolated as a yellow microcrystalline solid in 57% yield. ¹H NMR (CD₂Cl₂): 1.37 (s, 15H, Cp*), 2.78 (t, J_{HP} = 3.9 Hz, 6H, NMe), 7.10–7.80 (m, 20H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): 137.7. Anal. Calcd for C₃₆H₄₁ClN₂P₂Ru: C, 61.75; H, 5.90; N, 4.00. Found: C, 61.58; H, 5.97; N, 3.92.

Cp*Ru(PhO)₂PNMeNMeP(OPh)₂Cl (8**).** **8** was isolated as a yellow microcrystalline solid in 40% yield. ¹H NMR (CD₂Cl₂): 1.24 (t, 15H, J_{HP} = 2.7 Hz, Cp*), 2.97 (t, 6H, J_{HP} = 3.6 Hz, NMe), 7.12–7.60 (m, 20H, Ph). ³¹P{¹H} NMR (CD₂Cl₂): 166.7. Anal. Calcd for C₃₆H₄₁ClN₂O₄P₂Ru: C, 56.58; H, 5.41; N, 3.67. Found: C, 56.31; H, 5.90; N, 3.46.

Cp*Ru((C₄H₄N)₂PCH₂CH₂P(NC₄H₄)₂)Cl (9**).** **9** was isolated as a yellow microcrystalline solid in 77% yield. ¹H NMR (CD₂Cl₂): 1.54 (t, 15H, J_{HP} = 3.0 Hz, Cp*), 2.60 (m, 2H, CH₂CH₂), 2.90 (m, 2H, CH₂CH₂), 6.30 (s, 4H, NC₄H₄), 6.37 (s, 8H, NC₄H₄), 7.08 (d, 4H, NC₄H₄). ³¹P{¹H} NMR (CD₂Cl₂): 152.5. Anal. Calcd for C₂₈H₃₅ClN₄P₂Ru: C, 53.72; H, 5.63; N, 8.95. Found: C, 53.42; H, 5.59; N, 8.82.

Cp*Ru((EtO)₂C)₂C₄H₂N)₂PCH₂CH₂P(NC₄H₂(CO₂Et)₂)Cl (10**).** **10** was isolated as a yellow microcrystalline solid in 87% yield. ¹H NMR (CD₂Cl₂): 1.31 (m, 24H, OCH₂CH₃), 1.67 (s, 15H, Cp*), 2.85 (m, 2H, CH₂CH₂), 3.05 (m, 2H, CH₂CH₂), 4.26 (m, 16H, OCH₂CH₃), 6.95 (s, 4H, NC₄H₂), 7.55 (s, 4H, NC₄H₂). ³¹P{¹H} NMR (CD₂Cl₂): 156.9. Anal. Calcd for C₅₂H₆₇ClN₄O₁₆P₂Ru: C, 51.94; H, 5.62; N, 4.66. Found: C, 51.46; H, 6.13; N, 4.60.

NMR Titration. Prior to every set of calorimetric experiments involving a new reaction, an accurately weighed amount (\pm 0.1 mg) of the organoruthenium complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF-d₈ was subsequently added. The solution was titrated

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

$$\text{CpRu}(\text{COD})\text{Cl}_{(\text{soln})} + \text{PP}_{(\text{soln})} \xrightarrow[30\text{ }^\circ\text{C}]{\text{THF}} \text{CpRu}(\text{PP})\text{Cl}_{(\text{soln})} + \text{COD}_{(\text{soln})}$$

PP	$-\Delta H_{\text{reacn}}^b$
$(\text{EtO}_2\text{C})_2\text{C}_4\text{H}_2\text{N}_2\text{PCH}_2\text{CH}_2\text{P}(\text{NC}_4\text{H}_2(\text{CO}_2\text{Et})_2)_2$	24.0(0.4) ^c
$(\text{C}_4\text{H}_4\text{N})_2\text{PCH}_2\text{CH}_2\text{P}(\text{NC}_4\text{H}_4)_2$	29.1(0.1) ^c
$\text{Ph}_2\text{PNMeNMePPh}_2$	29.7(0.4) ^c
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	30.5(0.2) ^d
$(\text{PhO})_2\text{PNMeNMeP}(\text{OPh})_2$	32.4(0.3) ^c
$\text{Ph}_2\text{PCHCHPPh}_2$	32.7(0.2) ^d
$\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$	39.4(0.3) ^d
$\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$	39.7(0.3) ^d

^a Cp = C₅H₅; PP = chelating diphosphine. ^b Enthalpy values are reported with 95% confidence limits. ^c This work. ^d Taken from ref 12d.

with a solution of the reactant of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ¹H and ³¹P NMR spectroscopy, and the reactions were found to be rapid and quantitative, conditions necessary for accurate and meaningful calorimetric results. These criteria were satisfied for all organoruthenium reactions investigated.

Solution Calorimetry. Calorimetric Measurement for Reaction between CpRu(COD)Cl and Ph₂PNMeNMePPh₂.

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 CpRu(COD)Cl (**1**) was accurately weighed into the lower vessel, which was then closed and sealed with 1.5 mL of mercury. A 4 mL amount of a stock solution of Ph₂PNMeNMePPh₂ (350 mg of Ph₂PNMeNMePPh₂ 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 reached thermal equilibrium at 30.0 °C (ca. 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(Ph₂PNMeNMePPh₂)Cl was found to be quantitative under these reaction conditions. The enthalpy of reaction, -25.8 ± 0.3 kcal/mol, represents the average of three individual calorimetric determinations. The final enthalpy value listed in Table 1 (-29.7 ± 0.4 kcal/mol) represents the enthalpy of ligand substitution with all species in solution. The enthalpy of solution of **1** (3.9 ± 0.1 kcal/mol) has, therefore, been subtracted from the -25.8 ± 0.3 kcal/mol value. This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study. A compilation of enthalpies of reaction for all ligands investigated in the study is presented in Tables 1 and 2.

Structure Determination of CpRu(PhO)₂PNMeNMeP(OPh)₂Cl (4**).** Yellow crystals of **4** were obtained by slow diffusion of diethyl ether into a CH₂Cl₂ solution of **4**. A single crystal having approximate dimensions 0.24 × 0.35 × 0.20 mm was placed in a capillary tube and mounted on a Siemens X-ray diffractometer fitted with a CCD area detector. Data were collected using Mo Kα radiation at 110 K. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with 30° < 2θ < 46°. The structure was solved using direct methods (MULTAN80) and refined by full-matrix least-squares techniques. Crystal data for **4** are summarized in Table 3, and selected bond distances and angles are listed in Table 4. Figure 1 presents an ORTEP of this molecule.

Structure Determination of Cp*Ru(PhO)₂PNMeNMeP(OPh)₂Cl (8**).** Yellow crystals of **8** were obtained by slow

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

$$\text{Cp}^*\text{Ru}(\text{COD})\text{Cl}_{(\text{soln})} + \text{PP}_{(\text{soln})} \xrightarrow[30\text{ }^\circ\text{C}]{\text{THF}} \text{Cp}^*\text{Ru}(\text{PP})\text{Cl} + \text{COD}_{(\text{soln})}$$

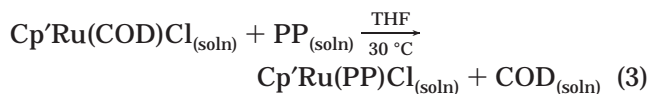
PP	$-\Delta H_{\text{reacn}}^b$
$(\text{EtO}_2\text{C})_2\text{C}_4\text{H}_2\text{N}_2\text{PCH}_2\text{CH}_2\text{P}(\text{NC}_4\text{H}_2(\text{CO}_2\text{Et})_2)_2$	19.4(0.2) ^c
$\text{Ph}_2\text{PNMeNMePPh}_2$	22.6(0.2) ^c
$(\text{C}_4\text{H}_4\text{N})_2\text{PCH}_2\text{CH}_2\text{P}(\text{NC}_4\text{H}_4)_2$	23.2(0.4) ^c
$(\text{PhO})_2\text{PNMeNMeP}(\text{OPh})_2$	26.4(0.2) ^c
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$	29.8(0.2) ^d
$\text{Ph}_2\text{PCHCHPPh}_2$	31.3(0.2) ^d
$\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$	34.8(0.2) ^d
$\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$	35.6(0.3) ^d

^a Cp* = C₅Me₅; PP = chelating diphosphine. ^b Enthalpy values are reported with 95% confidence limits. ^c This work. ^d Taken from ref 12c.

diffusion of diethyl ether into a CH₂Cl₂ solution of **8**. A single crystal having approximate dimensions 0.18 × 0.30 × 0.16 mm was placed in a capillary tube and mounted on a Siemens X-ray diffractometer fitted with a CCD area detector. Data were collected using Mo Kα radiation at 113 K. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with 30° < 2θ < 46°. The structure was solved using direct methods (MULTAN80) and refined by full-matrix least-squares techniques. Crystal data for **8** are summarized in Table 3, and selected bond distances and angles are listed in Table 5. Figure 2 presents an ORTEP drawing of this molecule.

Results

A facile entryway into the thermochemistry of Cp'Ru(PP)Cl (Cp' = C₅H₅ and C₅Me₅) complexes is made possible by the rapid and quantitative reaction of Cp'Ru(COD)Cl with the bidentate phosphine ligand (eq 3).

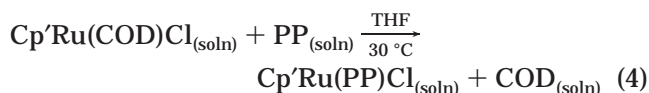


Cp' = C₅H₅, C₅Me₅; PP = chelating diphosphine

This type of bidentate 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. All reaction enthalpy data shown in Tables 1 and 2 refer to solution-phase values and include the enthalpy of solution of Cp'Ru(COD)Cl.

Discussion

Solution Thermochemistry. Recent work on Cp'Ru(COD)Cl (Cp' = Cp, Cp*) has shown that cyclooctadiene (COD) is very weakly bound to the Cp'RuCl moiety. The labile nature of these ruthenium–diene bonds has already been exploited in the investigation of phosphine substitution reactions as shown in eqs 1 and 2.^{6a,12i,f} This same approach was also tested with some bidentate ligands (eq 4) for which conversion of Cp'Ru(COD)Cl to Cp'Ru(PP)Cl complexes was also found to be quantitative.^{12c,d} The donor properties of tertiary phos-



PP =

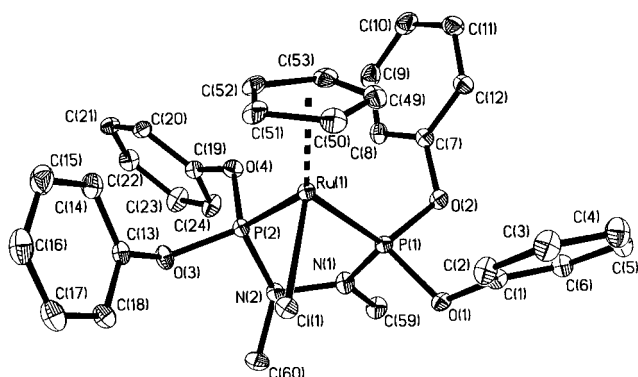
dppm, dmpm, dppb, dppe, dppp, dppv, depe, dmpe

Table 3. Crystallographic Data for 4 and 8

empirical formula	C ₃₁ H ₃₁ ClN ₂ O ₄ P ₂ Ru	C ₃₆ H ₄₁ ClN ₂ O ₄ P ₂ Ru
fw	694.04	764.17
temp, K	110(2)	113(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	triclinic
space group	P2 ₁	P1
unit cell dimens		
a, Å	15.5617(5)	12.1883(4)
b, Å	9.9700(3)	16.9193(6)
c, Å	20.3622(7)	18.7914(6)
α, deg	90	79.970(1)
β, deg	108.562(1)	75.140(1)
γ, deg	90	69.541(1)
V, Å ³	2994.9(2)	3493.9(2)
Z	4	4
D(calcd), g/cm ³	1.539	1.453
abs coeff, cm ⁻¹	0.759	0.658
F(000)	1416	1576
cryst size, mm	0.24 × 0.35 × 0.20	0.16 × 0.18 × 0.30
θ range for data collcn, deg	1.05–35.87	1.13–35.67
index ranges	–25 ≤ h ≤ 22, –16 ≤ k ≤ 16, –32 ≤ l ≤ 33	–7 ≤ h ≤ 7, –26 ≤ k ≤ 27, 0 ≤ l ≤ 30
no. of collcd reflns	49 044	63 310
no. of indep reflns	25 744 (R _{int} = 0.1535)	14 830 (R _{int} = 0.0851)
refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²
data/restraints/params	25744/1/744	14830/996/938
goodness of fit on F ²	0.488	1.219
final R index [I > 2σ(I)]	R1 = 0.0444, wR2 = 0.1346	R1 = 0.1066, wR2 = 0.2328
R indices (all data)	R1 = 0.0452, wR2 = 0.1377	R1 = 0.1376, wR2 = 0.2533
largest diff peak and hole, e Å ⁻³	2.079 and –1.941	2.849 and –2.159

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 4

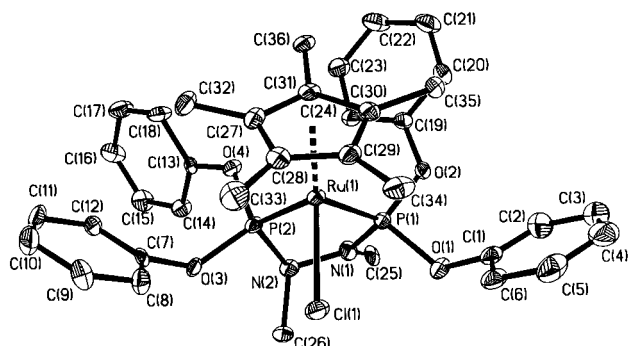
Bond Lengths			
Ru(1)–Cl(1)	2.4304(6)	P(1)–N(1)	1.668(2)
Ru(1)–P(1)	2.2129(6)	P(2)–N(2)	1.725(2)
Ru(1)–P(2)	2.1905(6)	N(1)–C(59)	1.463(3)
P(1)–O(1)	1.633(2)	P(2)–O(4)	1.613(2)
P(1)–O(2)	1.631(2)	N(1)–N(2)	1.433(3)
P(2)–O(3)	1.613(2)	N(2)–C(60)	1.473(3)
Ru(1)–Cp(c)	1.879(2)		
Bond Angles			
P(1)–Ru(1)–P(2)	80.39(2)	P(1)–N(1)–N(2)	119.3(2)
N(1)–N(2)–P(2)	106.2(2)	Ru(1)–P(1)–N(1)	111.02(8)
Ru(1)–P(2)–N(2)	113.50(7)	O(1)–P(1)–O(2)	93.15(10)
O(1)–P(1)–N(1)	103.28(10)	O(2)–P(1)–N(1)	102.53(10)
O(1)–P(1)–Ru(1)	122.82(7)	O(2)–P(1)–Ru(1)	120.73(7)
P(1)–N(1)–C(59)	125.4(2)	O(3)–P(2)–Ru(1)	125.75(7)
O(4)–P(2)–Ru(1)	110.71(7)	O(3)–P(2)–O(4)	102.20(10)
P(2)–N(2)–C(60)	118.1(2)	N(1)–N(2)–C(60)	111.6(2)
N(2)–N(1)–C(59)	115.2(2)	C(1)–O(1)–P(1)	116.6(2)
C(13)–O(3)–P(2)	122.0(2)	C(7)–O(2)–P(1)	123.4(2)
C(19)–O(4)–P(2)	127.8(2)	P(1)–Ru(1)–Cl(1)	90.46(2)
P(2)–Ru(1)–Cl(1)	90.99(2)		

Figure 1. ORTEP diagram of CpRu(PhO)₂PNMeNMeP(OPh)₂Cl (4). Ellipsoids are drawn in with 50% probability.

phine ligands can be modulated by electronic and steric parameter variation. This is usually achieved by variation of the substituents bound to the phosphorus atom. The binding affinities of specific phosphine ligands are commonly explained in terms of steric and electronic effects; yet these two factors are not easily separated. A common approach in physical inorganic/organome-

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 8

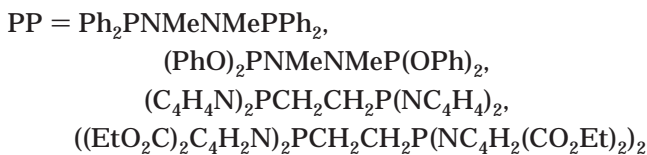
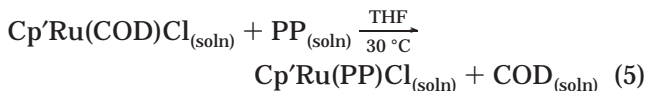
Bond Lengths			
Ru(1)–Cl(1)	2.438(2)	P(1)–N(1)	1.657(9)
Ru(1)–P(1)	2.221(2)	P(2)–N(2)	1.736(6)
Ru(1)–P(2)	2.213(3)	N(1)–C(25)	1.470(10)
P(1)–O(1)	1.633(6)	P(2)–O(4)	1.622(5)
P(1)–O(2)	1.637(7)	N(1)–N(2)	1.414(12)
P(2)–O(3)	1.611(8)	N(2)–C(26)	1.499(10)
Ru(1)–Cp*(c)	1.890(4)		
Bond Angles			
P(1)–Ru(1)–P(2)	80.03(10)	P(1)–N(1)–N(2)	119.7(5)
N(1)–N(2)–P(2)	107.5(5)	Ru(1)–P(1)–N(1)	111.8(3)
Ru(1)–P(2)–N(2)	112.8(4)	O(1)–P(1)–O(2)	93.6(4)
O(1)–P(1)–N(1)	100.8(3)	O(2)–P(1)–N(1)	102.6(4)
O(1)–P(1)–Ru(1)	122.8(2)	O(2)–P(1)–Ru(1)	121.5(2)
P(1)–N(1)–C(25)	125.7(8)	O(3)–P(2)–Ru(1)	126.6(2)
O(4)–P(2)–Ru(1)	110.9(3)	O(3)–P(2)–O(4)	103.9(4)
P(2)–N(2)–C(26)	116.8(6)	N(1)–N(2)–C(26)	112.1(7)
N(2)–N(1)–C(25)	114.4(8)	C(1)–O(1)–P(1)	120.8(5)
C(7)–O(3)–P(2)	124.3(6)	C(19)–O(2)–P(1)	128.0(7)
C(13)–O(4)–P(2)	128.9(6)	P(1)–Ru(1)–Cl(1)	91.61(7)
P(2)–Ru(1)–Cl(1)	89.98(8)		

Figure 2. ORTEP diagram of Cp*Ru(PhO)₂PNMeNMeP(OPh)₂Cl (8). Ellipsoids are drawn in with 50% probability.

tallic chemistry is to examine such effects while maintaining one of the two factors constant. Using this method, we have found from calorimetric studies that steric factors are the overwhelming component influencing the magnitude of the enthalpy of reaction in eqs 1 and 2.^{6a,12i,f} In reaction 4, the displacement of COD by bidentate phosphine ligands results in the incorporation of the Cp'RuCl moiety into the chelate structures,

producing metallacyclic rings. Enthalpies of this type of reaction showed that ligand displacements involving more basic alkyl-substituted phosphines prove to be more exothermic.

To study the binding of a transition metal with π -acceptor chelates and the relative importance of steric versus electronic ligand effects in the reaction of Cp^{*}Ru(COD)Cl with bidentate phosphine ligands, a thermochemical study of ligand substitution involving the newly reported ligands Ph₂PNMeNMePPh₂, (PhO)₂-PNMeNMeP(OPh)₂, (C₄H₄N)₂PCH₂CH₂P(NC₄H₄)₂, and ((EtO₂C)₂C₄H₂N)₂PCH₂CH₂P(NC₄H₂(CO₂Et)₂)₂ was undertaken (eq 5).



Ph₂PNMeNMePPh₂ and (PhO)₂PNMeNMeP(OPh)₂ are two representatives of the bis(phosphanyl) hydrazide chelating ligand family, which have chain lengths similar to Ph₂PCH₂CH₂PPh₂. However, their coordination chemistry with molybdenum and tungsten indicates that they are good π -acceptors.⁴ A variety of spectroscopic, structural, and thermochemical measurements have shown that *N*-pyrrolyl-substituted phosphines, which are isosteric with their phenylated counterparts, are good π -acceptors.^{5,6} It has been demonstrated that the substituent parameter X_i for the *N*-pyrrolyl functionality is approximately 12. The π -acceptor character of these ligands is thus found to exceed that of alkoxy/aryloxy- (–OPh, $X_i = 9.7$) and perfluoroaryl-substituted phosphines (–C₆F₅, $X_i = 11.2$) and approaches that found for fluoroalkylphosphines.¹⁹ On the basis of these observations, the diphosphine (C₄H₄N)₂PCH₂CH₂P(NC₄H₄)₂ and its carboethoxy derivative ((EtO₂C)₂C₄H₂N)₂PCH₂CH₂P(NC₄H₂(CO₂Et)₂)₂ were designed and expected to behave as good π -acceptor bidentate ligands. Moly and co-workers have found that the respective carbonyl stretching frequencies of Mo(CO)₄((EtO₂C)₂C₄H₂N)₂PCH₂CH₂P(NC₄H₂(CO₂Et)₂)₂ and Mo(CO)₄((C₄H₄N)₂PCH₂CH₂P(NC₄H₄)₂) are 32 and 23 cm^{–1} higher than that of Mo(CO)₄(Ph₂PCH₂CH₂PPh₂), clearly indicating that *N*-pyrrolyl-substituted bidentate phosphine ligands are good π -acceptors.⁶ It should also be mentioned that (C₄H₄N)₂PCH₂CH₂P(NC₄H₄)₂ and Ph₂PNMeNMePPh₂ are most likely isosteric with Ph₂PCH₂CH₂PPh₂.⁵ Enthalpy data are presented in Tables 1 and 2 for the CpRu(PP)Cl and Cp^{*}Ru(PP)Cl systems, along with selected data for previously investigated chelating phosphine ligands^{12c,d}

In the Cp system, the enthalpies of the reactions of CpRu(COD)Cl with Ph₂PNMeNMePPh₂ and (C₄H₄N)₂-PCH₂CH₂P(NC₄H₄)₂ are almost identical to that of Ph₂-PCH₂CH₂PPh₂. This result suggests that electronic effects have little influence over the magnitude of the enthalpy of this reaction, given that chelating ligands

Ph₂PNMeNMePPh₂, (C₄H₄N)₂PCH₂CH₂P(NC₄H₄)₂, and Ph₂PCH₂CH₂PPh₂ have similar steric but quite different electronic characters. Steric effects appear to again predominate, as illustrated by the reaction enthalpies of CpRu(COD)Cl with (PhO)₂PNMeNMeP(OPh)₂, which is less sterically demanding and more exothermic by 2.7 kcal/mol than Ph₂PNMeNMePPh₂ and (EtO₂C)₂C₄H₂N)₂-PCH₂CH₂P(NC₄H₂(CO₂Et)₂)₂, which is more sterically demanding and less exothermic by 5.7 kcal/mol than Ph₂PNMeNMePPh₂. The previously demonstrated importance of sterics in this system should not be construed as stating that ligand electronics do not contribute to the magnitude of the enthalpy of reaction. The electronic effects in the last two cases should not be ignored. We have shown that phosphite ligands are excellent binders to ruthenium in this system.^{12k} We also are aware that the carboalkoxy substituent on the pyrrolyl ring bound to the phosphine has a net electron-withdrawing effect. The observed effect must, therefore, represent a combination of steric and electronic effects.

In the Cp^{*}-based system, the reaction enthalpies of Cp^{*}Ru(COD)Cl with Ph₂PNMeNMePPh₂ and (C₄H₄N)₂-PCH₂CH₂P(NC₄H₄)₂ are almost identical but about 6 kcal/mol lower than that involving Ph₂PCH₂CH₂PPh₂. This difference must be an electronic effect since these ligands are thought to be isosteric. On the other hand, the reaction enthalpy of Cp^{*}Ru(COD)Cl with the π -acceptor (PhO)₂PNMeNMeP(OPh)₂ is 3 kcal/mol higher than that with Ph₂PNMeNMePPh₂ and 3 kcal/mol lower than that with Ph₂PCH₂CH₂PPh₂. As already stated, the phosphite functionality yields a better binder, the presence of the OPh and N(Me) groups within the ligand affords a phosphite which is less donating but still a phosphite. These observations suggest that ligand steric and electronic effects must both play a role in dictating the magnitude of the enthalpy of this reaction. A partitioning of the relative steric vs electronic parameters appears difficult in the present case. This is further complicated by the presence of π effects displayed by these ligand types. We do not presume to offer a definite answer as to the partitioning of σ and π effects in the present system but simply report the overall thermodynamic stability afforded by these ligands. Efforts to partition such contributions are in progress.²⁰ When the enthalpy data of the Cp and Cp^{*} systems are compared, a good linear fit ($R = 0.93$) is obtained (Figure 3), suggesting similar effects at play in both systems.

Comparison between the Cp and Cp^{*} data affords a look into the effects of electronic properties of the ancillary ligand as it contributes to the enthalpy of reaction. On average, there exists a difference between the enthalpies of reaction involving the same phosphine ligand of 6.4 kcal/mol, favoring the Cp system. Since the Cp^{*} is more electron donating than Cp, the Cp^{*} system accommodates less electron density from the incoming two-electron donor,^{2c} therefore leading to lower enthalpies of ligand substitution. This point has been described previously in our study on the CpRu(PR₃)₂Cl and Cp^{*}Ru(PR₃)₂Cl systems, where the average difference was 5.9 kcal/mol.^{12f}

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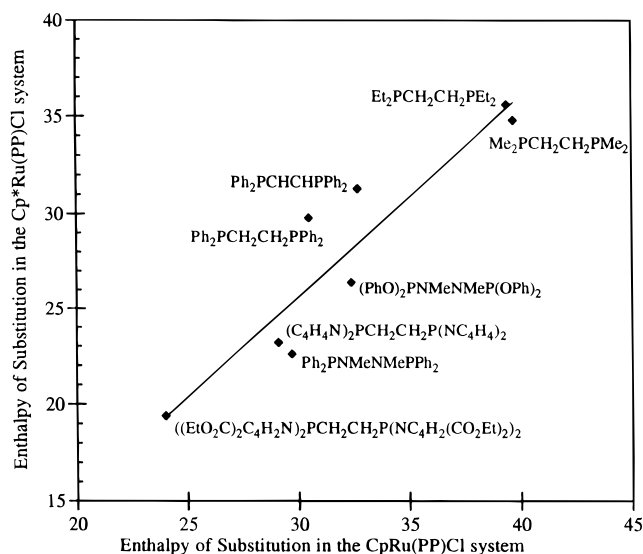


Figure 3. Enthalpies of reaction (kcal/mol) of Cp*Ru(PP)Cl versus CpRu(PP)Cl; slope = 1.04, $R = 0.93$.

Structural Studies of CpRu(PhO)₂PNMeNMeP(OPh)₂Cl (4) and Cp*Ru(PhO)₂PNMeNMeP(OPh)₂Cl (8). To help clarify the enthalpy trends observed, a structural study was conducted on two related complexes: CpRu((PhO)₂PNMeNMeP(OPh)₂)Cl (**4**) and Cp*Ru((PhO)₂PNMeNMeP(OPh)₂)Cl (**8**). As seen in Figures 1 and 2, the environment around the Ru atoms in **4** and **8** corresponds to a general three-legged piano-stool structure. The average Ru–P bond length in **4** is 2.2017(6) Å, clearly short when compared with that in CpRu(Ph₂PCH₂CH₂PPh₂)Cl (2.2776 Å).²¹ The phosphite donor property of the ligand appears to be attenuated by the N(Me) acceptor property. The difference in the Ru–P bond length qualitatively follows the reaction enthalpy trend: the reaction enthalpy value of (PhO)₂PNMeNMeP(OPh)₂ is 1.9 kcal/mol more exothermic than that of Ph₂PCH₂CH₂PPh₂. Similarly, the average Ru–P bond length (2.217(3) Å) in **8** is also much shorter than those observed for classical tertiary phosphine, which are usually in the range of 2.30–2.35 Å in [Cp*Ru(PR₃)₂L] neutral or cationic complexes,^{12d,22} and even shorter than those observed in Cp*Ru(P(NC₄H₄)₃)₂Cl (2.2598(11) Å)^{5a} and Cp*Ru(tmbp)Cl (2.2425(2) Å, tmbp = 4,4',5,5'-tetramethyl-2,2'-biphosphinine),²³ which contain the π -acceptors P(NC₄H₄)₃ and tmbp, respectively. The observed distance compares more closely to the Ru–P distance found in Cp*Ru(P(OMe)₃)₂Cl (2.232 Å).^{12k} In view of the metal basicity difference provided by Cp and Cp*, the Ru–P and Ru–Cp'(centroid) dis-

tances in **4** (Ru–P = 2.2017(6) Å, Ru–Cp = 1.879(2) Å) are shorter than those found in **8** (Ru–P = 2.217(3) Å, Ru–Cp* = 1.890(4) Å).

The average P–N distances obtained in **4** (1.697(2) Å) and **8** (1.697(9) Å) are similar to that observed in the complex Mo(CO)₄((PhO)₂PNMeNMeP(OPh)₂) (1.698(4) Å)^{4b} but shorter than typical P–N bonds (1.75–1.80 Å).^{4a,24} This is possibly due to the nitrogen–phosphorus $p\pi-d\pi$ interaction. It is also interesting to note that unequal Ru–C (carbon of the Cp or Cp* rings) distances are also found in **4** and **8**, similar to those in CpRu(Ph₂PCH₂CH₂PPh₂)Cl²¹ and CpRu(Ph₂CH₂CH(CH₃)PPh₂)Cl.²⁵ In each case, the shorter Ru–C distances are found trans to the chloro ligand, with longer Ru–C distances trans to P atoms, consistent with the differing trans influences of Cl and P.

A most interesting structural comparison is with CpRu(Ph₂PCH₂CH₂PPh₂)Cl,²¹ which does not contain a fragment that could provide a π contribution to the bonding. In **4**, the Ru–Cp(centroid) distance is 1.879 Å, compared to 1.853 Å in the diphos complex. Significant differences are also present in the Ru–P distances (2.2129 and 2.2863 Å for **4** and the diphos complex, respectively). Both variations in the metric parameters illustrate the push–pull influence of the presence of ligands with π -bonding capabilities.

Conclusion

A relative enthalpy scale has been established for the binding of π -acceptor chelating phosphine ligands to the CpRuCl and Cp*RuCl moieties that enables thermochemical comparisons with classical bidentate phosphine ligands. The labile nature of the COD ligand in CpRu(COD)Cl and Cp*Ru(COD)Cl was used to gain access into the thermochemistry of ligand substitution for bidentate π -acceptor ligands and also shows these reactions to be of synthetic use for isolation of these compounds. A combination of thermochemistry and X-ray diffraction investigations allows us to state that, as in previously investigated systems, the ligands investigated in this study display π -acceptor capabilities.

Acknowledgment. The National Science Foundation (Grant No. CHE-9631611) and Dupont (Educational Aid Grant) are gratefully acknowledged for financial support of this research.

Supporting Information Available: Tables of anisotropic thermal parameters, positional parameters, bond angles, and bond lengths for **4** and **8** (29 pages). Ordering and Internet access information are given on any current masthead page.

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