*Organometallics* **1994,** *13,* 3621−3627

# Enthalpies of Reaction of CpRu(COD)Cl ($Cp = \eta^5\text{-}C_5H_5$; COD = Cyclooctadiene) with Chelating Tertiary Phosphine Ligands. Solution Thermochemical Investigation of Ligand Substitution and Ring Strain Energies in $CpRu(R_2P(CH_2)_nPR_2)Cl$ Complexes

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*Received April 1, 1994*[⊗]

The enthalpies of reaction of CpRu(COD)Cl ($Cp = \eta^5\text{-}C_5H_5$; COD = $\eta^4$-cyclooctadiene) with a series of bidentate ligands, leading to the formation of CpRu(PP)Cl complexes, have been measured by anaerobic solution calorimetry in THF at 30.0 °C. The overall relative order of stability established for these complexes is as follows: dppm < dmpm < dppb < dppe < dppp < dppv < depe < dmpe. Comparison between enthalpies of these reactions and those of monodentate phosphine ligands affords a quantitative treatment of ring strain enthalpies in these organoruthenium metallacyclic compounds. Significant ring strain energy is displayed in the four-membered metallacycle and is on the order of 13 kcal/mol. A single crystal X-ray diffraction study has been performed on one of the new complexes, CpRu(dppv)Cl [dppv = bis(diphenylphosphino)ethylene] ($C_{31}H_{27}ClP_2Ru{\cdot}CH_2Cl_2$, $P\bar{1}$, $a = 10.344(2)$ Å, $b = 11.907(2)$ Å, $c = 13.183(1)$ Å, $\alpha = 67.89(1)°$, $\beta = 76.52(1)°$, $\gamma = 85.96(2)°$, $V = 1462.5(5)$ Å$^3$, and $Z = 2$). Comparisons of the thermochemical data with the $C_5Me_5$-based system and related metallacyclic complexes are also presented.

## Introduction

Chelating diphosphine ligands have been widely used in organometallic chemistry. Kinetic, catalytic, and structural studies have been performed on organometallic systems incorporating this ligand type.[1] One dramatic example of the effects of using 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] A factor influencing the metal−diphosphine complex reactivity and stability must certainly involve the metal−ligand bond enthalpy term. This bond disruption enthalpy (BDE) value can be viewed as a sum of the stabilizing metal−phosphorus interaction and of the destabilizing strain energy caused by steric and torsional forces present in the metallacyclic fragment.

Solution calorimetric studies have been useful in providing bonding and reactivity pattern information.[3−5] These have also proven insightful in directing the design of new metal-catalyzed transformations.[6] To date thermochemical information focusing on organo-group 8 complexes remains scarce.[7−12] We have recently reported on the solution thermochemistry of organoruthenium complexes bearing the Cp* ($Cp^* = \eta^5\text{-}C_5Me_5$) ancillary ligation:[13]

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

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0276-7333/94/2313-3621$04.50/0

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

$$\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5};\ \mathrm{R} = \text{alkyl, aryl}$$

Furthermore, we have most recently investigated the enthalpy of reaction associated with chelating diphosphine ligand displacement in this ruthenium system:[14]

$$\mathrm{Cp^*Ru(COD)Cl_{soln}} + \mathrm{P^\frown P_{soln}} \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(P^\frown P)Cl_{soln}} + \mathrm{COD_{soln}} \quad (2)$$

$$\mathrm{P^\frown P} = \text{chelating diphosphine}$$

We now wish to expand on our solution thermochemical studies of organo group 8 complexes by examining the effects of ancillary ligand modification on the enthalpies of ligand substitution for chelating phosphines. The ring strain energy present in this system will be quantitatively addressed by focusing on enthalpies of reaction of CpRu(COD)Cl with chelating diphosphine ligands.

## 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 oxygen and water. Ligands were purchased from Strem Chemicals and used as received. Solvents were dried and distilled under dinitrogen before use by employing the following drying agents: tetrahydrofuran (THF) (Na dispersion) and $CH_3CN$ ($P_2O_5$). Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. $^1H$ 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[15] or the enthalpy of solution of KCl in water.[16] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[17] 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.** CpRu(diene)Cl was synthesized as reported in the literature.[18] CpRu(PP)Cl complexes (PP = dppe,[19] dppm,[19] dppp,[20] dppb,[20] dmpe[21]) were identified by comparison with reported literature spectroscopic data. Experimental synthetic procedures, leading to isolation of crystalline materials, for all other complexes are reported below.

**$CpRu(PMe_2CH_2PMe_2)Cl$ (2).** A 25-mL flask was charged with 100 mg (0.32 mmol) of CpRu(COD)Cl, 10 mL of dried THF, and 65 $\mu$L (0.41 mmol) of $PMe_2CH_2PMe_2$. After stirring for 11 h, volatiles were removed in vacuum. A 10-mL mixture of hexane and THF (10:3) was vacuum transferred to the cooled flask (−78 °C) containing the residue. This solution was then allowed to warm to room temperature. 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 in vacuum, giving a 55-mg (50%) yield. $^1H$ NMR (300 MHz, THF-$d_8$, 25 °C): $\delta$ 1.54 (t, 6H, $-CH_3$), 1.66 (t, 6H, $-CH_3$), 3.29 (m, 1H, $-CH_2-$), 3.56 (m, 1H, $-CH_2-$), 4.39 (s, 5 H, Cp). Anal. Calcd for $RuClP_2C_{10}H_{19}$: C, 35.55; H, 5.67. Found: C, 35.88; H, 5.63.

**$CpRu(PEt_2(CH_2)_2PEt_2)Cl$ (3).** A 25-mL flask was charged with 100 mg (0.32 mmol) of CpRu(COD)Cl, 10 mL of THF, and 80 $\mu$L (10.33 mmol) of $PEt_2(CH_2)_2PEt_2$. After stirring for 12 h, the solvent was removed in vacuum and 40 mL of hexane was vacuum transferred to the cooled (−78 °C) flask containing the solid product. This mixture was filtered. The saturated solution was very slowly cooled to −78 °C and kept at this temperature overnight. After filtration, the collected orange crystals were washed with a small amount of hexane and dried in vacuo, giving a 75 mg (57%) yield. $^1H$ NMR (300 MHz, THF-$d_8$, 25 °C): $\delta$ 1.01 (m, 6H, $-CH_3$), 1.17 (m, 6H, $-CH_3$), 1.61 (br m, 8H, $-CH_2CH_3$), 1.97 (m, 2H, $-CH_2CH_2-$), 2.14 (m, 2H, $-CH_2CH_2-$), 4.51 (s, 5H, Cp). Anal. Calcd for $RuClP_2C_{15}H_{29}$: C, 44.17; H, 7.17. Found: C, 44.37; H, 7.27.

**$CpRu(PPh_2(CH{=}CH)PPh_2)Cl$ (4).** A 25-mL flask was charged with 150 mg (0.32 mmol) of CpRu(COD)Cl, 15 mL of dried THF, and 132 mg (0.33 mmol) of $PPh_2(CH{=}CH)PPh_2$. After stirring for 24 h, the solvent was removed in vacuum and an 8-mL solvent mixture of $CH_2Cl_2$ and pentane (1:5) was vacuum transferred to the cooled (−78 °C) solid product. The solution was warmed to room temperature, stirred for 15 min, and filtered. The solution was kept in an acetone bath overnight. After filtration, the orange crystals were collected and weighed, giving a 141-mg (49%) yield. $^1H$ NMR (300 MHz, THF-$d_8$, 25 °C): $\delta$ 4.40 (s, 5H, Cp), 7.18 (m, 4H, $-C_6H_5$), 7.25 (s, 6H, $-C_6H_5$), 7.34 (s, 6H, $-C_6H_5$), 7.71 (m, 1H, $-CH{=}CH-$), 7.91 (m, 1H, $-CH{=}CH-$), 8.00 (m, 4H, $-C_6H_5$). Anal. Calcd for $RuClP_2C_{31}H_{27}$: C, 62.26; H, 4.55. Found: C, 62.28; H, 4.48.

**$^1H$ 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 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 $^1H$ NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative, conditions necessary for accurate and meaningful calorimetric results. These criteria were satisfied for all organoruthenium reactions investigated.

**Calorimetric Measurement of the Reaction between CpRu(COD)Cl (1) and Bis(diphenylphosphino)ethane (dppe).** 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 was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of dppe (5 g of dppe 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

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

$$Cp'Ru(COD)Cl_{soln} + PP_{soln} \xrightarrow[30\ °C]{THF} Cp'Ru(PP)Cl_{soln} + COD_{soln}$$

$$Cp' = C_5Me_5 \text{ and } C_5H_5$$

| | P P | $-\Delta H_{rxn}$[a] | $-\Delta H_{rxn}$[b] |
|---|---|---|---|
| dppm | $Ph_2P$ $PPh_2$ | 19.4 (0.2) | 19.4 (0.2) |
| dmpm | $Me_2P$ $PMe_2$ | 23.8 (0.3) | 26.2 (0.2) |
| dppb | $Ph_2P$ $PPh_2$ | 24.7 (0.3) | 30.1 (0.3) |
| dppe | $Ph_2P$ $PPh_2$ | 29.8 (0.2) | 30.5 (0.2) |
| dppp | $Ph_2P$ $PPh_2$ | 30.7 (0.2) | 32.4 (0.2) |
| dppv | $Ph_2P$ $PPh_2$ | 31.3 (0.2) | 32.7 (0.2) |
| depe | $Et_2P$ $PEt_2$ | 35.6 (0.3) | 39.4 (0.3) |
| dmpe | $Me_2P$ $PMe_2$ | 34.8 (0.2) | 39.7 (0.3) |

[a] Enthalpies of reaction for the Cp*-based system[14] which are reported with 95% confidence limit. [b] Enthalpies of reaction for the Cp-based system also reported with 95% confidence limits.

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), the calorimeter was inverted, therby allowing the reactants to mix. After the reaction reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h), the vessels were removed from the calorimeter. Conversion from CpRu(COD)Cl to CpRu(dppe)Cl was found to be quantitative under these reaction conditions. The enthalpy of reaction, −26.6 ± 0.2 kcal/mol, represents the average of five individual calorimetric determinations. This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study. A tabulation of all calorimetric results (in solution) is presented in Table 1. These values include the enthalpy of solution of **1** in THF, +3.9 ± 0.1 kcal/mol.

## Results

**Synthesis and Thermochemistry.** On the basis of the available ruthenium diene thermochemical information,[13] the Cp*Ru(COD)Cl (**1**) complex was found to be one where the diene ligand is relatively weakly bound to the metal center. The thermodynamically weak and kinetically labile nature of the Ru−COD bond was exploited in a reaction which provides a facile entry into both syntheses and thermochemistry of CpRu(PP)Cl complexes.

$$CpRu(COD)Cl_{soln} + P\frown P_{soln} \xrightarrow[30\ °C]{THF} CpRu(P\frown P)Cl_{soln} + COD_{soln} \quad (3)$$

$$P\frown P = \text{chelating diphosphine}$$

**Table 2. Summary of Crystallographic Data for $CpRu(Ph_2PCH{=}CH)PPh_2)Cl$ (4)**

| | |
|---|---|
| empirical formula | $C_{31}H_{27}ClP_2Ru{\cdot}CH_2Cl_2$ |
| space group | $P\bar{1}$ (No. 2) |
| unit cell dimens | |
| $a$, Å | 10.344(2) |
| $b$, Å | 11.907(2) |
| $c$, Å | 13.183(1) |
| α, deg | 67.89(1) |
| β, deg | 76.52(1) |
| γ, deg | 85.96(2) |
| $V$, Å$^3$ | 1462.5(5) |
| $Z$, molecules/cell | 2 |
| density (calcd), g/cm$^3$ | 1.551 |
| wavelength, Å | 0.710 73 |
| monochromator | highly ordered graphite crystal |
| temp, K | 103(2) |
| abs corr | empirical (ψ-scan method) |
| diffractometer | Enraf-Nonius CAD 4 |
| scan type | $\theta-2\theta$ |
| data collcd | $-12 \le h \le 12$, $-14 \le k \le 14$, $0 \le l \le 15$ |
| $2\theta$ range, deg | 4.0−50.0 |
| no. of collcd reflns | 5151 |
| no. of ind reflns | 5140 |
| no. of obsd reflns | 4439 |
| $R_I$, % | 1.5 |
| $R_F$ (obsd data), % | 3.6 |
| $R_{wF}$, % | 5.1 |
| goodness of fit | 1.83 |
| no. of variables | 459 |

This type of diphosphine binding reaction appears to be general, and it was found to be rapid and quantitative for all ligands investigated by solution calorimetry at 30 °C in tetrahydrofuran. A compilation of diphosphine ligands and their respective enthalpy of reaction is given in Table 1. All reaction enthalpy values in Table 1 refer to the solution phase and were calculated from the experimentally determined $\Delta H$ using the previously determined enthalpy of solution for CpRu(COD)Cl.[22]

**Structure Determination of $CpRu(Ph_2P(CH{=}CH)PPh_2)Cl$ (4).** Crystal data and details concerning the experimental procedures are summarized in Table 2. A reguarly shaped yellow crystal having approximate dimensions 0.2 × 0.4 × 0.4 mm coated with Paratone N 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 Kα radiation at low temperatures under a stream of cold nitrogen gas generated by a locally modified Enraf-Nonius low temperature device. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with 20° < 2θ < 50°. The structure was solved using heavy-atom methods and refined by full matrix least-squares techniques. Hydrogen atoms in **4** were located in difference Fourier maps and included in the refinement with fixed temperature factors. Crystal data for **4** are summarized in Table 2, and selected bond distances and angles are listed in Tables 3. Positional and equivalent isotropic thermal parameters are presented in Table 4. All software used in the structure determinations were from the SPD package.[23]

## Discussion

Recent reports on the synthesis and high yield isolation of Cp*-based organoruthenium complexes provide

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(22) Cucullu, M. E.; Luo, L.; Fagan, P. J.; Jones, N.; Calabrese, J. C.; Nolan, S. P. Manuscript submitted for publication.

a direct thermodynamic entry into the solution calorimetric studies of ligand substitution in these systems.[24]

$$(Cp^{*}RuCl)_4 + 4\text{diene} \rightarrow 4Cp^{*}Ru(\text{diene})Cl \quad (4)$$

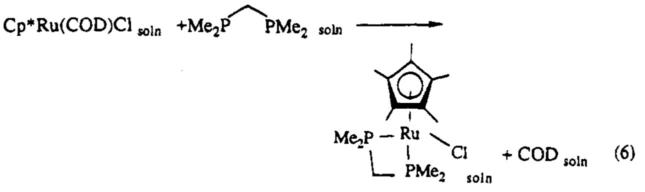
diene =
cyclohexadiene, norbornadiene, cyclooctadiene, etc.

Reaction 4 proceeds rapidly and quantitatively in THF at room temperature, and a solution calorimetric investigation of these reactions has already appeared.[13] From this solution thermochemical study, it was determined that cyclooctadiene (COD) was the more weakly bound diene to the Cp*RuCl moiety. The labile nature of these ruthenium–diene bonds has recently been exploited in the investigated of phosphine substitution reactions of the following type:[13]

$$Cp^{*}Ru(COD)Cl_{soln} + 2PMe_{3\ soln} \xrightarrow[30\ °C]{THF} Cp^{*}Ru(PMe_3)_2Cl_{soln} + COD_{soln} \quad (5)$$

$$\Delta H_{rxn} = -32.2 \pm 0.2\ \text{kcal/mol}$$

This same approach was tested for bidentate ligands and has proven quite efficient in leading to quantitative conversion of Cp*Ru(COD)Cl to Cp*Ru(PP)Cl complexes.[14]



(6)

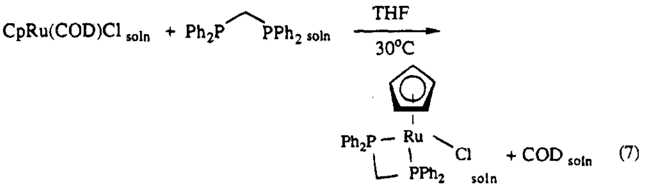
| Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for CpRu(Ph$_2$P(CH=CH)PPh$_2$)Cl (4) | | | |
|---|---|---|---|
| Bond Lengths | | | |
| Ru—Cl(1) | 2.4251(6) | Ru—P(1) | 2.2735(6) |
| Ru—P(2) | 2.2613(6) | Ru—C(1) | 2.229(3) |
| Ru—C(2) | 2.230(3) | Ru—C(3) | 2.167(3) |
| Ru—C(4) | 2.177(2) | Ru—C(5) | 2.240(3) |
| C(6)—C(7) | 1.325(4) | P(1)—C(6) | 1.821(3) |
| P(1)—C(20) | 1.821(3) | P(1)—C(26) | 1.836(3) |
| P(2)—C(7) | 1.827(3) | P(2)—C(8) | 1.831(3) |
| P(2)—C(14) | 1.827(3) | CpC—C(av) | 1.412(4) |
| Ru—Cp(centroid) | 1.854(1) | | |
| Bond Angles | | | |
| Cl(1)—Ru—P(1) | 87.60(2) | Cl(1)—Ru—P(2) | 92.96(2) |
| P(1)—Ru—P(2) | 83.45(2) | Ru—P(1)—C(6) | 109.94(9) |
| Ru—P(1)—C(20) | 119.65(8) | Ru—P(1)—C(20) | 119.65(8) |
| Ru—P(1)—C(26) | 118.53(8) | C(6)—P(1)—C(20) | 103.4(1) |
| C(6)—P(1)—C(26) | 100.3(1) | C(20)—P(1)—C(26) | 102.3(1) |
| Ru—P(2)—C(7) | 110.90(9) | Ru—P(2)—C(8) | 123.40(9) |
| Ru—P(2)—C(14) | 114.21(9) | C(7)—P(2)—C(8) | 102.1(1) |
| C(7)—P(2)—C(14) | 101.9(1) | C(8)—P(2)—C(14) | 101.6(1) |
| C(6)—P(1)—C(20) | 103.4(1) | Cl(1)—Ru-Cp(centroid) | 123.0(1) |
| P(1)—Ru—Cp(centroid) | 131.1(1) | P(2)—Ru—Cp(centroid) | 126.1(1) |

Table 4. Fractional Coordinates and Isotropic Thermal Parameters for CpRu(Ph$_2$P(CH=CH)PPh$_2$)Cl (4)[a]

| atom | *x* | *y* | *z* | *B* (Å$^2$) |
|---|---|---|---|---|
| Ru | 0.19702(2) | 0.24843(2) | 0.32724(2) | 1.204(5) |
| Cl(1) | −0.01036(8) | 0.25122(7) | 0.27050(6) | 2.01(2) |
| P(1) | 0.23882(8) | 0.43907(7) | 0.19588(6) | 1.33(2) |
| P(2) | 0.31538(8) | 0.19323(7) | 0.18662(6) | 1.23(2) |
| C(1) | 0.1046(4) | 0.1366(3) | 0.5051(3) | 2.30(7) |
| C(2) | 0.2222(4) | 0.0829(3) | 0.4736(3) | 2.31(7) |
| C(3) | 0.3262(3) | 0.1686(3) | 0.4430(3) | 2.15(7) |
| C(4) | 0.2709(3) | 0.2741(3) | 0.4589(2) | 1.96(7) |
| C(5) | 0.1310(4) | 0.2552(3) | 0.4991(3) | 2.12(7) |
| C(6) | 0.3222(3) | 0.4321(3) | 0.0606(3) | 1.57(6) |
| C(7) | 0.3580(3) | 0.3249(3) | 0.0557(2) | 1.49(6) |
| C(8) | 0.2540(3) | 0.0841(3) | 0.1406(2) | 1.47(6) |
| C(9) | 0.1328(3) | 0.0228(3) | 0.1972(3) | 2.30(7) |
| C(10) | 0.0866(4) | −0.0567(3) | 0.1587(3) | 3.07(8) |
| C(11) | 0.1567(4) | −0.0741(3) | 0.0641(3) | 2.58(7) |
| C(12) | 0.2774(4) | −0.0151(3) | 0.0086(3) | 2.05(7) |
| C(13) | 0.3263(3) | 0.0630(3) | 0.0461(3) | 1.79(7) |
| C(14) | 0.4791(3) | 0.1335(3) | 0.2063(2) | 1.52(6) |
| C(15) | 0.4920(3) | 0.0112(3) | 0.2702(3) | 1.73(7) |
| C(16) | 0.6119(4) | −0.0312(3) | 0.2971(3) | 2.26(7) |
| C(17) | 0.7202(3) | 0.0457(3) | 0.2609(3) | 2.44(8) |
| C(18) | 0.7097(4) | 0.1667(3) | 0.1959(3) | 2.46(8) |
| C(19) | 0.5899(3) | 0.2100(3) | 0.1688(3) | 2.03(7) |
| C(20) | 0.1011(3) | 0.5401(3) | 0.1634(2) | 1.51(6) |
| C(21) | 0.0200(3) | 0.5710(3) | 0.2489(3) | 0.93(7) |
| C(22) | −0.0832(3) | 0.6497(3) | 0.2281(3) | 2.28(8) |
| C(23) | −0.1093(3) | 0.6992(3) | 0.1211(3) | 2.21(8) |
| C(24) | −0.0311(3) | 0.6661(3) | 0.0361(3) | 2.21(7) |
| C(25) | 0.0733(3) | 0.5882(3) | 0.0567(3) | 1.88(7) |
| C(26) | 0.3563(3) | 0.5370(3) | 0.2113(2) | 1.48(6) |
| C(27) | 0.4710(3) | 0.4868(3) | 0.2465(3) | 1.94(7) |
| C(28) | 0.5615(3) | 0.5567(3) | 0.2608(3) | 2.28(7) |
| C(29) | 0.5371(4) | 0.6785(3) | 0.2413(3) | 2.24(7) |
| C(30) | 0.4248(4) | 0.7299(3) | 0.2053(3) | 2.20(7) |
| C(31) | 0.3352(3) | 0.6605(3) | 0.1890(3) | 1.80(7) |

[a] Numbers in parentheses are the estimated standard deviations.

In order to test the thermodynamic effects of ancillary ligand modification and considering recent reports on the catalytic role of the CpRu(phosphine) fragment,[25,26] a solution calorimetric investigation was performed on the related CpRu(PP)Cl complexes. A facile entry into the thermochemistry of CpRu(PP)Cl complexes is made possible by the quantitative and rapid nature of reactions such as eq 7. The enthalpies of ligand substitution for chelating diphosphine ligands are presented in Table 1. An apparent trend in examining Table 1 is that reactions involving alkyl substituted phosphines (more basic phosphines) prove to be more exothermic, resulting in more thermodynamically stable complexes. This trend also exists in the related Cp* system.[13,14]



(7)

$\Delta H_{rxn}$ = -19.4 ± 0.2 kcal/mol

A single crystal diffraction study was undertaken in order to examine the structural features of **4**. The ORTEP diagram of **4** shows a short C(6)—C(7) distance, 1.325 Å, indicative of a double bond. The structure of a related complex, CpRu(Ph$_2$PCH(Me)CH$_2$PPh$_2$)Cl (**5**),

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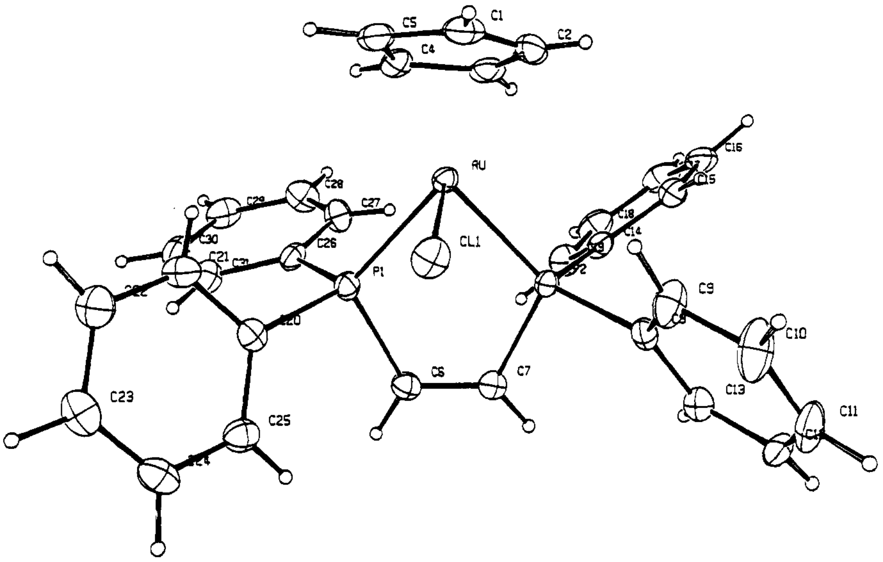


**Figure 1.** ORTEP drawing of CpRu(Ph$_2$P(CH=CH)PPh$_2$)Cl (**4**) with ellipsoids drawn with 50% probability.

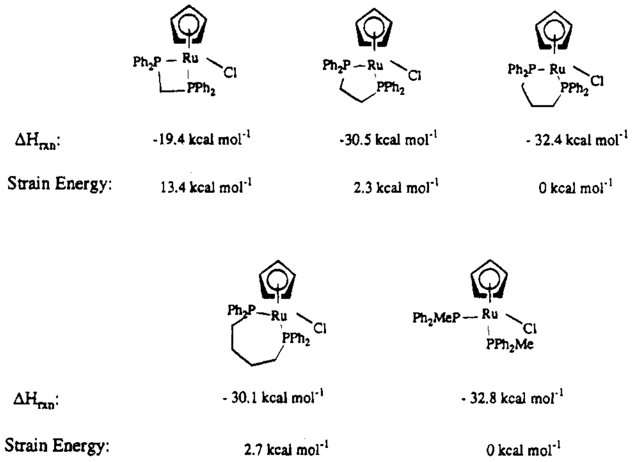
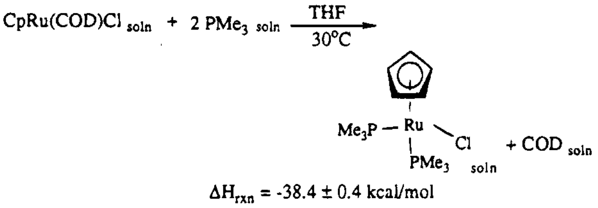


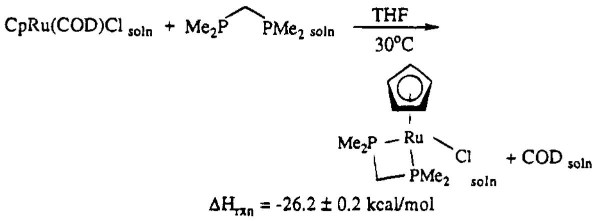
**Figure 2.** Enthalpies of reaction and ring strain estimates for metallacycles in the CpRu(PP)Cl system.

has previously been elucidated.[27] The related C(6)—C(7) distance in **5** is 1.525 Å and is the only significant difference between all common bond distances and angles for the two structures. Structural studies aimed at clearly addressing the effects of the tether length on the stability of the complexes are in progress.

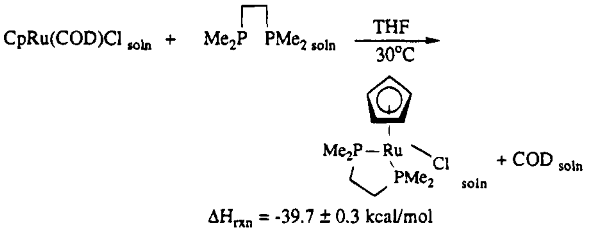
The strain energies in cyclic organic compounds have been extensively investigated. Ring strain estimates for four-, five-, and six-membered rings are on the order of 26, 6, and 0 kcal/mol, respectively.[28] Incorporation of a metal center into the chelate structures, shown below, produces four- to seven-membered metallacyclic rings with enthalpies of reaction as shown in Figure 2. The five-, six-, and seven-membered ring complexes based on 1,2-(diphenylphosphino)ethane (dppe), 1,2-(diphenylphosphino)propane) (dppp), and 1,2-(diphenylphosphino)butane (dppb) are most stable, their enthalpies of reaction being of the same order of magnitude as 2 equiv of PPh$_2$Me. The least stable of the metallacycles investigated is the four-membered ring where ring strain is estimated as 13.4 kcal/mol. This 13.4 kcal/mol strain energy is on the same order of magnitude as strain energy estimates for a thorium metallacyclobutane complex (10 kcal/mol).[29] This energy is also in relatively good agreement with more closely related four-membered organomolybdenum, (Ph$_2$PCH$_2$PPh$_2$)Mo(CO)$_4$ (8.3 kcal/mol),[30] organoiron, (Ph$_2$PCH$_2$PPh$_2$)Fe(CO)$_3$ (12.6 kcal/mol),[12b] and Cp*Ru(Ph$_2$PCH$_2$PPh$_2$)Cl (10 kcal/mol)[14] complexes. An estimate for the ring strain energies for the four- and five-membered metallacyclic complexes with phosphine ligands bearing alkyl groups is made possible by comparing their relative enthalpies of reaction with the enthalpy of reaction 8.



(8)



(9)



(10)

Here again a difference of ca. 13 kcal/mol exists between the dmpm and the bis(trimethylphosphine) complexes. The very small enthalpy difference between the five-membered metallacycle and the bis(monodentate) phosphine indicates no appreciable strain energy. In spite

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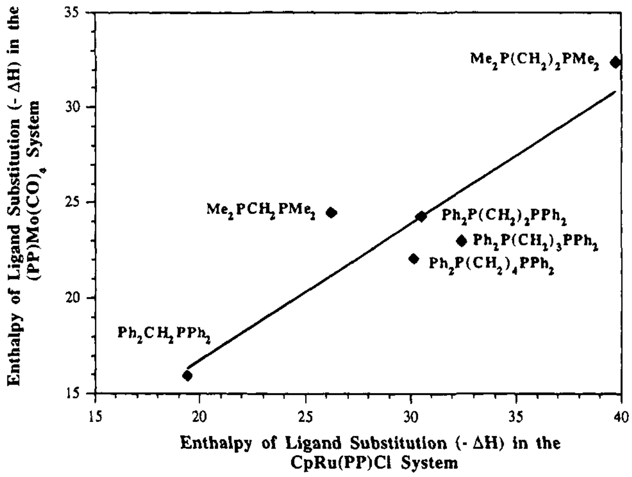

**Figure 3.** Comparison between enthalpies of ligand substitution in the CpRu(PP)Cl and $(PP)Mo(CO)_4$ systems. $R = 0.91$, slope = 0.71.

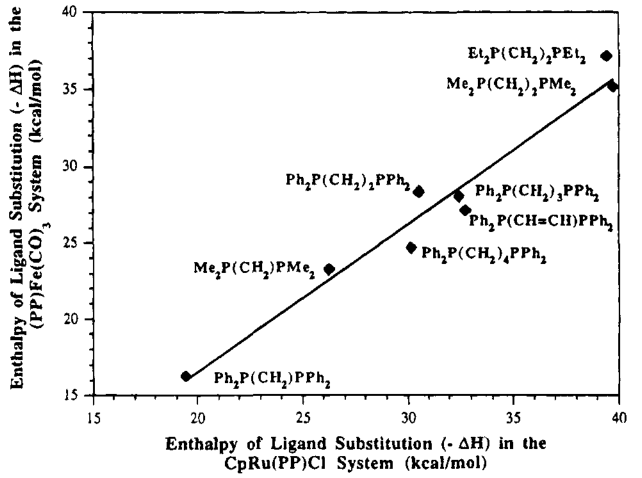

**Figure 4.** Comparison between enthalpies of ligand substitution in the CpRu(PP)Cl and $(PP)Fe(CO)_3$ systems. $R = 0.98$, slope = 0.98.

of the presence of a double bond in the Ru–dppv complex, rendering the structure more rigid, no ring strain appears to be present in this five-membered metallacycle.

The present enthalpy data allow for comparisons of the entire series with other bidentate phosphine substitution reactions investigated by solution calorimetry. The first such study examined by Hoff and co-workers was focused on the $(PP)Mo(CO)_4$ system.[30] When the relative enthalpy data for a series of ligands common to the two systems are compared, a linear fit ($R = 0.91$) is obtained (Figure 3). This may be surprising in view of the different number of available coordination sites in the two systems. The relative order of stability for the molybdenum system is generally the same as the one observed for the present ruthenium data. A better comparison is the one with the $(PP)Fe(CO)_3$ system. Similar steric and electronic trends are expected to be present in a comparison between members of a same chemical group. This relationship is presented in Figure 4. This relationship exhibits a remarkable fit ($R = 0.98$) considering the difference in ancillary ligations between the two systems. The exact reasons for such a good correlation are at this time unclear. A more informative comparison exists between the present system and the recently investigated Cp*Ru(PP)Cl system. A direct comparison of these enthalpies of reaction is illustrated in Figure 5 and shows the presence of a good correlation between the two sets of data. On average there exists a difference between enthalpies of reaction involving the same ligand of 2.9 kcal/mol, favoring the Cp system. We take this thermodynamic preference as an illustration of the increased metal basicity on going from a Cp to a Cp* ancillary ligation. This point has previously been described in our report on the $CpRu(PR_3)_2Cl$ system[22] where the average difference was 5.9 kcal/mol, favoring the Cp system. The smaller difference here can be attributed to the tether which effectively locks the bidentate ligand into a specific configuration, therefore inhibiting an increase in the R–Ru–P angle which could lead to greater orbital overlap with the metal orbitals and therefore to the formation of stronger bonds. This point is actually nicely represented by the seven-membered ring metallacycle where a greater tether length, being able to afford a greater bite to the phosphine, leads to an enthalpy of reaction some 5.4 kcal/mol more exothermic than its Cp* parent; this difference is equal to the average enthalpy difference between the Cp and Cp* bis(monodentate) ligand values, where no strain exists. Steric and electronic factors both appear to play important roles in determining the overall thermodynamic stability of these and other metallacyclic complexes. The offered comparisons with all other known systems clearly illustrate that electronic and steric factors affecting the thermodynamic stability of metallacyclic complexes may in fact be general.

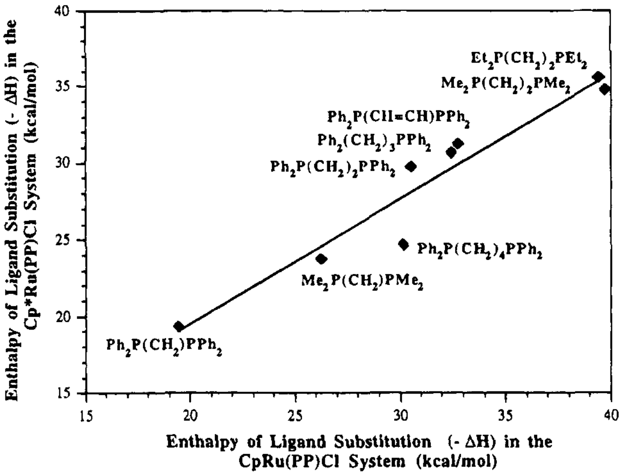

**Figure 5.** Comparison between enthalpies of ligand substitution in the CpRu(PP)Cl and Cp*Ru(PP)Cl systems. $R = 0.96$, slope = 0.82.

## Conclusion

A relative enthalpy scale has been established for the binding of chelating phosphine ligands to the CpRuCl moiety. The labile nature of the COD ligand in CpRu(COD)Cl was used to gain access into the thermochemistry of ligand substitution for bidentate arsine/phosphine ligands. Reactions of bidentate ligands with **1** also shows this reaction to be of synthetic use for isolation of complexes of formulation CpRu(PP)Cl. The ring strain energies present in these metallacycles have been estimated from enthalpy data for the monodentate system. Only the four-membered ring complex displays any considerable strain energy and is on the order of

13 kcal/mol. The overall enthalpy of reaction trend is similar to results recently obtained for organoiron and related organoruthenium systems. The increased exothermicity in enthalpies of reaction is understood as an illustration of the increased metal basicity in this CpRu(PP)Cl system over its Cp* relative. Further thermochemical and mechanistic investigations focusing on this and related systems are presently underway.

**Acknowledgment.** The donors of the Petroleum Research Fund, administered by the American Chemical Society, the Board of Regents of the Louisiana Education Quality Support Fund (LEQSF(RF/1993-96)-RD-A-47), and the National Science Foundation (Grant No. CHE-9305492) are gratefully acknowledged for support of this research. The authors are indebted to Johnson-Matthey for the generous loan of ruthenium salts.

**Supplementary Material Available:** Tables of atomic coordinates, selected distances and angles, anisotropic thermal displacement parameters, and hydrogen bond distances for **4** (13 pages). Ordering information is given on any current masthead page.

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