Enthalpies of Reaction of Cp*Ru(COD)Cl (Cp* = η^5-C_5Me_5; COD = Cyclooctadiene) with Chelating Tertiary Phosphine Ligands. Solution Thermochemical Investigation of Ligand Substitution and Ring Strain Energies in Cp*Ru(PP)Cl Complexes

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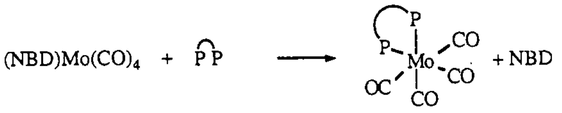
The enthalpies of reaction of Cp*Ru(COD)Cl (Cp* = η^5-C_5Me_5: COD = cyclooctadiene) with a series of bidentate ligands, leading to the formation of Cp*Ru(PP)Cl complexes, have been measured by anaerobic solution calorimetry in THF at 30.0 °C. The overall relative order of stability established for these complexes is as follows: dppm < arphos, dmpm, dppb < dppe, dppp, dppv < dmpe, depe. Comparisons of enthalpies of reaction with monodentate phosphine ligands afford a quantitative treatment of ring strain enthalpies in these organoruthenium metallacyclic compounds. The ring strain energies exhibited by four- and seven-membered metallacycles are on the order of 10 and 5 kcal/mol, respectively. Results of a single crystal X-ray diffraction study performed on one of the metallacyclic complexes, Cp*Ru(arphos)Cl, are reported. Comparisons with other 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] Complexation of chelating diphosphine ligands to transition metal catalysts has been shown to influence product selectivities. One dramatic example is the different linear to branched product ratios obained when monodentate *versus* bidentate phosphine ligands are bound to metals used to mediate the oxo process.[2] Entropy must play a role in these metal-chelating diphosphine systems since creation of a vacant site at the metal center by metal–phosphine bond breakage leaves the chelating ligand still anchored to the metal by the other phosphine moiety which can therefore easily reattach to the metal. Another 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] Hoff and coworkers have examined, using solution calorimetric techniques, the enthalpy of reaction and ring strain energies associated with molybdenum-chelating disphosphine binding interactions:[7]



(1)

NBD = norbornadiene

However, few solution thermochemical investigations

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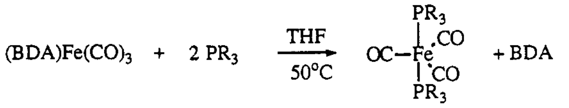
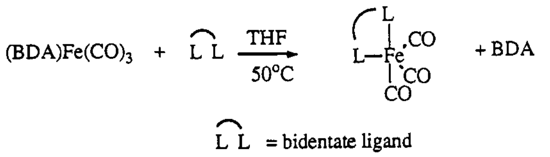
focusing on complexes involving group 8 metal–ligand bonds have been performed.[8–11] Our initial efforts in this area focused on substitution reactions of mono- and diphosphine ligands with (BDA)Fe(CO)$_3$ (BDA = PhCH=CHC(O)Me, benzylideneacetone) (eqs 2 and 3).[12]



(2)



(3)

Combining the two studies allowed the determination of an estimate for the ring strain enthalpy in the iron metallacyclic complexes. Furthermore, we most recently investigated the enthalpy of reaction associated with ligand displacement in a ruthenium system:[13]

$$\mathrm{Cp^*Ru(COD)Cl} + 2\mathrm{PR_3} \rightarrow \mathrm{Cp^*Ru(PR_3)_2Cl} + \mathrm{COD} \tag{4}$$

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

We now wish to expand on our solution thermochemical studies of organo group 8 complexes and quantitatively address the ring strain energy present in organoruthenium metallacyclic systems by focusing on the enthalpies of reaction of Cp*Ru(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$_3$CN (P$_2$O$_5$). 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[14] or the enthalpy of solution of KCl in water.[15] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[16] 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. (Cp*RuCl)$_4$ and Cp*Ru(diene)Cl were synthesized as reported in the literature.[17c] Experimental synthetic procedures, leading to isolation of crystalline materials, for all other complexes are reported below.

Cp*Ru(PMe$_2$CH$_2$PMe$_2$)Cl. A 25-mL flask was charged with 300 mg (0.79 mmol) of Cp*Ru(COD)Cl, 10 mL of dried THF, and 300 μL (2.0 mmol) of PMe$_2$CH$_2$PMe$_2$. After stirring for 1 h, the solvent was removed in vacuum. A 10-mL mixture of hexane and THF (8:2) 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 214-mg (66%) yield. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.39 (t, 6 H, –CH$_3$), 1.53 (t, 6 H, –CH$_3$), 1.74 (t, 15 H, Cp*), 3.15 (m, 1 H, –CH$_2$–), and 3.34 (m, 1H, –CH$_2$–). Anal. Calcd for RuClP$_2$C$_{15}$H$_{29}$: C, 44.17; H, 7.16. Found: C, 44.53; H, 7.26.

Cp*Ru(PMe$_2$(CH$_2$)$_2$PMe$_2$)Cl. A 25-mL flask was charged with 250 mg (0.66 mmol) of Cp*Ru(COD)Cl, 10 mL of dried THF, and 400 μL (2.4 mmol) of PMe$_2$(CH$_2$)$_2$PMe$_2$. After stirring for 2 h, the solvent was removed in vacuum. A 5-mL mixture of solvents (hexane and THF in 3:2 ratio) was vacuum transferred to the cooled (−78 °C) flask containing the residue. This solution was allowed to warm to room temperature. After filtration, the solution was very slowly cooled to −78 °C. Cold filtration afforded orange crystals that were washed with a small amount of hexane and dried in vacuum, giving a 58-mg (21%) yield. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.34 (m, 6 H, –CH$_3$); 1.44 (m, 6 H, –CH$_3$), 1.66 (t, 2 H, –CH$_2$CH$_2$–), 1.71 (t, 15 H, Cp*), 1.75 (t, 2 H, –CH$_2$-CH$_2$–). Anal. Calcd for RuClP$_2$C$_{16}$H$_{31}$: C, 45.55; H, 7.41. Found: C, 45.75; H, 7.03.

Cp*Ru(PEt$_2$(CH$_2$)$_2$PEt$_2$)Cl. A 25-mL flask was charged with 300 mg (0.79 mmol) of Cp*Ru(COD)Cl, 10 mL of THF, and 300 μL (1.3 mmol) of PEt$_2$(CH$_2$)$_2$PEt$_2$. After stirring for 2 h, the solvent was removed in vacuum and about 5 mL of the solvent mixture (hexane and THF (3:2)) was vacuum transferred to the cooled (−78 °C) flask containing the solid product. This mixture was warmed to 40 °C, stirred, and filtered. The saturated solution was very slowly cooled to −78 °C and kept at this temperature overnight. After filtration, the collected orange needles were washed with a small amount of hexane and dried in vacuum, giving a 220-mg (58%) yield. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.05 (m, 12 H, –CH$_3$), 1.51 and 1.55 (br m, 8 H, –CH$_2$CH$_3$), 1.70 (s, 15 H, Cp*), 2.02 (m, 4 H, –CH$_2$CH$_2$–). Anal. Calcd for RuClP$_2$C$_{20}$H$_{39}$: C, 50.26; H, 8.22. Found: C, 50.21; H, 8.17.

Cp*Ru(PPh$_2$(CH$_2$)$_2$AsPh$_2$)Cl. A 25-mL flask was charged with 300 mg (0.79 mmol) and Cp*Ru(COD)Cl, 15 mL of THF, and 300 μL (1.59 mmol) of PPh$_2$CH$_2$CH$_2$AsPh$_2$. After stirring for 24 h, the solution was filtered, the solvent was removed in vacuum, and 5 mL of hexane was vacuum transferred to the cooled (−78 °C) flask containing the solid product. Then this solution was warmed to 40 °C, stirred for 15 min, and filtered. At room temperature, this solution was kept in an acetone bath overnight. After filtration, the orange red crystals were washed with a small amount of hexane and dried in vacuum, giving a 380-mg (72%) yield. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.47 (s, 15 H, Cp*), 2.36 (m, 2 H, –CH$_2$CH$_2$–), 2.62 (m, 2 H, –CH$_2$-CH$_2$–), 7.07 (d, 2 H, –C$_6$H$_5$), 7.31 (m, 14 H, –C$_6$H$_5$), 7.72 (m, 4 H, –C$_6$H$_5$). Anal. Calcd for RuAsClPC$_{36}$H$_{39}$: C, 60.55; H, 5.50. Found: C, 60.64; H, 5.24.

Cp*Ru(PPh$_2$(CH$_2$)PPh$_2$)Cl. A 25-mL flask was charged with 270 mg (0.71 mmol) of Cp*Ru(COD)Cl, 15 mL of dried THF, and 625 mg (2.38 mmol) of PPh$_2$CH$_2$PPh$_2$. After stirring for 3 h the solvent was removed in vacuum and an 8-mL solvent mixture of hexane and THF (2:6) was vacuum transferred to the cooled (−78 °C) solid product. This was warmed to room temperature, stirred for 15 min, and filtered. Then at room temperature, the solution was kept in an acetone bath overnight to let the crystals slowly

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grow. After filtration, the orange crystals were washed with a small amount of hexane and dried in vacuum, giving a 230-mg (44%) yield. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.66 (s, 15 H, Cp*), 4.18 (m, 1 H, $-CH_2-$), 4.94 (m, 1 H, $-CH_2-$), 7.27 (m, 16 H, *o*- and *m*-C_6H_5), 7.53 (t, 4 H, *p*-C_6H_5). Anal. Calcd for $RuClP_2C_{35}H_{37}$: C, 64.07; H, 5.68. Found: C, 63.95; H, 5.34.

Cp*Ru(PPh$_2$(CH$_2$)$_2$PPh$_2$)Cl. A 25-mL flask was charged with 250 mg (0.66 mmol) of Cp*Ru(COD)Cl, 10 mL of dry THF, and 370 μL (0.93 mmol) $PPh_2(CH_2)_2PPh_2$. After stirring for 70 min, the solvent was removed in vacuum and a 6-mL mixture of hexane and THF (2:1) was vacuum transferred to the cooled (−78 °C) solid product. This was warmed to room temperature, stirred for 15 min, and filtered. Then the solution was slowly cooled to −30 °C and kept overnight at this temperature to let the crystals grow. After filtration, the red orange crystals were washed with a small amount of hexane and dried in vacuum, giving a 200-mg (46%) yield. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.41 (s, 15 H, Cp*), 2.14 (m, 2 H, $-CH_2CH_2-$), 2.66 (m, 2 H, $-CH_2CH_2-$), 7.20 (t, 8 H, *m*-C_6H_5), 7.31 (d, 8 H, *o*-C_6H_5), 7.69 (t, 4 H, *p*-C_6H_5). Anal. Calcd for $RuClP_2C_{36}H_{39}$: C, 64.52; H, 5.87. Found: C, 64.28; H, 5.89.

Cp*Ru(PPH$_2$(CH$_2$)$_2$PPh$_2$)Cl. A 25-mL flask was charged with 300 mg (0.79 mmol) of Cp*Ru(COD)Cl, 10 mL of dried THF, and 370 mg (0.90 mmol) of $PPh_2(CH_2)_3PPh_2$. After stirring for 2 h, the solvent was removed in vacuum and an 8-mL solvent mixture (hexane and THF (2:6)) was vacuum transferred to the cooled (−78 °C) reaction flask. This mixture was warmed to room temperature, stirred for 15 min, and filtered. Then the solution was kept in an acetone bath overnight. After filtration, the dark red crystals were washed with a small amount of hexane and dried under vacuum, giving a 290-mg (53%) yield. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.28 (s, 15 H, Cp*), 1.50 (m, br w, 2 H, $-CH_2CH_2CH_2-$), 2.35 (m, 2 H, $-CH_2CH_2CH_2-$), 3.17 (m, 2 H, $-CH_2CH_2CH_2-$), 7.23 (m, 16 H, *o*- and *m*-C_6H_5), 7.62 (t, 4 H, *p*-C_6H_5). Anal. Calcd for $RuClP_2C_{37}H_{41}$: C, 64.95; H, 6.04. Found: C, 65.07; H, 6.14.

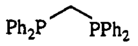
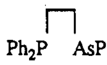
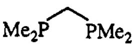
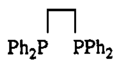
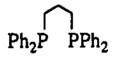
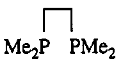
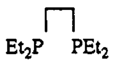
Cp*Ru(PPh$_2$(CH$_2$)$_4$PPh$_2$)Cl. A 25-mL flask was charged with 300 mg (0.79 mmol) of Cp*Ru(COD)Cl, 15 mL of dried THF, and 470 μL (1.1 mmol) of $PPh_2(CH_2)_4PPh_2$. After stirring for 70 min, the solvent was removed in vacuum and a 5-mL solvent mixture (hexane and THF (1:4)) was vacuum transferred to the cooled (−78 °C) solid product. Then it was allowed to warm to room temperature, stirred for 15 min, and filtered, then the solution was very slowly cooled to −78 °C and kept at this temperature overnight. After cold filtration, the orange crystals were washed with a small amount of hexane and dried in vacuum, giving a 210-mg (57%) yield. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.11 (s, 15 H, Cp*), 1.29 (m, br w, 2 H, $-CH_2CH_2CH_2CH_2-$), 1.76 (m, br w, 2 H, $-CH_2CH_2CH_2CH_2-$), 1.99 (m, br w, 2 H, $-CH_2CH_2CH_2CH_2-$), 3.33 (m, 2 H, $-CH_2CH_2CH_2CH_2-$), 7.27 (s, 6 H, $-C_6H_5$), 7.43 (s, 10 H, $-C_6H_5$), 7.60 (s, 4 H, $-C_6H_5$). Anal. Calcd for $RuClP_2C_{38}H_{43}$: C, 65.37; H, 6.21. Found: C, 65.52; H, 6.33.

Cp*Ru(PPh$_2$(CH=CH)PPh$_2$)Cl. A 25-mL flask was charged with 300 mg (0.79 mmol) of Cp*Ru(COD)Cl, 10 mL of dried THF, and 320 mg (0.82 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 THF and toluene (2:6) 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 washed with a small amount of hexane and dried in vacuum, giving a 190-mg (35%) yield. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.45 (s, 15 H, Cp*), 7.15 (t, 4 H, $-C_6H_5$), 7.32 (m, 12 H, $-C_6H_5$), 7.38 (m, 1 H, $-CH{=}CH-$), 7.58 (m, 1 H, $-CH{=}CH-$), 7.70 (t, 4 H, $-C_6H_5$). Anal. Calcd for $RuClP_2C_{36}H_{37}$: C, 64.71; H, 5.58. Found: C, 64.39; H, 5.28.

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

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

$$Cp^*Ru(COD)Cl_{(soln)} + \overset{\frown}{PP}_{(soln)} \xrightarrow[30\,°C]{THF} Cp^*Ru(\overset{\frown}{PP})Cl_{(soln)} + COD_{(soln)}$$

	$\overset{\frown}{PP}$	$-\Delta H_{rxn}$[a]
dppm		19.4 (0.2)
arphos		23.7 (0.3)
dmpm		23.8 (0.3)
dppb		24.7 (0.3)
dppe		29.8 (0.2)
dppp		30.7 (0.2)
dppv		31.3 (0.2)
dmpe		34.8 (0.2)
depe		35.6 (0.3)

[a] Enthalpies of reaction are reported with 95% confidence limits.

Calorimetric Measurement of the Reaction between Cp*Ru(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 Cp*Ru(COD)Cl was accurately weighed into the lower vessel, it was closed and sealed with 1.5 mL of mercury. A stock solution (4 mL) 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 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, thereby 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 Cp*Ru(COD)Cl to Cp*Ru(dppe)Cl was found to be quantitative under these reaction conditions. The enthalpy of reaction, −24.9 ± 0.1 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 is presented in Table 1.

Crystallographic Study of Cp*Ru(Ph$_2$As(CH$_2$)$_2$PPh$_2$)Cl. An orange crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm^3, grown by slow solvent evaporation from a tetrahydrofuran solution, was mounted on an Enraf-Nonius CAD 4, and data were collected using Mo Kα radiation at 110 K. The structure was solved by direct methods and refined by full-matrix least-squares techniques. The crystal data and data collection parameters are summarized in Table 2. The structure contains

Table 2. Summary of Crystallographic Data for $Cp^*Ru(Ph_2As(CH_2)_2PPh_2)Cl$

empirical formula	$C_{36}H_{39}PAsClRu$
space group	$P2_1/n$
unit cell dimens	
a, Å	17.356(4)
b, Å	11.461(3)
c, Å	31.223(10)
α, deg	90
β, deg	91.12(2)
γ, deg	90
V, Å^3	6209(4)
Z, molecule/cell	8
density (calcd), g/cm^3	1.754
wavelength, Å	0.710 73
monochromator	highly ordered graphite crystal
temp, K	110(2)
abs corr	empirical (ψ-scan method)
diffractometer	Enraf-Nonius CAD 4
scan type	θ–2θ
data collected	$+h,+k,\pm l$
2θ range, deg	2.0–50.0
no. of collected reflns	11 927
no. of indep reflns	10 540
no. of obsd reflns	6437
R_f (obsd data), %	4.4
R_{wF}, %	5.8
goodness of fit	1.65
no. of variables	721

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) and Torsion Angles (deg) for $Cp^*Ru(Ph_2As(CH_2)_2PPh_2)Cl$

	Bond Lengths		
Ru(1)–As(1)	2.365 (1)	Ru(2)–As(2)	2.376 (1)
Ru(1)–P(1)	2.343 (1)	Ru(2)–P(2)	2.320 (1)
Ru(1)–Cl(1)	2.450 (2)	Ru(2)–Cl(2)	2.441 (2)
Ru(1)–C(av)	2.210 (5)	Ru(2)–C(av)	2.993 (5)
As(1)–C(1)	1.943 (7)	As(2)–C(2)	1.937 (6)
As(1)–C(11)	1.933 (6)	As(2)–C(31)	1.936 (6)
As(1)–C(21)	1.923 (6)	As(2)–C(41)	1.927 (6)
P(1)–C(3)	1.868 (6)	P(2)–C(4)	1.875 (6)
P(1)–C(51)	1.868 (6)	P(2)–C(71)	1.850 (6)
P(1)–C(61)	1.862 (7)	P(2)–C(81)	1.859 (6)
C(1)–C(3)	1.532 (9)	C(2)–C(4)	1.544 (8)
Ru–Cp*(1)(centroid)	1.848 (4)	Ru–Cp*(2)(centroid)	1.827 (4)
	Bond and Torsion Angles		
As(1)–Ru(1)–P(1)	80.52 (4)	As(2)–Ru(2)–P(2)	82.31 (4)
As(1)–Ru(1)–Cl(1)	89.78 (5)	As(2)–Ru(2)–Cl(2)	88.77 (4)
P(1)–Ru(1)–Cl(1)	85.11 (5)	P(2)–Ru(2)–Cl(2)	82.44 (5)
Ru(1)–As(1)–Cl(1)	110.5 (2)	Ru(2)–As(2)–Cl(2)	110.3 (2)
As(1)–C(1)–C(3)	109.6 (5)	As(2)–C(2)–C(4)	109.0 (4)
P(1)–C(3)–C(1)	110.1 (5)	P(2)–C(4)–C(2)	109.6 (4)
Ru(1)–P(1)–C(3)	106.3 (3)	Ru(2)–P(2)–C(4)	107.9 (2)
As(1)–Ru(1)–Cp*(1)	130.2 (4)	As(2)–Ru(2)–Cp*(2)	130.7 (4)
P(1)–Ru(1)–Cp*(1)	136.6 (4)	P(2)–Ru(2)–Cp*(2)	135.7 (4)
Cl(1)–Ru(1)–Cp*(1)	119.2 (3)	Cl(2)–Ru(2)–Cp*(2)	120.6 (3)
As(1)–C(1)–C(3)–P(1)	36.6 (7)	As(2)–C(2)–C(4)–P(2)	42.6 (6)

two independent molecules in the asymmetric unit. Inspection of thermal parameters after refinement indicated a disorder resulting from a partial interchange of the phosphorus and arsenic atoms in both independent molecules. This disorder was modeled in the least-squares refinement by including both a phosphorus and an arsenic atom at each site, constrained to have the same positional and thermal parameters. The occupancy parameters of As(1) and As(2), c(As1) and c(As2) respectively, were refined, with the constraints $c(P1) = c(As1)$; $c(P1') = c(As1') = 1 - c(As1)$; $c(P2) = c(As2)$; and $c(P2') = c(As2') = 1 - c(As2)$. The resulting occupancies were $c(As1) = 0.708(6)$ and $c(As2) = 0.806(6)$. Selected bond distances, bond angles, and torsion angles are listed in Table 3. All software used in the structure determination was from the SPD package.[18]

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 was 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 entryway into both syntheses and thermochemistry of Cp*Ru(PP)Cl complexes.

$$Cp^*Ru(COD)Cl_{(soln)} + \mathrm{P}\frown\mathrm{P}_{(soln)} \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(\mathrm{P}\frown\mathrm{P})Cl_{(soln)} + COD_{(soln)} \quad (5)$$

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

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 are listed in Table 1. All reaction enthalpy values refer to solution phase values including the previously determined enthalpy of solution of Cp*Ru(COD)Cl.[13]

Diffraction Study. Inspection of Figure 1 and Table 3 shows the geometries of the two independent molecules found in the unit cell to be very similar with the exception of the orientation of the phenyl rings. The partial disorder resulting from interchange of As and P atom positions precluded a detailed analysis of the bond distances in the ring. Both rings, however, show similar conformations with a torsion angle of ca. 40° about the C–C bond. In both rings, both carbon atoms lie on the same side of the plane defined by the Ru, As, and P atoms as the Cl atom, with the C atom bonded to the P atom showing the greatest deviation from the plane.

Discussion

Recent reports on the synthesis and high yield isolation of organoruthenium complexes provide a direct thermodynamic entryway into the solution calorimetric studies of ligand substitution in these systems.[17] Fagan and coworkers have communicated results illustrating the easy access to complexes of the type Cp*Ru(diene)Cl from the tetrameric $(Cp^*RuCl)_4$ compound.[17c]

$$(Cp^*RuCl)_4 + 4\text{diene} \rightarrow 4Cp^*Ru(\text{diene})Cl \quad (6)$$

diene = cyclohexadiene, norbornadiene, cyclooctadiene, etc.

Reaction 6 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 one of the more weakly bound dienes to the Cp*RuCl moiety. The labile nature of these ruthenium–diene bonds was exploited in the investigation

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

(18) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1982.

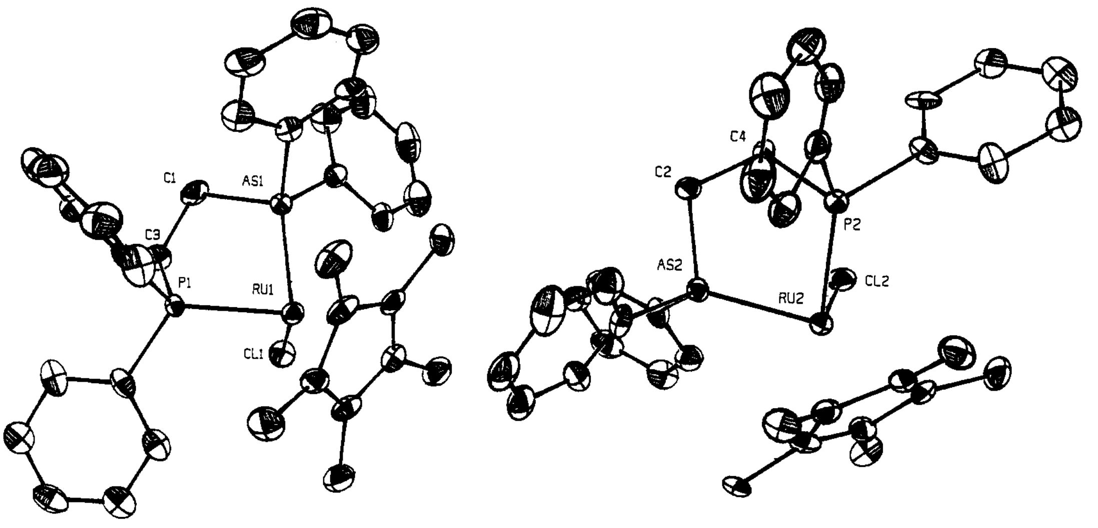


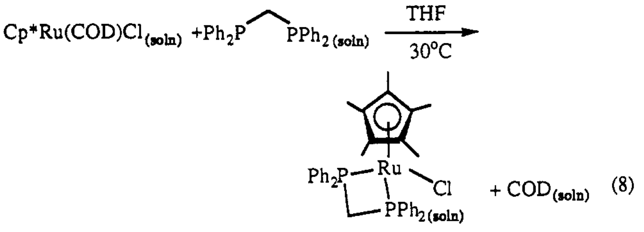
Figure 1. ORTEP drawing of Cp*Ru(Ph₂P(CH₂)₂AsPh₂)Cl with ellipsoids at 50% probability.

of phosphine substitution reactions of type[19]

$$\mathrm{Cp^*Ru(COD)Cl_{(soln)} + 2PMe_{3(soln)} \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(PMe_3)_2Cl_{(soln)} + COD_{(soln)}} \quad (7)$$

$$\Delta H_{\mathrm{rxn}} = -32.2 \pm 0.4\ \mathrm{kcal/mol}$$

The same approach was tested for bidentate ligands and has proven quite efficient in leading to quantitative conversion of 1 to Cp*Ru(PP)Cl complexes.



$$\mathrm{Cp^*Ru(COD)Cl_{(soln)} + Ph_2P\frown PPh_{2\,(soln)} \xrightarrow[30^\circ C]{THF}} \quad \mathrm{+ COD_{(soln)}} \quad (8)$$

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

The enthalpies of ligand substitution for chelating diphosphine ligands are presented in Table 1. A trend that is quite clear 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. The substitution of one mixed phosphine–arsine ligand (arphos) has been investigated. The measured enthalpy of reaction is 6.1 kcal/mol less exothermic for arphos than for the symmetrical diphosphine parent, dppe. This same difference of 6.1 kcal/mol is found to be the difference between the average Ru–As vs Ru–P bond in the thermochemical investigation of monodentate ligands.[13] This trend of arsenic based ligands being weaker donors has been observed in other organometallic solution calorimetric investigations.[7,20]

$$\mathrm{Cp^*Ru(COD)Cl_{(soln)} + 2AsEt_{3(soln)} \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(AsEt_3)_2Cl_{(soln)} + COD_{(soln)}} \quad (9)$$

$$\Delta H_{\mathrm{rxn}} = -15.0 \pm 0.2\ \mathrm{kcal/mol}$$

$$\mathrm{Cp^*Ru(COD)Cl_{(soln)} + 2PEt_{3(soln)} \xrightarrow[30\ ^\circ C]{THF} Cp^*Ru(PEt_3)_2Cl_{(soln)} + COD_{(soln)}} \quad (10)$$

$$\Delta H_{\mathrm{rxn}} = -27.2 \pm 0.2\ \mathrm{kcal/mol}$$

An X-ray single crystal diffraction study was undertaken to clarify the structural features associated with the Cp*Ru(PPh₂(CH₂)₂AsPh₂)Cl complex. The structure, whose ORTEP representation is provided in Figure 1, clearly shows the complex to be monomeric in the solid state. The crystal structure determination was complicated by the existence of two independent molecules in the unit cell. Comparisons with other Cp*Ru(PP)Cl complexes are made difficult in view of the scarcity of structural information concerning these compounds. Such a structural study focusing on Cp*Ru(PP)Cl and Cp*Ru(PR₃)₂Cl is presently being performed.[21]

The strain energies in cyclic organic compounds have been extensively investigated. Ring strain estimates for four-, five-, and six-membered hydrocarbon rings are on the order of 26, 6, and 0 kcal/mol, respectively.[22] Incorporation of a metal center into the chelate structures, shown below, produce four- to seven-membered metallacyclic rings with enthalpies of reaction as shown in Figure 2.

The five- and six-membered ring complexes based on 1,2-(diphenylphosphino)ethane (dppe) and 1,2-(diphenylphosphino)propane (dppp) are most stable, their enthalpies of reaction being of the same order of magnitude as that of 2 equiv of PPh₂Me. The seven-membered ring is less stable with an enthalpy of reaction 4.7 kcal/mol less than that of 2 equiv of PPh₂Me, a difference which is attributed to the ring strain energy. The attempted

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(19) The labile nature of the COD ligand in the related CpRu(COD)Cl complexes has been examined: (a) Albers, M. O.; Oosthuizen, H. E.; Robinson, D. J.; Shaver, A.; Singleton, E. *J. Organomet. Chem.* **1985**, *282*, C49–C52. (b) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199–2205. Thermochemical studies on these systems are presently ongoing.

(20) Nolan, S. P.; de la Vega, R.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529–2537.

(21) Luo, L.; Nolan, S. P.; Fagan, P. J.; Calabrese, J. Manuscript in preparation.

(22) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970.

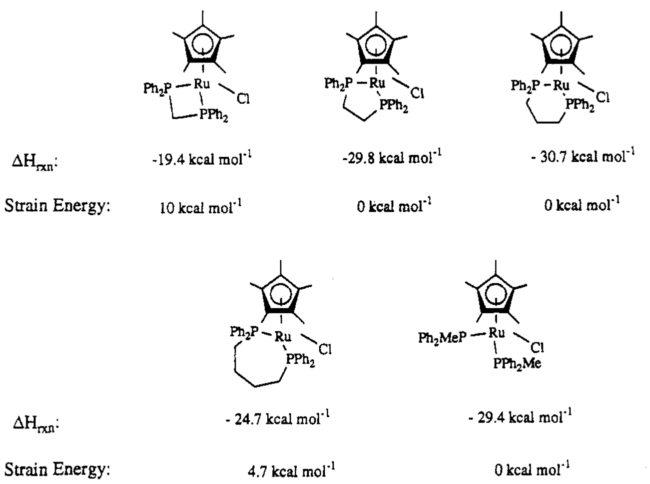
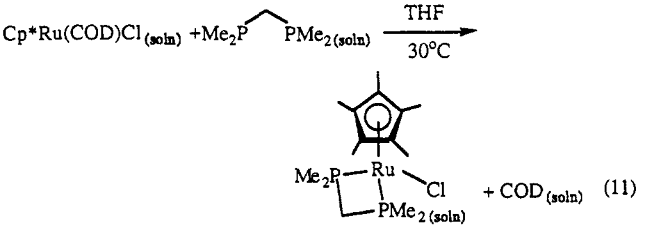


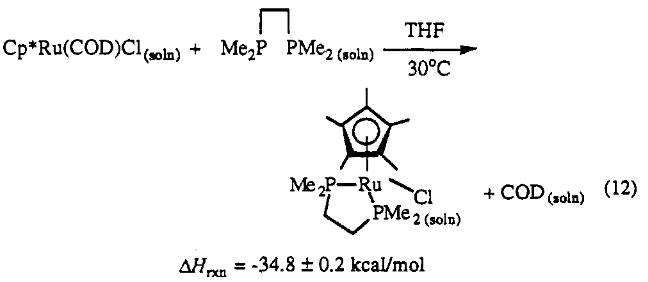
Figure 2. Enthalpies of reaction and ring strain estimates for metallacycles in the Cp*Ru(PP)Cl system.

synthesis of this seven-membered metallacyclic complex from $[Cp^*RuCl_2]_n$ could not be achieved. Instead, a solvated species, $Cp^*Ru(\eta^1\text{-}Ph_2P(CH_2)_4PPh_2)(CHCl_3)Cl$, was isolated.[23] This solvato complex appears to be a thermodynamically more stable complex, and the absence of a cyclic arrangement possessing some 5 kcal/mol of ring strain is taken as a major factor favoring the noncyclic structure. The least stable of the metallacycles investigated is the four-membered ring where ring strain is estimated as 10 kcal/mol. This 10 kcal/mol strain energy is of the same order of magnitude as strain energy estimates for a thorium metallacyclobutane complex (10 kcal/mol).[24] This energy is also in good agreement with more closely related four-membered organomolybdenum, $(Ph_2PCH_2PPh_2)Mo(CO)_4$ (8.3 kcal/mol),[7] and organoiron, $(Ph_2PCH_2PPh_2)Fe(CO)_3$ (12.6 kcal/mol),[12b] complexes. Comparison of ring strain energies for the four- and five-membered metallacyclic complexes can also be estimated for phosphine bearing alkyl groups. Here again a difference of ca. 10 kcal/mol exists between the dmpm and dmpe complexes.



(11)

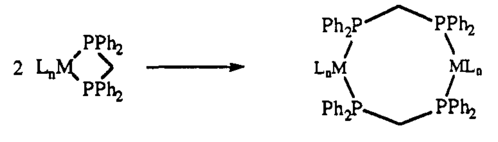
ΔH_{rxn} = -23.8 ± 0.3 kcal/mol



(12)

ΔH_{rxn} = -34.8 ± 0.2 kcal/mol

Phosphine ligands having small "bites" are known to form bridged structures as shown in eq 13.[1] The entropy of reaction 13 should be unfavorable and can be estimated to be on the order of10 kcal/mol at 25 °C.[25] For the present



(13)

L_n = ancillary ligation

ruthenium system, the enthalpy of reaction 13 is estimated to be exothermic by some 20 kcal/mol, representing relief of ring strain in 2 equiv of $Cp^*Ru(Ph_2PCH_2PPh_2)Cl$. This favorable enthalpy term is clear enough to offset the unfavorable entropy factor. Therefore, the mononuclear complex should probably best be considered a kinetic product.

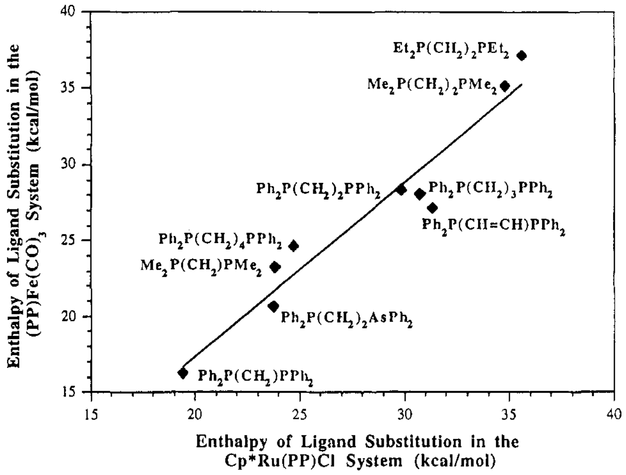


Figure 3. Comparison between enthalpies of ligand substitution in the Cp*Ru(PP)Cl and $(PP)Fe(CO)_3$ systems. R = 0.96, slope = 1.15.

The present enthalpy data allow for comparisons with other bidentate phosphine substitution reactions investigated by solution calorimetry. The first comparison examined was with the $(PP)Mo(CO)_4$ system studied by Hoff and co-workers.[7] When the relative enthalpy data for a series of ligands common to the two systems are compared, a poor linear fit (R = 0.86) is obtained. This may not be too surprising in view of the different number of available coordination sites in the two systems. This difference in coordination number and geometry may well explain different steric and electronic factor contributions to the enthalpies of reaction. 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 the same chemical group. This relationship is presented in Figure 3. This relationship exhibits a remarkable fit (R = 0.96) considering the dissimilarities in ancillary ligations of the two systems.

Conclusion

A relative enthalpy scale has been established for the binding of chelating phosphine ligands to the Cp*RuCl moiety. The labile nature of the COD ligand in Cp*Ru(COD)Cl was used to gain access into the thermochemistry

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[23] Oshima, N.; Suzuki, H.; Moro-Oka, Y. *Chem. Lett.* **1984**, 1161–1164.

[24] Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832.

[25] Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449–459.

of ligand substitution for bidentate arsine/phosphine ligands. Reactions of bidentate ligands with 1 also show this reaction to be of synthetic use for isolation of complexes of formulation Cp*Ru(PP)Cl. The ring strain energies present in these metallacycles have been estimated from enthalpy data for the monodentate system. Only the four- and seven-membered rings display any considerable strain energies. The overall enthalpy of reaction trend is similar to results recently obtained for an organoiron system. 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, and the National Science Foundation (Grant No. CHE-9305492) are gratefully acknowledged for support of this research. The Louisiana Board of Regents is also acknowledged for allocating funds allowing the purchase of NMR spectrometers (Grant No. ENH-53, 1990–1991). The authors are indebted to Johnson-Matthey for the generous loan of ruthenium salts.

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