Solution Thermochemical and Structural Studies of Ligand Substitution of *N*-Pyrrolyl Phosphine Ligands in the (*p*-cymene)RuCl₂(PR₃) System

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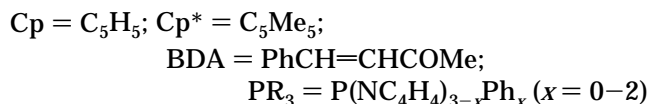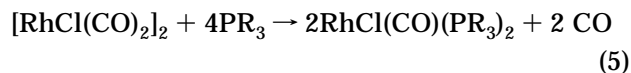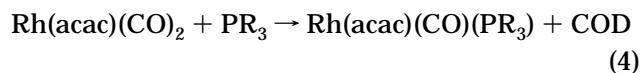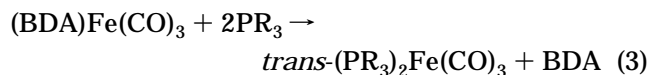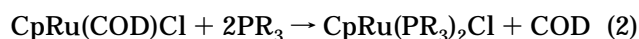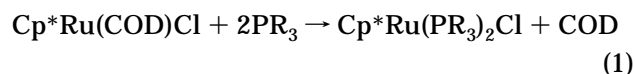
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The enthalpies of reaction of [(*p*-cymene)RuCl₂]₂ (*p*-cymene = $(CH_3)_2CHC_6H_4CH_3$) with a series of N-substituted tertiary phosphine ligands, leading to the formation of (*p*-cymene)-RuCl₂(PR₃) complexes (PR₃ = tertiary phosphine) have been measured by solution calorimetry in CH_2Cl_2 at 30 °C. The overall relative order of stability, within this series, is as follows: $P(NC_4H_4)_3 < P(NC_4H_4)_2(C_6H_5) < P(NC_4H_4)(C_6H_5)_2 < P(NC_4H_8)_3$. Structural studies have been performed on three complexes in the (*p*-cymene)RuCl₂(PR₃) system, PR₃ = $P(NC_4H_4)_3$, $P(NC_4H_4)_2(C_6H_5)$, and PBz₃. Thermochemical and structural data are compared to provide an understanding of the bonding involving these *N*-pyrrolyl-substituted phosphine ligands.

Introduction

The utilization of tertiary phosphine ligands in organometallic chemistry and catalysis is widespread.[1,2] In spite of the vast amount of information focusing on PR₃−transition-metal complexes,[3] few thermodynamic data regarding heats of binding of these ligands to metal centers exist, eqs 1−5.[4−8] Interesting catalytic developments involving organoruthenium complexes would

$$Cp^*Ru(COD)Cl + 2PR_3 \rightarrow Cp^*Ru(PR_3)_2Cl + COD \quad (1)$$

$$CpRu(COD)Cl + 2PR_3 \rightarrow CpRu(PR_3)_2Cl + COD \quad (2)$$

$$(BDA)Fe(CO)_3 + 2PR_3 \rightarrow$$
$$\textit{trans-}(PR_3)_2Fe(CO)_3 + BDA \quad (3)$$

$$Rh(acac)(CO)_2 + PR_3 \rightarrow Rh(acac)(CO)(PR_3) + COD \quad (4)$$

$$[RhCl(CO)_2]_2 + 4PR_3 \rightarrow 2RhCl(CO)(PR_3)_2 + 2 CO \quad (5)$$

$$Cp = C_5H_5; Cp^* = C_5Me_5;$$
$$BDA = PhCH=CHCOMe;$$
$$PR_3 = P(NC_4H_4)_{3-x}Ph_x \ (x = 0-2)$$

surely benefit from a better understanding of ligand binding affinity/thermochemical studies. Enthalpies of reaction involving a variety of phosphine ligands and

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ruthenium,[9] iron,[10] and rhodium[11] systems have been investigated. We have recently focused our thermochemical research efforts in the direction of a new class of pyrrolyl-substituted tertiary phosphine ligands. These ligands bind to metal centers with variable degrees of σ- and π-interactions.[12] In the hope of delineating the relative σ and π contributions, we present in this paper a combination of thermochemical and structural data probing the role of these ligands in the [(*p*-cymene)-RuCl₂(PR₃)] system.

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. Methylene chloride was distilled from P_2O_5 into flame-dried glassware prior to use. Only materials of high purity, as indicated by NMR spectroscopy, were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[13] or the enthalpy of solution of KCl in water.[14] The experimentally-determined enthalpies for these two standard calibration reactions are the same within experimental error to literature values. This calorimeter has been previously described,[15] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

¹H NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organoruthenium complex was placed in a Wilmad screw-capped NMR tube fitted with a septum and CD_2Cl_2 was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ¹H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and mean-

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

$$[RuCl_2(p\text{-cymene})]_{2(soln)} + 2L_{(soln)} \xrightarrow[\text{30 °C}]{CH_2Cl_2}$$

$$2RuCl_2(p\text{-cymene})(PR_3)_{(soln)}$$

L	complex	$-\Delta H_{rxn}{}^{a,b}$
P(NC₄H₄)₃	RuCl₂(*p*-cymene)(P(NC₄H₄)₃))	30.3 ± 0.3[c]
P(C₆H₅)(NC₄H₄)₂	RuCl₂(*p*-cymene)(PPh(NC₄H₄)₂)	31.1 ± 0.3[c]
P(*p*-CF₃C₆H₄)₃	RuCl₂(*p*-cymene)(P(*p*-CF₃C₆H₄)₃)	33.4 ± 0.1
P(C₆H₅)₂(NC₄H₄)	RuCl₂(*p*-cymene)(PPh₂(NC₄H₄))	34.4 ± 0.1[c]
PCy₃	RuCl₂(*p*-cymene)(PCy₃)	34.4 ± 0.2
PCy₂Ph	RuCl₂(*p*-cymene)(PCy₂Ph)	34.6 ± 0.1
P(*p*-ClC₆H₄)₃	RuCl₂(*p*-cymene)(P(*p*-ClC₆H₄)₃)	34.8 ± 0.2
P(OPh)₃	RuCl₂(*p*-cymene)(P(OPh)₃)	35.5 ± 0.3
P^iPr₃	RuCl₂(*p*-cymene)(P^iPr₃)	35.6 ± 0.2
PPh₃	RuCl₂(*p*-cymene)(PPh₃)	36.3 ± 0.1
P(*p*-FC₆H₄)₃	RuCl₂(*p*-cymene)(P(p-FC₆H₄)₃)	36.5 ± 0.3
P(*p*-MeC₆H₄)₃	RuCl₂(*p*-cymene)(P(p-MeC₆H₄)₃)	37.6 ± 0.3
PCyPh₂	RuCl₂(*p*-cymene)(PCyPh₂)	38.8 ± 0.4
P(*p*-MeOC₆H₄)₃	RuCl₂(*p*-cymene)(P(p-MeOC₆H₄)₃)	39.0 ± 0.5
P^iBu₃	RuCl₂(*p*-cymene)(P^iBu₃)	39.6 ± 0.1
PBz₃	RuCl₂(*p*-cymene)(PBz₃)	40.7 ± 0.3
P(NC₄H₈)₃	RuCl₂(*p*-cymene)(P(NC₄H₈)₃)	44.0 ± 0.2[c]
PEtPh₂	RuCl₂(*p*-cymene)(PEtPh₂)	45.2 ± 0.2
PPh₂Me	RuCl₂(*p*-cymene)(PPh₂Me)	45.6 ± 0.3
P(OMe)₃	RuCl₂(*p*-cymene)(P(OMe)₃)	45.9 ± 0.4
PEt₃	RuCl₂(*p*-cymene)(PEt₃)	51.3 ± 0.3
PPhMe₂	RuCl₂(*p*-cymene)(PPhMe₂)	52.5 ± 0.3
PMe₃	RuCl₂(*p*-cymene)(PMe₃)	55.3 ± 0.2

ingful calorimetric results and were satisfied for all organoruthenium reactions investigated. Only reactants and products were observed in the course of the NMR titration.

Calorimetric Measurement of Reaction between [(*p*-cymene)RuCl₂]₂ (1) and P(NC₄H₄)₃. 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 [(*p*-cymene)RuCl₂]₂ was accurately weighed into the lower vessel, and it was closed and sealed with 1.5 mL of mercury. Four milliliters of a 25% stock solution of the tris-(pyrrolyl)phosphine (1 g of P(NC₄H₄)₃ in 25 mL of CH₂Cl₂) 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 (about 2 h), it was inverted, thereby allowing the reactants to mix. The reaction was considered complete after the calorimeter had once again reached thermal equilibrium. The vessels were then removed from the calorimeter, taken into the glovebox, opened, and analyzed using ¹H NMR spectrocopy. Conversion to (*p*-cymene)RuCl₂(P(NC₄-H₄)₃) was found to be quantitative under these reaction conditions. The enthalpy of reaction, −25.2 ± 0.3 kcal/mol, represents the average of five individual calorimetric determinations. The enthalpy of solution of [(*p*-cymene)RuCl₂]₂ was then added to this value to obtain a value of −30.3 ± 0.3 kcal/mol for all species in solution. All enthalpy data measured for this study are presented in Table 1.

Calorimetric Measurement of Enthalpy of Solution of [(*p*-cymene)RuCl₂]₂ (1) in CH₂Cl₂. In order to consider all species in solution, the enthalpies of solution of [(*p*-cymene)-RuCl₂]₂ had to be directly measured. This was performed by using a similar procedure to the one described above with the exception that no ligand was added to the reaction cell. This enthalpy of solution represents the average of five individual determinations, +5.1 ± 0.1 kcal/mol.

Synthesis. The compound [(*p*-cymene)RuCl₂]₂ (**1**) was synthesized according to the literature procedure.[16] The synthesis of (*p*-cymene)RuCl₂(P(CH₂C₆H₅)₃) has been previ-

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Table 2. Crystallographic Data for the X-ray Diffraction Analyses of 2, 4, and 6

empirical formula	$C_{22}H_{26}Cl_2N_3PRu$ (**2**)	$C_{24}H_{27}Cl_2N_2PRu$ (**4**)	$C_{31}H_{35}Cl_2PRu$ (**6**)
fw	535.40	546.42	610.53
temp	208(2) K	208(2) K	295(2) K
wavelength	0.710 73Å	0.710 73 Å	0.710 73 Å
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
unit cell dimens	a, 17.158(4) Å α, 90°	a, 17.206(4) Å α, 90°	a, 9.381(2) Å α, 93.70(1)°
	b, 8.851(2) Å β, 99.394(4)°	b, 8.811(2) Å β, 97.758(4)°	b, 10.046(1) Å β, 96.44(1)°
	c, 14.626(4) Å γ, 90°	c, 14.857(3) Å γ, 90°	c, 15.181(1) Å γ, 93.60(2)°
volume, Z	2191.3(9) Å^3, 4	2231.9(9) Å^3, 4	1415.3(3) Å$_3$, 2
calcd density	1.623 g/cm3	1.626 g/cm3	1.433 g/cm^3
abs coeff	1.047 mm^{-1}	1.028 mm^{-1}	0.817 mm^{-1}
$F(000)$	1088	1112	628
cryst dimens	$0.33 \times 0.25 \times 0.10$ mm	$0.30 \times 0.18 \times 0.08$ mm	$0.16 \times 0.22 \times 0.48$ mm
θ range for data collection	2.41−30.00°	2.39−30.06°	2.04−25.00°
index ranges	$-23 \leq h \leq 23, -11 \leq k \leq 12,$	$-24 \leq h \leq -23, -12 \leq k \leq 12,$	$0 \leq h \leq 11, -11 \leq k \leq 11,$
	$-20 \leq l \leq 20$	$-20 \leq l \leq 20$	$-18 \leq l \leq 17$
no of reflns collected	31 754	33 478	5276
no. of indep reflns	6018 (R_{int} = 0.1342)	6223 (R_{int} = 0.0867)	4949 (R_{int} = 0.0295)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	Full-matrix least-squares on F^2
data/restraints/params	6018/0/262	6223/0/271	4636/0/319
goodness-of-fit on F^2	1.038	0.956	1.027
final R indices [$I > 2\sigma(I)$]	R1 = 0.0692, wR2 = 0.1398	R1 = 0.0417, wR2 = 0.0882	R1 = 0.0384, wR2 = 0.0856
R indices (all data)	R1 = 0.1363, wR2 = 0.1675	R1 = 0.0844, wR2 = 0.1022	R1 = 0.0590, wR2 = 0.0946
largest diff peak and hole	1.723, −1.193 e Å^{-3}	1.602, −1.007 e Å^{-3}	0.748, −0.347 e Å^{-3}

ously reported.[9h] Ligands were synthesized as reported in the literature.[12] Experimental synthetic procedures, leading to isolation of previously unreported complexes, are described below.

(*p*-cymene)RuCl₂(P(NC₄H₄)₃) (2). A 50 mL flask was charged with 188 mg (0.82 mmol) of P(pyrrole)₃, 250 mg (0.41 mmol) of [RuCl₂(*p*-cymene)]₂, and 15 mL of CH₂Cl₂. The clear wine-red solution was stirred at room temperature for 15 min, after which the solvent was removed under vacuum. The residue was washed with *ca.* 50 mL of hexane, filtered, and dried under vacuum, which afforded 370 mg of the product (yield 85%). ¹H NMR (300 MHz, CDCl₃, 25 °C): 1.25 (d, 6H, 2CH₃), 1.99 (s, 3H, −CH₃), 2.95 (sp, 1H, −CH), 5.27 (d, 2H, −C₆H₄), 5.57 (d, 2H, −C₆H₄), 6.31 (s, 6H, pyrrole), 7.02 (s, 6H, pyrrole). Anal. Calcd for C₂₂H₂₆RuCl₂PN₃: C, 49.35; H, 4.89; N, 7.85. Found: C, 49.70; H, 5.13; N, 7.61.

(*p*-cymene)RuCl₂(PPh₂(NC₄H₄)) (3). In a similar fashion as described for **2**, **3** was isolated in 81% yield. ¹H NMR (300 MHz, CDCl₃, 25 °C): 1.13 (d, 6H, 2CH₃), 1.90 (s, 3H, −CH₃), 2.85 (sp, 1H, −CH), 5.09 (d, 2H, −C₆H₄), 5.32 (d, 2H, −C₆H₄), 6.30 (s, 2H, −pyrrole), 7.12 (2H, −pyrrole), 7.38 (m, 6H, C₆H₅), 7.70 (m, 4H, C₆H₅). Anal. Calcd for C₂₆H₂₈RuCl₂PN: C, 56.02; H, 5.06; N, 2.51. Found: C, 55.75; H, 4.90; N, 2.42.

(*p*-cymene)RuCl₂(PPh(NC₄H₄)₂) (4). In an analogous manner, **4** is isolated in 79% yield. ¹H NMR (300 MHz, CDCl₃, 25 °C): 1.16 (d, 6H, 2CH₃), 1.94 (s, 3H, −CH₃), 2.87 (sp, 1H, −CH), 5.21 (d, 2H, −C₆H₄), 5.43 (d, 2H, −C₆H₄), 6.28 (s, 4H, −pyrrole), 7.08 (s, 4H, −pyrrole), 7.40 (m, 5H, C₆H₅). Anal. Calcd for C₂₄H₂₇RuCl₂PN₂: C, 52.72; H, 4.98; N, 5.13. Found: C, 52.97; H, 4.90; N, 4.96.

(*p*-cymene)RuCl₂(P(NC₄H₈)₃) (5). Following an identical procedure, **5** is isolated in 88% yield. ¹H NMR (300 MHz, CDCl₃, 25 °C): 1.33 (d, 6H, 2CH₃), 1.74 (s, 12H, −pyrrolidinyl), 2.16 (s, 3H, −CH₃), 3.21 (s, 12H, −pyrrolidinyl), 5.07 (d, 2H, −C₆H₄), 5.50 (d, 2H, −C₆H₄). Anal. Calcd for C₂₂H₃₈RuCl₂-PN₃: C, 48.26; H, 7.00; N, 7.67. Found: C, 48.20; H, 6.69; N, 7.32.

Crystal Structure Determination of (*p*-cymene)RuCl₂-(P(NC₄H₄)₃) (2) and (*p*-cymene)RuCl₂(PPh(NC₄H₄)₂) (4). Data for these two red crystals, **2** and **4**, were collected using a Siemens SMART CCD area detector diffractometer. At each series of four orientations about the ϕ angle, the crystal was scanned in ω by 688 steps of 0.3° (frames). The first 50 frames

were repeated at the end to check for crystal decay. In both cases, examination revealed a small twin component, the orientation of which could not be determined. Integration of the three-dimensional intensity profiles was, therefore, based upon a well-defined orientation matrix for the major (90%) component and yielded 33, 748 and 31, 754 reflections for **2** and **4**, respectively, providing reciprocal space coverage to resolution $d \geq 0.71$ Å of 93.9% and 94.6%, respectively. Intensity data were corrected for the effects of absorption by an empirical method using repeated and symmetry-equivalent reflections and based on the method of Blessing.[17] Slightly elevated residual densities and R_{int} values are a result of a failure to account for the minor component of the twin but in our view do not significantly detract from the accuracy of the structure determinations. The structures were solved by direct methods; all non-hydrogen atoms were refined using aniso-tropic displacement parameters, hydrogen atoms were included in calculated positions with fixed isotropic displacement parameters, and refined according to a riding model. All calculations were performed using the Siemens/SHELXTL suite of crystallographic programs.[18] The refined lattice parameters and other pertinent crystallographic information are summarized in Table 2. The refined positional parameters with equivalent isotropic displacement parameters for **2** and **4** are provided in the Supporting Information, and the inter-atomic distances and bond angles are listed in Tables 3 and 4, respectively. ORTEP diagrams of **2** and **4** are presented in Figures 1 and 2.

Crystal Structure Determination of (*p*-cymene)RuCl₂-(P(CH₂C₆H₅)₃) (6). A red crystal of (*p*-cymene)RuCl₂P-(CH₂C₆H₅)₃ (**6**) was sealed in a capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The reflections that were used for the deter-mination of the dimensions of the triclinic unit cell were located and indexed by the automatic peak search routine XSCANS.[19] The corresponding lattice parameters and orien-tation matrix were provided from a nonlinear least-squares fit of the orientation angles of 38 reflections (10° < 2θ < 24°) at 22 °C. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 2.

(16) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74−79.

(17) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.
(18) (a) *SMART, SAINT*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996. (b) *SHELXTL 5.0*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.
(19) *XSCANS*, version 2.0; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1991.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for (*p*-cymene)RuCl₂P(NC₄H₄)₃ (2)

Bond Lengths[a]

Ru−Cl(1)	2.396(2)	Ru−Cl(2)	2.398(2)
Ru−P	2.282(2)	Ru−Ar(c)[b]	1.723
P−N(1)	1.696(5)	P−N(2)	1.692(5)
P−N(3)	1.713(5)	N(1)−C(11)	1.385(8)
N(2)−C(24)	1.382(7)	N(3)−C(34)	1.369(8)

Bond Angles[a]

P(1)−Ru(1)−Cl(1)	89.27(5)	P(1)−Ru(1)−Cl(2)	91.48(5)
Cl(1)−Ru(1)−Cl(2)	88.72(6)	N(2)−P(1)−N(1)	103.5(3)
N(2)−P(1)−N(3)	98.6(2)	N(1)−P(1)−N(3)	99.1(3)
N(2)−P(1)−Ru(1)	121.4(2)	N(1)−P(1)−Ru(1)	115.3(2)
N(3)−P(1)−Ru(1)	115.4(2)	C(1)−Ru(1)−P(1)	112.8(2)
C(1)−Ru(1)−Cl(1)	157.8(2)	C(4)−Ru(1)−Cl(1)	86.6(2)
C(2)−Ru(1)−Cl(2)	123.4(2)	C(5)−Ru(1)−Cl(2)	108.4(2)

[a] Numbers in parentheses are the estimated standard deviations. [b] Ar(c) designates the centroid of the arene ring.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for (*p*-cymene)RuCl₂P(C₆H₅)(NC₄H₄)₂ (4)

Bond Lengths[a]

Ru−Cl(1)	2.388(1)	Ru−Cl(2)	2.392(1)
Ru−P	2.292(1)	Ru−Ar(c)[b]	1.710
Ru−C(30)	1.792(3)	P−N(1)	1.703(3)
P−N(2)	1.706(3)	N(1)−C(14)	1.378(5)
N(1)−C(11)	1.396(5)	N(2)−C(21)	1.368(4)
		N(2)-C(24)	1.381(4)

Bond Angles[a]

P(1)−Ru−Cl(2)	91.65(3)	Cl(1)−Ru−Cl(2)	88.72(3)
N(1)−P1−N(2)	102.9(2)	N(1)−P(1)−C(30)	102.4(2)
N(2)−P(1)−C(30)	101.3(2)	N(1)−P(1)−Ru	114.4(1)
N(2)−P(1)−Ru	120.9(1)	C(30)−P(1)−Ru	112.6(1)
C(14)−N(1)−C(11)	107.5(3)	C(14)−N(1)−P(1)	128.6(3)
C(11)−N(1)−P(1)	122.7(2)	C(21)−N(2)−C(24)	107.5(3)
C(21)−N(2)−P(1)	126.9(2)	C(24)−N(2)−P(1)	125.2(3)

[a] Numbers in parentheses are the estimated standard deviations. [b] Ar(c) designates the centroid of the arene ring.
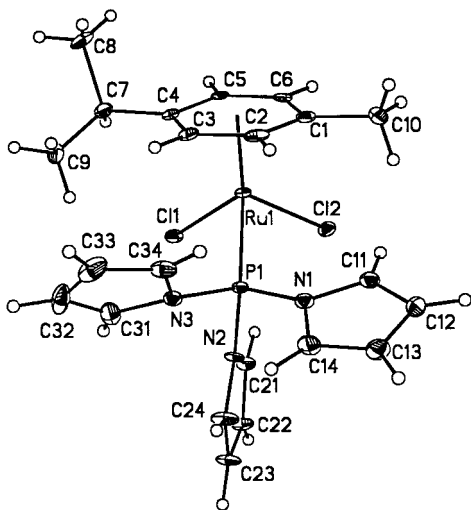
Figure 1. ORTEP of (*p*-cymene)RuCl₂(P(NC₄H₄)₃) (**2**) with ellipsoids drawn at 40% probability.

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and variable ω scans (4.0−10.0 deg/min). Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured periodically during data collection and gave no indication of crystal decay or sample movement. The data were corrected for Lorentz−polarization, and the symmetry-equivalent reflections were averaged. An empirical absorption correction (range of transmission coefficients: 0.708−
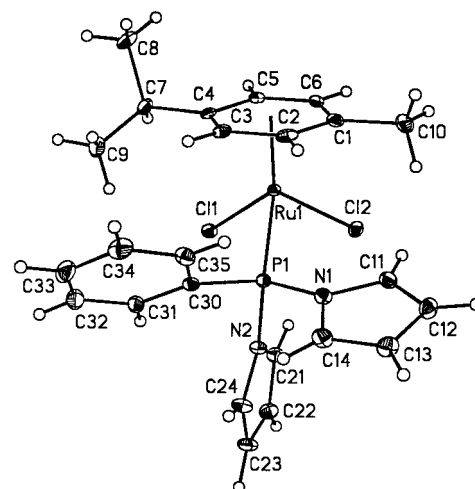
Figure 2. ORTEP of (*p*-cymene)RuCl₂(PPh(NC₄H₄)₂) (**4**) with ellipsoids drawn at 40% probability.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for (*p*-cymene)RuCl₂P(CH₂C₆H₅)₃ (6)

Bond Lengths[a]

Ru−Cl(1)	2.416(1)	Ru−Cl(2)	2.412(1)
Ru−P	2.359(1)	Ru−Ar(c)[b]	1.708
P−C(11)	1.848(4)	P−C(18)	1.839(4)
P−C(25)	1.861(4)	C(1)−C(2)	1.395(6)
C(1)−C(6)	1.433(6)	C(1)-C(7)	1.507(6)

Bond Angles[a]

|			
P−Ru−Cl(1)	81.93(4)	P−Ru−Cl(2)	83.45(4)
P−Ru−Ar(c)	134.9	Cl(1)−Ru−Cl(2)	90.88(4)
C(11)−P−Ru	111.3(1)	C(11)−P−C(18)	106.0(2)
C(11)−P−C(25)	103.9(2)	C(18)−P−Ru	118.4(1)
C(18)−P−C(25)	101.9(2)	C(25)−P−Ru	114.1(1)

[a] Numbers in parentheses are the estimated standard deviations. [b] Ar(c) designates the centroid of the arene ring.

0.783) based upon the ψ scans measured for six reflections ($\chi \approx -90°$, $2\theta = 13-31°$) was applied.

The initial coordinates of the Ru atom were determined by Patterson methods, and the coordinates for the remaining non-hydrogen atoms were obtained from subsequent Fourier summations calculated with the algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Hydrogen atoms were included in calculated positions with fixed isotropic displacement parameters and refined according to a riding model. The refined positional parameters with equivalent isotropic displacement parameters **6** are provided in the Supporting Informaiton, and the interatomic distances and bond angles are listed in Table 5. An ORTEP of **6** is presented in Figure 3.

Results and Discussion

A facile entryway into the thermochemistry of (*p*-cymene)Ru(PR₃)Cl₂ complexes is made possible by the rapid and quantitative reaction of [(*p*-cymene)RuCl₂]₂ (**1**) with a variety of phosphine ligands, eq 6. This type

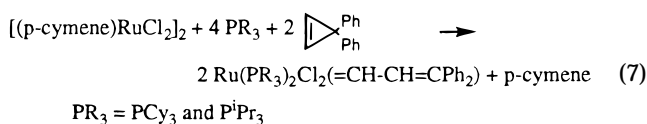$$ \text{PR}_3 = \text{Tertiary Phosphine} \qquad (6) $$
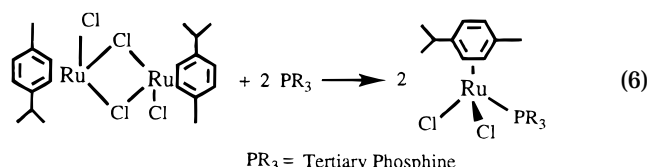
of phosphine binding reaction is rapid and quantitative for all ligands calorimetrically investigated at 30.0 °C in methylene chloride. We have previously examined
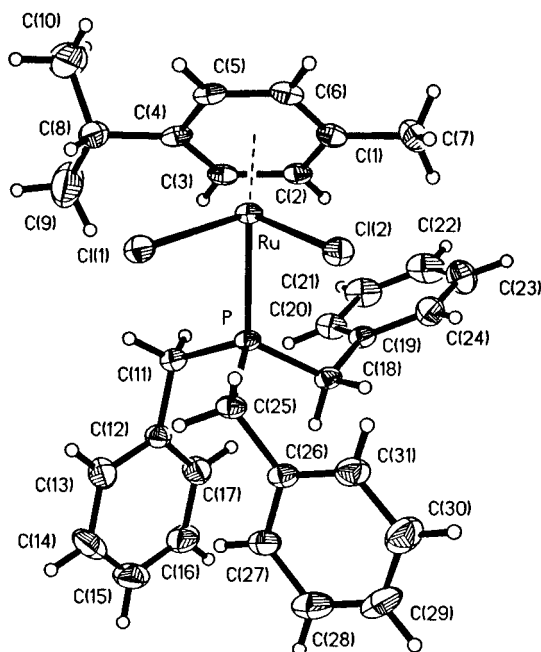
Figure 3. ORTEP of (*p*-cymene)RuCl$_2$(P(CH$_2$C$_6$H$_5$)$_3$) (**6**) with ellipsoids drawn at 30% probability.
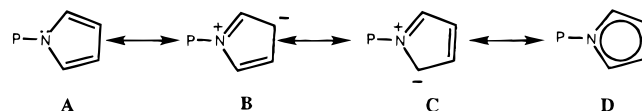
similar substitution reactions for a wide variety of phosphine ligands. The present enthalpy of reaction data along with that previously reported on this system are compiled in Table 1.

The complex [(*p*-cymene)RuCl$_2$]$_2$ (**1**) and some of its phosphine derivatives have been demonstrated as efficient catalyst/catalyst precursors. For example, Noels and co-workers have shown **1** and some of its phosphine derivatives to be efficient precursors for the ring-opening metathesis polymerization of olefins.[20] Grubbs and Nguyen, in synthetic studies related to their investigations on ring-opening and ring-closing metathesis reactions,[21] have used **1** as a synthon, leading to the isolation of catalytically active ruthenium carbene complexes, (PR$_3$)$_2$Cl$_2$Ru(CH=CH=CPh$_2$), eq 7.[22] In view of the

[(p-cymene)RuCl$_2$]$_2$ + 4 PR$_3$ + 2 ⟶

2 Ru(PR$_3$)$_2$Cl$_2$(=CH-CH=CPh$_2$) + p-cymene   (7)

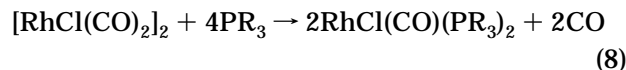PR$_3$ = PCy$_3$ and P^{i}Pr$_3$

reactivity displayed by **1**, thermochemical studies were undertaken to obtain quantitative data about the enthalpic driving forces behind the fragmentation and ligand binding trends for this dimeric complex.

The *N*-pyrrolyl-substituted phosphine series has been shown to act as a potent electron-withdrawing group, rendering the phosphine a poor σ donor and a good π-acceptor.[12] Pertinent resonance structures for the *N*-pyrrolyl phosphines can be drawn as follows:
Aromatic delocalization of the nitrogen lone pair into the pyrrole ring, as depicted in structures B and C, has

(20) (a) Demonceau, A.; Noels, A. F.; Saive, E.; Hubert, A. J. *J. Mol. Catal.* **1992**, *76*, 123−132. (b) Demonceau, A.; Stumpf, A. W.; Saive, E.; Noels, A. F. *Macromolecules* **1997**, *30*, 3127−3136.
(21) (a) Nguyen, S. T.; Johnson, L. K. Grubbs, R. H.: Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (b) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857. (c) Nguyen, S. T.; Grubbs, R. H.: Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859.
(22) Nguyen, S. T.; Grubbs, R. H. Personnal communication.

the effect of placing a partial positive charge on the nitrogen. This would be expected to reduce the basicity of the adjacent phosphorus atom. Structure D suggests that *N*-pyrrolyl phosphines will be poorer donors than the corresponding phenyl phosphines since the more electronegative nitrogen replaces carbon. Moloy[12] has shown these ligands to undergo quantitative binding to the RhCl(CO) fragment, eq 8. The pyrrolyl moiety,

$$[RhCl(CO)_2]_2 + 4PR_3 \rightarrow 2RhCl(CO)(PR_3)_2 + 2CO$$
(8)

PR$_3$ =
 P(NC$_4$H$_4$)$_3$; P(NC$_4$H$_4$)$_2$Ph; P(NC$_4$H$_4$)Ph$_2$; P(NC$_4$H$_8$)$_3$

known for its π-involvement, has been shown by the vibrational spectroscopic data obtained for a related series of rhodium compounds to affect the binding ability of the phosphine. The thermochemical information subsequently gathered for this rhodium system quantitatively supports[11] that the phosphine donor strength decreases with increasing number of pyrrolyl substituents on phosphorus.

In the present ruthenium study, this same phosphine ligand series was examined. From the data in Table 1, it is evident that the pyrrolyl-substituted phosphines are in fact among the most weakly bound ligands investigated in this system. The pyrrolyl- and pyrrolidinyl-substituted phosphines are isosteric, having a cone angle of 145°.[12,23] Therefore, any observed enthalpy difference can be essentially attributed to electronic effects. The reaction enthalpy data in Table 1 clearly show that these addition reactions become less exothermic as the number of pyrrolyl substituents on the phosphine increases. The observed trend has been observed in other ruthenium systems.[9j] A stepwise increase of this reaction enthalpy as a function of pyrrolyl substitution is graphically represented in Figure 4.[24] The totally saturated P(NC$_4$H$_8$)$_3$ ligand is more closely related to a trialkylphosphine than to its pyrrolyl congener. This remark was previously supported by the enthalpy data measured in other rhodium[11a] and ruthenium[9j] systems, where enthalpies of reactions for P(NC$_4$H$_8$)$_3$ are closer to PEt$_3$. The enthalpy scale trend present in the (*p*-cymene)RuCl$_2$(PR$_3$) (PR$_3$ = P(NC$_4$H$_4$)$_3$, P(NC$_4$H$_4$)$_2$(C$_6$H$_5$), P(NC$_4$H$_4$)(C$_6$H$_5$)$_2$ and P(NC$_4$H$_8$)$_3$) system is, therefore, consistent with the thermochemical data measured for these previously investigated systems.

To determine the relative importance of the σ- and π-bonding components of the phosphine ligand, single-crystal X-ray diffraction studies were performed on three complexes. Two of these compounds bear pyrrolyl substituents, (*p*-cymene)RuCl$_2$(P(NC$_4$H$_4$)$_3$) (**2**) and (*p*-cymene)RuCl$_2$(P(NC$_4$H$_4$)$_2$(C$_6$H$_5$) (**4**), on the phosphine,
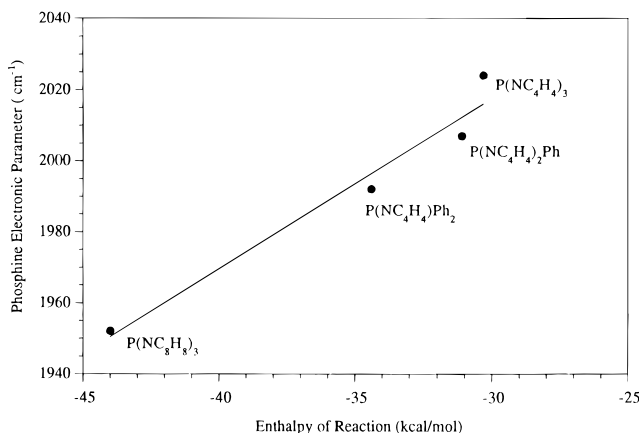
(23) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(24) The electronic parameter used in this relationship is the one determined in ref 12, which is the carbonyl stretching frequency of Rh(CO)Cl(PR$_3$)$_2$.

Figure 4. Enthalpy of reaction (kcal/mol) vs phosphine electronic factor in the [(p-cymene) RuCl$_2$(PR$_3$)] system. Slope = 4.79; R = 0.98

Table 6. Selected Bond Distances (Å) and Enthalpy of Ligand Substitution (kcal/mol) for [*p*-cymeneRuCl$_2$(PR$_3$)] Complexes

	2 (P(NC$_4$H$_4$)$_3$)	**4**(PPh(NC$_4$H$_4$)$_2$)	**6** (PBz$_3$)
Ru−P	2.282(2)	2.292(1)	2.359(1)
Ru−Cl(1)	2.396(2)	2.388(1)	2.416(1)
Ru−Cl(2)	2.398(2)	2.392(1)	2.412(1)
Ru−Ar(c)	1.723	1.710	1.708
−ΔH	30.3(0.3)	31.1(0.3)	40.7(0.3)

and the third provides a standard for comparison due to the presence of a simple trialkyl phosphine ligand in (*p*-cymene)RuCl$_2$(PCH$_2$C$_6$H$_5$)$_3$ (**6**). The pertinent crystallographic bond distances and angles are summarized in Table 6. From a comparison of the structural data for **2** and **4**, it is apparent that the replacement of a pyrrolyl with a phenyl substituent on the phosphine produces only a modest increase of 0.01 Å[25] in the Ru−P bond distance. However, a substantially larger increase of 0.07 Å in the Ru−P distance is observed when the three pyrrolyl groups of **2** are replaced by the three benzyl substituents of **6**. On the basis of the observed variation in the Ru−P distances for these three compounds, the least exothermic enthalpy of reaction corresponds to the Ru phosphine complex, **2**, with the shortest Ru−P bond. However, any reasonable interpretation must also consider any reorganization energy illustrated by changes in bond lengths between the metal and the *p*-cymene and Cl ligands. It should be kept in mind that the present enthalpy data does not represent "bond strength" but is a sum of a number of enthalpic contributions which include bond strength differences and fragment relaxation enthalpies. This relaxation enthalpy can be explained in terms of bond length/bond strength reorganization resulting from differing π-bonding involved in the incoming phosphine ligand. In the case of complex **6**, which contains the most basic phosphine ligand and the longest Ru−P distance, one finds the shortest Ru−Ar(c) distance of 1.708 Å and the longest average Ru−Cl distance of 2.414 Å. Apparently, the weaker π-acceptor ability of the tribenzylphosphine ligand in **6** is compensated by a greater π-back-donation from the Ru to the arene. In

contrast, for the π-activated tris(pyrrolyl)phosphine in **2**, its enhanced π-acceptor ability reduces the degree of π-back-donation into the arene, thus leading to a longer Ru−Ar(c) distance of 1.723 Å. The observed variation in Ru−Cl bond distances appears to be consistent with the π-donor character of the Cl ligand, with the longer average Ru−Cl distance in **6** being associated with a more electron-rich Ru center.

We have previously reported on the thermochemistry and structural features of this ligand series within the Cp*Ru(PR$_3$)$_2$Cl system.[9j] The enthalpy trend observed in this system is P(NC$_4$H$_4$)(C$_6$H$_5$)$_2$ < P(NC$_4$H$_4$)$_3$ < P(NC$_4$H$_4$)$_2$(C$_6$H$_5$) < P(NC$_4$H$_8$)$_3$. The structural trend in that study shows an increase in the average Ru−P bond length within this series, correlating with an increase in reaction exothermicity, A trend that is counterintuitive if the bonding is solely considered in terms of σ donation. It was, therefore, concluded that the bonding in the pyrrolyl-substituted phosphines appeared to involve some π-back-donation as well. In the present system, the observed enthalpy trend is P(NC$_4$H$_4$)$_3$ < P(NC$_4$H$_4$)$_2$(C$_6$H$_5$) < P(NC$_4$H$_4$)(C$_6$H$_5$)$_2$ < P(NC$_4$H$_8$)$_3$, more along the lines of the π-bonding ability of the series. The structural features of the first two complexes in this series (**2** and **4**) show a slight shortening of the Ru−P bond length on going from **2** to **4**. The present system appears to be much more sensitive to the electronic π−back-donation. The two systems contain different ancillary ligands, which will surely influence (in a different manner) the amount of electron density available for back-donation. Furthermore, the Cp*Ru(PR$_3$)$_2$-Cl system contains two phosphine ligands competing for back-donation, compared to a single phosphine in the (*p*-cymene)RuCl$_2$PR$_3$ system. In the case of the presence of a unique phosphine ligand, a marked increase of the π-back-donation from Ru into pyrrolyl substituent antibonding orbitals should be expected. The trend of increased pyrrolyl substitution accompanied by a shorter Ru−P bond length and lower enthalpy values clearly illustrates this effect.[26]

Conclusion

The lability of the chloride bridges in [(*p*-cymene)-RuCl$_2$]$_2$ (**1**) provides a suitable entry to probe the thermochemistry associated with ligand binding for pyrrolyl- and pyrrolidinyl-substituted phosphine ligands. By holding the steric factor constant for the phosphines examined within this Ru series, the observed trend in the measured reaction enthalpies can be accounted for by considering the differences in the relative σ-donor and π -acceptor bonding contributions for these phosphine ligands. Further thermochemical, mechanistic, and catalytic investigations focusing on this and related ligand system are presently underway.

(25) This distance difference, although metrically real, may not be chemically significant, see: Martin, A.; Orpen, A. G. *J. Am. Chem. Soc.*, **1996**, *118*, 1464−1470.

(26) It should also be stated that such a simple analysis does not take into account the importance of steric repulsive effects in the Cp*Ru(PR$_3$)$_2$Cl system.[9j]

Supporting Information Available: Tables of crystal and intensity data, atomic coordinates, selected distances and angles, anisotropic thermal displacement parameters, and hydrogen bond distances for **2**, **4**, and **6** (18 pages). Ordering information is given on any current masthead page.

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