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Organoruthenium Thermochemistry. Enthalpies of Reaction of $(Cp^*RuCl)_4$ and $Cp^*Ru(COD)Cl$ (Cp^* = η^5-C_5Me_5, COD = Cyclooctadiene) with Dienes and Tertiary Phosphine Ligands

Lubin Luo and Steven P. Nolan*

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

Paul J. Fagan

Central Research and Development, E. I. du Pont de Nemours & Co., Inc.,
Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880–0328

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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 monodentate ligands, leading to the formation of $Cp^*Ru(ER_3)_2Cl$ (E = P, As), have been measured by anaerobic solution calorimetry in THF at 30 °C. The enthalpies of reaction associated with the rapid and quantitative reaction of the $(Cp^*RuCl)_4$ complex with diene ligands in THF at 30 °C, producing $Cp^*Ru(diene)Cl$ complexes, have also been investigated. Reaction of $(Cp^*RuCl)_4$ with excess phosphine ligand, at 30 °C, has been shown to quantitatively yield the corresponding $Cp^*Ru(PR_3)_2Cl$ complex and allows for the design of a thermochemical cycle assuring the internal consistency of the thermochemical data. The overall relative order of stability established for the preceding complexes is as follows: for monodentate ligands, $AsEt_3 < PPh_3 < P^nBu_3 < PEt_3 < PPh_2Me < P(OPh)_3 < PPhMe_2 < PMe_3 < P(OMe)_3$; for dienes, 2,3-dimethyl-1,3-butadiene < 1,3-cyclohexadiene < cyclooctadiene < 1,3-pentadiene < norbornadiene. Comparisons with other organometallic systems and insight into factors influencing the Ru–L bond disruption enthalpies are discussed.

Introduction

Thermochemical studies performed on organometallic systems have gained recognition as an area of research that could provide important insights into reactivity and bonding patterns.[1–4] In spite of this recognition, the paucity of thermochemical information for certain transition-metal groups is noticeable. The solution thermochemistry of systems such as those revolving around group 8 metal centers is a good example of an area where more information is needed.[1a,b] Considering the large number of catalytic processes mediated by organoruthenium systems (ranging from hydrogenation of olefins to ring-opening metathesis polymerization),[5] the limited number of thermochemical studies performed on these systems is remarkable.

Ligand substitution reactions are at the heart of catalytic transformation, since creation of vacant coordination sites oftentimes requires liberation of one or more ligands from the coordination sphere of the metal.[6] The few studies focusing on organoruthenium complexes have included the kinetic determination of relative bond enthalpy data for the $Cp^*(PMe_3)_2Ru$–X system reported by Bercaw and co-workers:[7]

$$Cp^*(PMe_3)_2Ru{-}OH + HL \rightarrow Cp^*(PMe_3)_2Ru{-}L + H_2O \quad (1)$$

$$L = CCPh, NHPh, SH, CN, H$$

Collman has examined the kinetics of cleavage of one of

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the Ru–ethyl bonds in the (OEP)Ru(Et)$_2$ system:[8]

$$(OEP)Ru(Et)_2 \rightarrow (OEP)Ru(Et) + Et \tag{2}$$

Parker and Tilset have most recently estimated absolute bond disruption enthalpies for a number of transition-metal hydrides, including H–Ru(CO)$_2$Cp,[9] and Halpern and Mancuso have reported a kinetic determination of *D*(Ru–R) in Cp(CO)$_2$RuCH(CH$_3$)C$_6$H$_5$.[10] To our knowledge, with the exclusion of our recent report on the thermodynamic driving forces behind the binding affinity of the Cp*Ru$^+$ fragment to arenes,[11] no solution calorimetric investigation of ruthenium systems has been performed:[12]

$$Cp^*Ru(CH_3CN)_3OTf + arene \rightarrow Cp^*Ru(arene)OTf + 3CH_3CN \tag{3}$$

$$OTf = O_3SCF_3$$

Recent reports on the synthesis and high-yield isolation of organoruthenium complexes provide a thermodynamic entryway into the solution calorimetric studies of ligand substitution in these systems. Fagan and co-workers have communicated results illustrating the easy access to complexes of type Cp*Ru(diene)Cl from the tetrameric (Cp*RuCl)$_4$ compound:[13]

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

diene =
cyclohexadiene, norbornadiene, cyclooctadiene, etc.

Reaction 4 proceeds rapidly and quantitatively in THF at room temperature. These researchers also have shown that the (Cp*RuCl)$_4$ complex could act as a useful synthon leading to the formation of Cp*Ru(PR$_3$)$_2$Cl complexes:[13c]

$$(Cp^*RuCl)_4 + 8PMe_3 \rightarrow 4Cp^*Ru(PMe_3)_2Cl \tag{5}$$

On the basis of these recent observations concerning the reactivity of the (Cp*RuCl)$_4$ complex, we have undertaken thermochemical studies aimed at quantifying the enthalpic driving forces behind the observed chemistry. In the present study, we wish to report on the enthalpies of reaction associated with diene coordination to the Cp*RuCl fragment as well as those related to tertiary phosphine substitution in the Cp*Ru(COD)Cl 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. Ligands were purchased from Strem Chemicals and used as received. Solvents were dried and distilled under dinitrogen before use, 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 IR and NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300-MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[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)$_4$, Cp*Ru(diene)Cl, and Cp*Ru(PMe$_3$)$_2$Cl were synthesized as reported in the literature.[13c] Experimental synthetic procedures, leading to isolation of crystalline materials, for all other complexes are reported below.

Cp*Ru(AsEt$_3$)$_2$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 (2.13 mmol) of AsEt$_3$. After the mixture was stirred for 2 h, the solvent was removed under vacuum. About 10 mL of hexane was then vacuum-transferred to the cooled (−78 °C) flask containing the solid residue. The solution was warmed to room temperature and stirred; it was then filtered and slowly cooled to −78 °C, at which temperature it was kept overnight. Cold filtration afforded orange-yellow needles that were washed with small amounts of hexane and dried under vacuum. This procedure affords an isolated yield of 200 mg (42%). ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.14 (q, 18 H, CH$_2$C*H*$_3$), 1.63 (s, 15 H, Cp*), 1.67–1.88 (t, 12 H, C*H*$_2$CH$_3$). Anal. Calcd for RuAs$_2$ClC$_{22}$H$_{45}$: C, 44.29; H, 7.61. Found: C, 44.09; H, 7.64.

Cp*Ru(P(OPh)$_3$)$_2$Cl. A 25-mL flask was charged with 250 mg (0.66 mmol) of Cp*Ru(COD)Cl, 10 mL of dried THF, and 450 μL (1.71 mmol) of P(OPh)$_3$. After the mixture was stirred for 2 h, the solvent was removed under vacuum. A 10-mL mixture of hexane and THF (1:1) then was vacuum-transferred to the cooled (−78 °C) flask containing the solid residue. This solution was warmed to room temperature and stirred. After filtration, the solution was very slowly cooled down to −78 °C and kept at that temperature overnight to let crystals grow. The yellow crystals were then collected by cold filtration, washed with a small amount of hexane, and dried under vacuum, giving 250 mg (43%) of product. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.38 (s, 15 H, Cp*), 6.96 (t, 6H, *p* C$_6$*H*$_5$), 7.13 (t, 12 H, *m* C$_6$*H*$_5$), 7.26 (d, 12H, *o* C$_6$*H*$_5$). Anal. Calcd for RuClP$_2$O$_6$C$_{46}$H$_{45}$: C, 61.92; H, 5.08. Found: C, 61.83; H, 5.15.

Cp*Ru(P(OMe)$_3$)$_2$Cl. A 25-mL flask was charged with 250 mg (0.66 mmol) of Cp*Ru(COD)Cl, 10 mL of dried THF, and 250 μL (2.13 mmol) of P(OMe)$_3$. After the mixture was stirred for 2 h, the solvent was removed under vacuum. About 10 mL of pentane then was vacuum-transferred to the cooled (−78 °C) flask containing the solid product. The solution was warmed up with hot water (40 °C) to make a saturated solution. After filtration, the saturated solution was very slowly cooled to −78 °C and kept at the temperature overnight to let the crystal grow finely. The yellow crystals were filtered, washed with a small amount of pentane, and dried under vacuum, giving 226 mg (66%) of product. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 1.65 (s, 15 H, Cp*), 3.60 (s, 18H, –C*H*$_3$). Anal. Calcd for RuClP$_2$O$_6$C$_{16}$H$_{33}$: C, 36.96; H, 6.40. Found: C, 36.93; H, 6.21.

Cp*Ru(PPh$_2$Me)$_2$Cl. A 25-mL flask was charged with 300 mg (0.79 mmol) of Cp*Ru(COD)Cl, 15 mL of dried THF, and 300

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μL (1.59 mmol) of PPh_2Me. After the mixture was stirred for 2 days, the solvent was removed under vacuum. A 5-mL portion of hexane then was vacuum-transferred to the cooled (−78 °C) flask containing solid product. The solution was warmed to 40 °C and stirred for 15 min. The saturated solution was filtered and placed in a dry ice/acetone bath overnight to let the crystal grow. After filtration, the orange-red crystals were washed with a small amount of hexane and dried under vacuum, giving 380 mg (72%) of product. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 1.25 (s, 15 H, Cp*), 1.32 (m, 6 H, $-CH_3$), 7.10 (t, 8H, *M* C_6H_5), 7.37 (t, 8H, *o* C_6H_5), 7.62 (d, 4 H, *p* C_6H_5). Anal. Calcd for $RuClP_2C_{36}H_{41}$: C, 64.33; H, 6.15. Found: C, 64.32; H, 6.19.

Cp*Ru(PEt_3)$_2$Cl. A 25-mL flask was charged with 250 mg (0.66 mmol) of Cp*Ru(COD)Cl, 10 mL of THF, and 360 μL (2.6 mmol) of PEt_3. After the mixture was stirred for 2 h at room temperature, the solvent was removed under vacuum. A 10-mL portion of hexane was then vacuum-transferred to the cooled (−78 °C) flask containing the solid residue. The solution was warmed to room temperature and then filtered and slowly cooled to −78 °C, at which temperature it was kept overnight. Cold filtration afforded orange-yellow needles that were washed with a small amount of hexane and dried under vacuum. This procedure affords an isolated yield of 160 mg (48%) of product. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 1.08 (m, 18 H, $-CH_2CH_3$), 1.58 (s, 15 H, Cp*), 1.85 (m, 12 H, $-CH_2CH_3$). Anal. Calcd for $RuClP_2C_{22}H_{45}$: C, 52.01; H, 8.93. Found: C, 52.13; H, 9.05.

Cp*Ru(P^nBu_3)$_2$Cl. A 25-mL flask was charged with 250 mg (0.65 mmol) of Cp*Ru(COD)Cl, 15 mL of dried THF, and 350 μL (1.41 mmol) of P^nBu_3. After the mixture was stirred for 1 h, the solvent was removed under vacuum. The oily product was subjected to high vacuum and heated to 40 °C with a water bath for 24 h to remove any excess phosphine. A 10-mL portion of hexane was vacuum-transferred to the cooled (−78 °C) flask containing a solid residue. After the volume was reduced by half, the saturated solution was slowly cooled to −78 °C. After filtration, the orange crystals were washed with a very small amount of hexane and dried under vacuum, giving 200 mg (57%) of product. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 0.93 (m, 18 H, $-CH_3$), 1.58 (s, 15 H, Cp*), 1.40 (m, 12 H, $-CH_2CH_2CH_2CH_3$), 1.47 (m, 12 H, $-CH_2CH_2CH_2CH_3$), 1.80 (m, 12 H, $-CH_2CH_2CH_2CH_3$). Anal. Calcd for $RuClP_2C_{34}H_{69}$: C, 60.38; H, 10.28. Found: C, 60.61; H, 10.39.

Cp*Ru($PPhMe_2$)$_2$Cl. A 25-mL flask was charged with 250 mg (0.66 mmol) of Cp*Ru(COD)Cl, 15 mL of dried THF, and 300 μL (2.10 mmol) of PPh_2Me. After the mixture was stirred for 2 h, the solvent was removed under vacuum. Because the product was oily, it was placed under high vacuum and heated to 40 °C to remove any excess phosphine. A 10-mL mixture of hexane and THF (1:1) then was vacuum-transferred to the cooled (−78 °C) flask containing the solid residue. After it was warmed to 40 °C and stirred, the solution was filtered and then slowly cooled to −40 °C and kept overnight at this temperature. After filtration, the red-orange crystals were washed with a small amount of hexane and dried under vacuum, giving 177 mg (49%) of product. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 1.23 (s, 15 H, Cp*), 1.60 (m, 12H, $-CH_3$), 7.30 (t, 2H, *p* C_6H_5), 7.33 (t, 4 H, *m* C_6H_5), 7.81 (t, 4 H, *o* C_6H_5). Anal. Calcd for $RuClP_2C_{26}H_{37}$: C, 56.98; H, 6.80. Found: C, 56.89; H, 6.78.

Cp*Ru(PPh_3)$_2$Cl. A 25-mL flask was charged with 270 mg (0.71 mmol) of Cp*Ru(COD)Cl, 15 mL of dry THF, and 625 mg (2.38 mmol) of PPh_3. After the mixture was stirred for 2 h, the solvent was removed under vacuum. A 40-mL portion of THF was then vacuum-transferred to the cooled (−78 °C) flask containing the solid residue. To make a saturated solution, the flask was placed in a hot water bath (40 °C) for about 30 min; then the solution was filtered. Reduction of the volume by half followed by filtration yielded orange needles, which were washed with a small amount of hexane and dried under vacuum, giving 500 mg (88%) of product. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 1.03 (s, 15 H, Cp*), 7.03 (m, 12 H, *m* C_6H_5), 7.12 (m, 6 H, *p* C_6H_5) and 7.50 (m, 12 H, *o* C_6H_5). Anal. Calcd for $RuClP_2C_{46}H_{45}$: C, 69.38; H, 5.70. Found: C, 69.64; H, 5.57.

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 under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organoruthenium reactions investigated. Only reactants and products were observed in the course of the NMR titration.

Solution Calorimetry. Calorimetric Measurement of Reaction between (Cp*RuCl)$_4$ (1) and Cyclooctadiene (COD). 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*RuCl$_4$) was accurately weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of COD (5 mL of COD 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 had reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h), the vessels were removed from the calorimeter. Conversion to Cp*Ru(COD)Cl was found to be quantitative under these reaction conditions. The enthalpy of reaction, −39.8 ± 0.4 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.

Calorimetric Measurement of the Enthalpy of Solution of Cp*Ru(COD)Cl (2) in THF. In order to consider all species in solution, the enthalpies of solution of Cp*Ru(COD)Cl had to be directly measured. This was performed by using a procedure similar 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 and is determined to be 4.9 [illegible] 0.2 kcal/mol.

Results

A facile entryway into the thermochemistry of Cp*Ru(diene)Cl complexes is made possible by the rapid and quantitative reaction of (Cp*RuCl)$_4$ (1) with a variety of different diene ligands:[13c]

$$(\mathrm{Cp^*RuCl})_4(\mathrm{s}) + 4\mathrm{CHD}(\mathrm{soln}) \xrightarrow[30\,^\circ\mathrm{C}]{\mathrm{THF}} 4\mathrm{Cp^*Ru(CHD)Cl}(\mathrm{soln}) \quad (6)$$

CHD = cyclohexadiene

$$\Delta H_{\mathrm{rxn}} = -39.3 \pm 0.5\ \mathrm{kcal/mol}$$

This type of diene binding reaction appears to be general, and it was found to be rapid and quantitative for all dienes calorimetrically investigated at 30 °C in tetrahydrofuran. A compilation of diene ligands and their respective enthalpies of reaction are listed in Table I.

With the diene information in hand, the Cp*Ru(COD)Cl (2) complex was found to have the diene ligand more weakly

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

$$(\mathrm{Cp^*RuCl})_4(\mathrm{s}) + 4\mathrm{diene(soln)} \xrightarrow[30\,^\circ\mathrm{C}]{\mathrm{THF}} 4\mathrm{Cp^*Ru(diene)Cl(soln)}$$

diene	complex	$-\Delta H_{rxn}$[a]
2,3-dimethyl-1,3-butadiene	$Cp^*Ru(Me_2butadiene)Cl$	39.0 (0.2)
1,3-cyclohexadiene	Cp*Ru(CHD)Cl	39.3 (0.5)
cyclooctadiene	Cp*Ru(COD)Cl	39.8 (0.4)
trans,trans-2,4-hexadiene	Cp*Ru(*t,t*-hexadiene)Cl	44.2 (0.5)
1,3-pentadiene	Cp*Ru(1,3-pd)Cl	46.1 (0.2)
norbornadiene	Cp*Ru(NBD)Cl	52.1 (0.2)

[a] Enthalpy values are reported with 95% confidence limits in parentheses.

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

$$\mathrm{Cp^*Ru(COD)Cl(soln)} + 2\mathrm{L(soln)} \xrightarrow[30\,^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(L)_2Cl(soln)}$$

L	complex	$-\Delta H_{rxn}$[a]
$AsEt_3$	$Cp^*R(AsEt_3)_2Cl$	15.0 (0.2)
PPh_3	$Cp^*Ru(PPh_3)_2Cl$	18.1 (0.2)
P^nBu_3	$Cp^*Ru(P^nBu_3)_2Cl$	26.0 (0.2)
PEt_3	$Cp^*Ru(PEt_3)_2Cl$	27.2 (0.2)
PPh_2Me	$Cp^*Ru(PPh_2Me)_2Cl$	29.4 (0.2)
$P(OPh)_3$	$Cp^*Ru(P(OPh)_3)_2Cl$	31.2 (0.2)
$PPhMe_2$	$Cp^*Ru(PPhMe_2)_2Cl$	31.8 (0.3)
PMe_3	$Cp^*Ru(PMe_3)_2Cl$	32.2 (0.4)
$P(OMe)_3$	$Cp^*Ru(P(OMe)_3)_2Cl$	37.5 (0.4)

[a] Enthalpy values are reported with 95% confidence limits in parentheses.

bound to the metal center. The labile nature of the Ru-COD bond was exploited in reaction 7. Table II lists the large variety of phosphine and arsine ligands able to readily substitute for COD in this system.

$$\mathrm{Cp^*Ru(COD)Cl(soln)} + 2\mathrm{PEt_3(soln)} \xrightarrow[30\,^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(PEt_3)_2Cl(soln)} + \mathrm{COD(soln)} \quad (7)$$

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

Certain steric and electronic limitations exist in this diene system (vide infra), and phosphine compounds with very large cone angles were found to substitute to a lesser degree and much more slowly than smaller, more basic phosphine ligands. An alternative reaction pathway had to be used to obtain enthalpies of reaction for these complexes, and this is illustrated in reaction 8. In order to compare the magnitude of the enthalpy of reaction 8 with that of other monodentate ligands, reactions between 1 and a number of sterically less demanding phosphine ligands were investigated:

$$(\mathrm{Cp^*RuCl})_4(\mathrm{s}) + 4\mathrm{PCy_3(soln)} \xrightarrow[30\,^\circ\mathrm{C}]{\mathrm{THF}} 4\mathrm{Cp^*Ru(PCy_3)Cl(soln)} \quad (8)$$

$$\Delta H_{rxn} = -41.9 \pm 0.9\ \mathrm{kcal/mol}$$

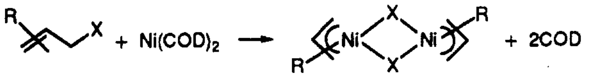
$$(\mathrm{Cp^*RuCl})_4(\mathrm{s}) + 8\mathrm{PEt_3(soln)} \xrightarrow[30\,^\circ\mathrm{C}]{\mathrm{THF}} 4\mathrm{Cp^*Ru(PEt_3)_2Cl(soln)} \quad (9)$$

$$\Delta H_{rxn} = -147.5 \pm 0.6\ \mathrm{kcal/mol}$$

Table III summarizes the enthalpy of reaction associated with phosphine binding to the Cp*RuCl fragment from 1.

Discussion

The lability of a number of metal-diene complexes is well-known. These complexes are often used to stabilize a catalytically active organometallic fragment. For example, the $Ni(COD)_2$ complex readily loses cyclooctadiene ligands to form nickel allyl complexes in the presence of allylic halides[17] (eq 10). These nickel allyl complexes have found great utilization in organic chemistry in the formation of C-C bonds.[17] It is, however, quite intriguing that few thermodynamic data are available describing such systems. Important questions must be answered in order to gain a better understanding of the factors controlling the stability of metal-diene interactions.



(10)

In the present ruthenium system, on the basis of the present enthalpic data, certain important trends are observed. The complexes of general formulation Cp*Ru-(diene)Cl can be viewed as a potential source of the 14-electron Cp*RuCl fragment. Depending on the binding energy associated with the Ru-diene interaction, this fragment will or will not be readily accessible by substitution pathways. In the series of diene ligands investigated, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, and cyclooctadiene ligands possess similar affinity for the Cp*RuCl moiety. The hexadiene and pentadiene are more strongly bound to the ruthenium center, and norbornadiene is the most strongly bound diene observed in the study. Therefore, it would appear that NBD represents the poorest choice for a diene leaving group in the present series. We have experimentally tested this observation and have observed that indeed reaction 11 did not proceed quantitatively under calorimetric conditions when norbornadiene was the diene bound to ruthenium. Reaction 11 did, however, proceed to completion under fairly mild conditions when the diene was cyclooctadiene (COD). This relative order of stability has previously been observed in other organometallic systems. The CpCo(COD) complex, which has been found to be a catalyst precursor for the cooligomerization of methylacetylene with acetonitrile leading to the formation of trimethylpyridine,[18] was also found to directly substitute a norbornadiene for a cy-

$$\mathrm{Cp^*Ru(NBD)Cl} + 2\mathrm{PPh_3} \nrightarrow \mathrm{Cp^*Ru(PPh_3)_2Cl} + \mathrm{NBD} \quad (11)$$

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[17] For reviews, see: (a) Semmelhack, M. F. *Org. React.* **1972**, *19*, 115-198. (b) Baker, R. *Chem. Rev.* **1973**, *73*, 487-530. (c) Hegedus, L. S. *J. Organomet. Chem. Libr.* **1976**, *1*, 329-359. (d) Billington, D. C. *Chem. Soc. Rev.* **1985**, *14*, 93-120.

[18] (a) Wakatsuki, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2715-2716. (b) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W.; Mynott, R. *J. Organomet. Chem.* **1984**, *272*, 231-249. (c) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248-262.

Scheme I[a]

		ΔH_{rxn} (kcal/mol)	
$^{1}/_{4}(Cp^*RuCl)_4(s) + 2P(OMe)_3$	$\longrightarrow Cp^*Ru(P(OMe)_3)_2Cl$	-47.6 ± 0.2	(17)
$Cp^*Ru(NBD)Cl$	$\longrightarrow {}^{1}/_{4}(Cp^*RuCl)_4(s) + NBD$	13.0 ± 0.2	(18)
$Cp^*Ru(P(OMe)_3)_2Cl + COD$	$\longrightarrow Cp^*Ru(COD)Cl + 2P(OMe)_3$	37.5 ± 0.4	(19)
$Cp^*Ru(COD)Cl + 2PPh_3$	$\longrightarrow Cp^*Ru(PPh_3)_2Cl + COD$	-18.1 ± 0.2	(20)
$Cp^*Ru(NBD)Cl + 2PPh_3$	$\longrightarrow Cp^*Ru(PPh_3)_2Cl + NBD$	-15.2 ± 0.3	(21)

[a] Unless otherwise stated, all species are in solution.

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

$$(Cp^*RuCl)_4(s) + 8L(soln) \xrightarrow[30\ °C]{THF} 4Cp^*Ru(L)_2Cl(soln)$$

L	complex	$-\Delta H_{exptl}$[a]
PCy_3	$Cp^*Ru(PCy_3)Cl$	41.9 (0.2)[b]
P^nBu_3	$Cp^*Ru(P^nBu_3)_2Cl$	144.9 (0.4)
PEt_3	$Cp^*Ru(PEt_3)_2Cl$	147.5 (0.6)
$P(OMe)_3$	$Cp^*Ru(P(OMe)_3)_2Cl$	190.3 (0.4)

[a] Enthalpy values are reported with 95% confidence limits in parentheses. [b] Enthalpy refers to substitution of only one PCy_3 ligand.

clooctadiene ligand at elevated temperatures:[19]

$$CpCo(COD) + NBD \xrightarrow[130\ °C]{CH_3CN} CpCo(NBD) + COD \quad (12)$$

Two possible factors can account for this different behavior exhibited by the aforementioned ruthenium–diene complexes. This might represent a qualitative example of the apparent stronger M–NBD vs M–COD bonding interaction. In the present ruthenium system, a quantitative evaluation of this binding energy difference can be obtained. The exchange of COD for NBD can be estimated when eq 14 is subtracted from eq 13, leading directly to the enthalpy of the diene exchange. The calculated

		ΔH_{rxn} (kcal/mol)	
$(Cp^*RuCl)_4(s) + 4NBD(soln)$	$\longrightarrow 4Cp^*Ru(NBD)Cl(soln)$	-52.1 ± 0.2	(13)
$(Cp^*RuCl)_4(s) + 4COD(soln)$	$\longrightarrow 4Cp^*Ru(COD)Cl(soln)$	-39.8 ± 0.4	(14)
$4Cp^*Ru(COD)Cl(soln) + 4NBD(soln)$	$\longrightarrow 4Cp^*Ru(NBD)Cl(soln) + 4COD(soln)$	-12.3 ± 0.4	(15)

enthalpy of reaction 15 corresponds to the exchange of four COD for four NBD ligands. Equation 16 provides a view of the diene exchange process on a per mole basis.

$$Cp^*Ru(COD)Cl(soln) + NBD(soln) \rightarrow Cp^*Ru(NBD)Cl(soln) + COD(soln) \quad (16)$$

$$\Delta H_{calcd} = -3.1 \pm 0.4 \text{ kcal/mol}$$

Reaction 16 is calculated to be exothermic by some 3.1 kcal/mol. This relative increased thermodynamic stability might not entirely explain the fact that reaction 11 does not proceed extensively at 30 °C. An enthalpy of reaction can be estimated from the present data (Scheme I). This exothermic value clearly indicates reaction 21 to be enthalpically favored. It appears then that the dominating factor behind our inability to observe eq. 11 must then not be a thermodynamic one but a kinetic one.

Furthermore, the enthalpy difference between reactions 20 and 21 (−2.9 kcal/mol) is the same within experimental error as the previously determined value for eq 16 (−3.1 kcal/mol). This further emphasizes the internal consistency of the present data. This estimate is in very close agreement with an enthalpy estimate of 2.0 kcal/mol for the preferential binding of NBD over COD in the (diene)Mo(CO)$_4$ system:[20]

$$(COD)Mo(CO)_4(soln) + NBD(soln) \rightarrow (NBD)Mo(CO)_4(soln) + COD(soln) \quad (22)$$

$$\Delta H_{calcd} = -2.0 \pm 0.4 \text{ kcal/mol}$$

Both these trends for the ruthenium and molybdenum systems are found to be opposite to the heat of binding to Pd(II), where cyclooctadiene was found to be 1.7 kcal/mol more stable than norbornadiene.[1b,21]

Taking advantage of the labile nature of the COD ligand in **2**, we investigated reactions involving the displacement of the COD ligand by 2 equiv of monodentate ligands by solution calorimetry at 30 °C;

$$Cp^*Ru(COD)Cl(soln) + 2AsEt_3(soln) \xrightarrow[30\ °C]{THF} Cp^*Ru(AsEt_3)_2Cl(soln) + COD(soln) \quad (23)$$

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

These reactions were found to be quantitative and rapid under the experimental calorimetric conditions. Arsine and phosphine ligands were investigated in view of their importance as catalyst modifiers.[22] Enthalpies of reaction are reported in Table II. As might be expected, in view of its steric bulk and mild electronic donating ability, the $AsEt_3$ ligand is the weakest bound ligand studied. A similar trend has been observed for $(AsEt_3)_2Fe(CO)_3$[23] and $(AsEt_3)_2Mo(CO)_4$[19] complexes. The binding enthalpy of the arsine can be compared with that of its phosphine analog by simply taking the difference in enthalpies of reaction listed in Table II:[24]

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(19) Wakatsuki, Y.; Yamazaki, H.; Kobayashi, T.; Sugawara, Y. *Organometallics* **1987**, *6*, 1191–1196.

(20) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; de la Vega, R. *Inorg. Chem.* **1988**, *27*, 81–85.

(21) Partenheimer, W. *Inorg. Chem.* **1972**, *11*, 743–746.

(22) (a) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (b) See ref 6.

(23) Luo, L.; Nolan, S. P. *Inorg. Chem.* **1993**, *32*, 2410–2415.

(24) The enthalpy of ligand exchange of any two entries in Table II can be calculated by subtracting the appropriate enthalpy values.

(25) Luo, L.; Nolan, S. P. *Organometallics* **1992**, *11*, 3483–3486.

$$\mathrm{Cp^*Ru(AsEt_3)_2Cl(soln) + 2PEt_3 \rightarrow Cp^*Ru(PEt_3)_2Cl(soln) + 2AsEt_3(soln)} \quad (24)$$

$$\Delta H_{\mathrm{calcd}} = -12.2 \pm 0.4 \text{ kcal/mol}$$

The phosphine ligand, PEt_3, displays an enthalpy of reaction 12.2 kcal/mol more exothermic than its arsenic relative. Similar enthalpy differences (12.4 ± 0.3 kcal/mol) have been observed in the *cis*-$(L)_2Mo(CO)_4$ complexes[20] (L = arsine and phosphine ligands). A recent study of the diaxial $(L)_2Fe(CO)_3$ system[23,25] also shows important similarities as far as the binding of arsenic vs phosphorus donors. Taking into consideration the estimated enthalpy of isomerization (axial–equatorial to diaxial) of −5.4 kcal/mol, the calculated the difference in enthalpies of binding of $AsEt_3$ vs PEt_3 to be 12.5 kcal/mol in this iron system. Reasons for similarities may be more obvious in the iron and molybdenum systems, since they revolve around the same ancillary ligation. The reasons behind a similar enthalpy trend existing in the $Cp^*Ru(L)_2Cl$ complexes are not obvious, and we therefore only point out the enthalpic similarity.

Other monodentate phosphine ligands have been calorimetrically investigated, and the respective enthalpies of ligand substitution are reported in Table II. The data can be examined in terms of steric and electronic contributions to the enthalpy of reaction, the relative importance of which can be quantified in terms of the respective A_1/A_2 ratios obtained in a treatment first proposed by Tolman,[26] where enthalpies of reaction are correlated with steric (θ, cone angle) and electronic (ν, A_1 carbonyl stretching frequency in $Ni(CO)_3L$, L = tertiary phosphine) factors:

$$-\Delta H^\circ = A_0 + A_1\theta + A_2\nu \quad (25)$$

A correlation factor (R) of 0.95 is obtained when enthalpic data are fitted to eq 25. The A_1/A_2 ratio obtained can be taken as a measure of the relative importance of steric versus electronic factors. It would be expected that steric factors play a major role in the ruthenium system in view of the cis arrangement of phosphine ligands and the steric bulk of the Cp* ligand. A value of 2.32 is calculated for the A_1/A_2 ratio and quantitatively denotes the overwhelming influence of steric factors. This compares to a value of 1.42 for the $(L)_3Mo(CO)_3$ system,[27] which exhibits a considerable influence of steric factors in comparison to the data for the parent $(L)_2Mo(CO)_4$ system (A_1/A_2 = 0.81).[20] Another comparison which facilitates an understanding of the relative importance of steric factors in the present system is the one with the diaxial $(L)_2Fe(CO)_3$ system.[25] In that instance, the A_1/A_2 ratio is only 0.008 and, as might be expected, the steric factors play a minor role since the phosphine ligands have adopted a mutually trans arrangement. Since the steric factors have such a profound influence on the enthalpy of reaction, a direct relationship between the enthalpy of reaction and the phosphine cone angle was established (Figure 1) and the linear relationship emphasizes the major role played by steric effects in the present system. It appears from the experimental enthalpy data that trimethyl phosphite leads to the formation of the most stable organoruthenium complex. This is not obvious, even though similar high binding affinities of this ligand to transition metals have previously been observed.[27] This fact can possibly be explained in terms of back-donation from the metal into orbitals on the phosphite ligand (phosphorus–oxygen σ^* orbitals).

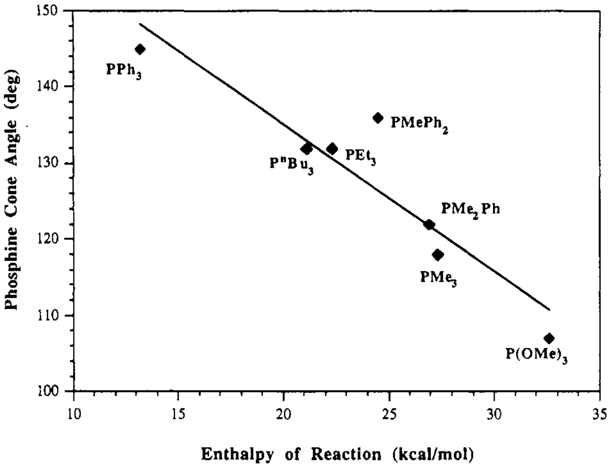

Figure 1. Enthalpy of reaction vs phosphime cone angle for a series of tertiary phosphine ligands in the $Cp^*Ru(PR_3)_2Cl$ system (slope −1.94; R = 0.93).

However, not all phosphine ligands react with **2** to yield the corresponding $Cp^*Ru(PR_3)_2Cl$ complex. For example, reaction of **2** with excess PCy_3 proceeds very slowly; even after the mixture is stirred overnight at room temperature, the reaction is still incomplete, and this is explained in terms of a very large cone angle for PCy_3 (170°).[26a] The investigation of the enthalpy of ligand substitution for such a sterically demanding phosphine ligand had to be performed using a different approach. Fagan had reported the direct synthesis of the $Cp^*Ru(PMe_3)_2Cl$ complex from $(Cp^*RuCl)_4$ (**1**).[13c] This route was tested for PCy_3 and did lead to the isolation of a unique organoruthenium complex:

$$\mathrm{(Cp^*RuCl)_4(s) + 4PCy_3(soln) \rightarrow 4Cp^*Ru(PCy_3)Cl(soln)} \quad (26)$$

$$\Delta H_{\mathrm{rxn}} = -41.9 \pm 0.4 \text{ kcal/mol}$$

This coordinatively unsaturated complex has recently been isolated in high yield by Tilley and co-workers[28] and is reminiscent of the group 6 metal complexes investigated by Kubas[29] and Hoff.[30] NMR spectroscopy confirms the identity of the species generated in the course of calorimetric experiments.[28] In order to compare the enthalpy of binding of PCy_3 to other phosphines and phosphites obtained by reactions similar to eq 18, the enthalpy associated with the binding of phosphorus donors to the Cp*RuCl fragment and breakup of the Ru–Cl cubic core of **1** were measured. The data are listed in Table III, and it is readily observed that PCy_3 is the largest cone angle phosphine studied and the most weakly bound to ruthenium. This might prove quite interesting in terms of

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[26] (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348. (b) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1955–1986. (c) Tolman, C. A.; Reutter, D. W.; Seidel, W. C. *J. Organomet. Chem.* **1976**, *117*, C30–C33.

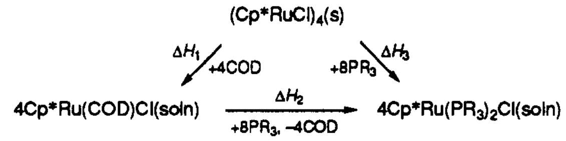
[27] Nolan, S. P.; de la Vega, R.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529–2537.

[28] Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278–280.

[29] Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128 and references therein.

[30] Gonzalez, A. A.; Murkerjee, S. L.; Chou, S.-J.; Zhang, K.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419–4421.

Scheme II



reactivity of this unsaturated fragment. Tilley and coworkers have already shown Cp*Ru(PCy$_3$)Cl to be capable of oxidatively adding a primary silane:[28]

$$\mathrm{Cp^*Ru(P)Cl + H_3SiPh \xrightarrow{CH_2Cl_2} Cp^*Ru(P)(H)(H_2SiPh)Cl(soln)} \quad (27)$$

$$\mathrm{P = PCy_3, PPr^i_3}$$

With the available thermodynamic information on hand, a check of the internal consistency of our enthalpic data was possible. Scheme II represents the thermochemical cycle devised and used to perform this verification. This check of the internal consistency of our results was performed for three phosphine/phosphite ligands, and calculated and experimental enthalpic results are listed in Table IV. The experimental and calculated enthalpies of reaction 3 of Scheme II are in excellent agreement and confirm the accuracy of the enthalpic data.

Conclusion

A relative enthalpy scale has been established for the binding of dienes to the Cp*RuCl moiety. This shows COD to be less strongly bound to Ru than NBD. The labile nature of the COD ligand in Cp*Ru(COD)Cl was used to gain access into the thermochemistry of ligand substitution for monodentate arsine/phosphine/phosphite ligands. The enthalpy trend can be explained in terms of electronic and steric contributions to the enthalpy of reaction, with the steric constituent playing a major role. Reactions of monodentate ligands with **2** are also of synthetic use for isolation of complexes of formulation Cp*Ru(L)$_2$Cl. A direct entryway into the thermochemistry of binding of a large-cone-angle phosphine, leading to coordinatively unsaturated Ru(II) complexes, was also successfully achieved with the PCy$_3$ ligand. A thermochemical cycle was constructed to confirm the internal consistency of the enthalpy data. Further thermochemical and mechanistic investigations focusing on this and related systems are presently underway.

Table IV. Calculated and Experimental Enthalpies (kcal/mol) of the Reactions

$$\mathrm{(Cp^*RuCl)_4(s) + 8PR_3 \xrightarrow[30\ ^\circ C]{THF} 4Cp^*Ru(PR_3)_2Cl(soln)} \quad \Delta H_3$$

PR$_3$	$-\Delta H_1$[a,b]	$-\Delta H_2$[a]	$-\Delta H_{3,\mathrm{calcd}}$[a]	$-\Delta H_{3,\mathrm{exptl}}$[a]
P^{n}Bu$_3$	39.8 (0.4)	104.0 (0.8)	143.8 (1.2)	144.9 (0.4)
PEt$_3$	39.8 (0.4)	108.8 (0.8)	148.6 (1.2)	147.5 (0.6)
P(OMe)$_3$	39.8 (0.4)	150.0 (2.0)	189.8 (2.0)	190.3 (0.4)

[a] Enthalpy values are reported with 95% confidence limits in parentheses. [b] Enthalpy of reaction refer to equations in Scheme I (see text).

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