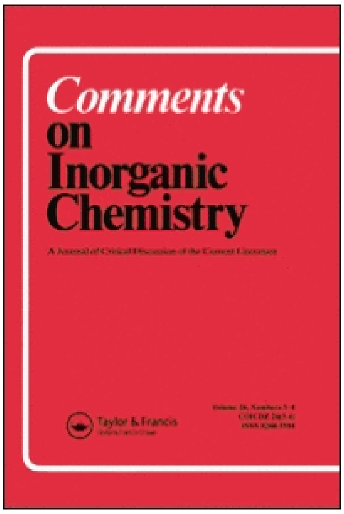

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Solution Thermochemistry of Ligand Substitution Reactions Involving Organoruthenium Complexes

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The solution thermochemistry of ruthenium-based organometallic complexes is outlined. Until recently, very little thermodynamic information was available concerning organogroup VIII systems. Bond enthalpy data for metal–hydride, metal–arene, metal–diene and metal–phosphine bonds have only recently been determined and will be presented and discussed in the following contribution. Developments in organometallic thermochemistry have demonstrated the considerable insight into bonding and reaction chemistry that metal–ligand bond disruption enthalpy data can provide. Such thermodynamic data will prove to be of fundamental importance to both theoretical and applied research in organometallic chemistry and catalysis.

Key Words: *bond enthalpy data, solution calorimetry, ancillary ligand influence, ligand substitution reactions, tertiary phosphine, ligand steric and electronic factors, thermochemistry*

A. INTRODUCTION

Large scale catalytic transformations of organic molecules mediated by transition metal complexes are increasingly attractive in view of

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the growing importance of energy and materials resources conservation. This has led to rapid developments in the area of organometallic chemistry, efforts mainly focused on the synthesis of new homogeneous catalysts, kinetic investigations of known catalysts and understanding catalytic systems from a theoretical standpoint. Any catalytic cycle is comprised of a series of reactions involving metal bond-breaking and bond-making processes resulting in overall net thermoneutrality of the metal itself. The energy produced comes totally from the organic reaction. While the total energy for a given process is fixed, and usually well known, the individual steps composing metal-catalyzed processes are not. A high energy barrier among various steps can greatly impede the catalytic behavior of metal complexes. It would therefore prove quite valuable to determine the energetics of important catalytic steps and examine how these vary with modulations in the metal coordination sphere. Recent developments in organometallic thermochemistry have demonstrated the considerable insight into bonding and reaction chemistry that metal–ligand bond disruption enthalpy (Eq. (1) for the adiabatic, homolytic process of Eq. (2)) information can provide.

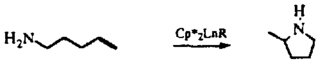
$$D(L_nM-R) = \Delta H_f^\circ(L_nM) + \Delta H_f^\circ(R^\bullet) - \Delta H_f^\circ(L_nM-R) \qquad (1)$$

$$L = \text{ancillary ligands}$$

$$L_nM-R \rightarrow L_nM + R^\bullet \qquad (2)$$

It is therefore a surprise that few thermodynamic studies have been performed to date on transition metal systems playing an important role in catalysis.[1-3]

The thermodynamics of important steps involved in catalytic cycles must be better understood. Solution calorimetric measurements can shed light on the thermodynamic contribution of individual steps to overall catalytic processes. Such thermodynamic investigations can also help clarify the necessary metal ancillary modifications required to improve catalytic activity. As an example of the power of this approach, solution calorimetric studies by Marks and coworkers[4] on the catalytically active Cp_2^*Ln-R [$Cp^* = \eta^5$ - $C_5(CH_3)_5$; Ln = lanthanide; R = hydrocarbyl, hydride, amido, halide, alkoxide] systems have led to the prediction of the thermodynamic feasibility of both steps (olefin insertion (i) and alkyl protonation (ii)) involved in the organolanthanide-mediated insertion of an olefin into a nitrogen–hydrogen bond (hydroamination). With this information in hand, Marks and co-workers proceeded to investigate the organolanthanide-catalyzed cyclization of N-unprotected aminoolefins.[5]



(3)

$$\Delta H = -11 \text{ kcal/mol}$$

Solution calorimetric investigations of Group 6 metal carbonyl complexes[6] have allowed Hoff and co-workers to propose alternative synthetic routes leading to a number of organomolybdenum complexes.[7]

$$\text{(p-xylene)Mo(CO)}_3 + C_5H_6 \xrightarrow{\text{THF}} \text{HMo}(C_5H_5)(\text{CO})_3 + \text{p-xylene} \quad (4)$$

The molybdenum thermochemical data have also provided valuable information regarding the thermodynamic requirements for each step of the hydroformylation or oxo process.[1b,8,9]

			ΔH(kcal/mol)
$[C_5H_5(CO)_3Mo]_2 + H_2$	→	$2\ HMo(CO)_3C_5H_5$	+6.3
$HMo(CO)_3C_5H_5 + C_2H_4$	→	$R\text{-}Mo(CO)_3C_5H_5$	−5.6
$R\text{–}Mo(CO)_3C_5H_5 + CO$	→	$R\overset{\overset{O}{\|}}{C}Mo(CO)_3C_5H_5$	−13
$R\overset{\overset{O}{\|}}{C}Mo(CO)_3C_5H_5$ + $HMo(CO)_3C_5H_5$	→	$R\overset{\overset{O}{\|}}{C}H + [C_5H_5(CO)_3Mo]_2$	−16
$C_2H_4 + H_2O + CO$	→	$R\overset{\overset{O}{\|}}{C}H$	−28.3

Keeping in mind the important insights provided by thermochemical studies on the lanthanide and Group 6 complexes, it is interesting to notice that few such studies have been conducted on Group 8 organometallic complexes. Connor and co-workers have examined a small number of iron carbonyl complexes by solution calorimetry,[10] but few absolute BDE are available to facilitate a comparison with other systems. Ligand substitution reactions are at the heart of catalytic transformations since creation of vacant coordination sites oftentimes requires liberation of one or more ligands from the coordination sphere of the metal.[9] The few thermodynamic 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.[11]

$$Cp^*(PMe_3)_2Ru{-}OH + HL \rightarrow Cp^*(PMe_3)_2Ru{-}L + H_2O \qquad (5)$$

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

Collman has examined the kinetics of cleavage of one of the Ru–ethyl bonds in the $(OEP)Ru(Et)_2$ system.[12]

$$(OEP)Ru(Et)_2 \rightarrow (OEP)Ru(Et)^{\bullet} + Et^{\bullet} \qquad (6)$$

Parker and Tilset have most recently estimated absolute bond disruption enthalpies for a number of transition metal hydrides including $H{-}Ru(CO)_2Cp$[13]

$$Cp(CO)_2Ru{-}H \rightarrow Cp(CO)_2Ru^{\bullet} + H^{\bullet} \qquad (7)$$

and Halpern and Mancuso have reported a kinetic determination of D(Ru–R) in the $Cp(CO)_2RuCH(CH_3)C_6H_5$.[14]

$$Cp(CO)_2Ru{-}CH(CH_3)Ph \rightarrow Cp(CO)_2Ru^{\bullet} + {}^{\bullet}CH(CH_3)Ph \qquad (8)$$

To our knowledge, and prior to our recent contributions, no solution calorimetric investigation of either iron or ruthenium systems had been performed.[15,16] This paucity of thermodynamic information is rather surprising considering the involvement of Group 8 organometallic complexes in homogeneous catalysis. A large number of organoruthenium complexes of CO and/or phosphines are involved in catalysis. Catalysis requires ligand exchange reactions as liberation of one labile ligand to produce a vacant coordination site enabling substrate binding. These specific ligand exchange reactions are at the origin of the catalytic activity exhibited by Group 8 organometallic complexes, but little thermodynamic information is available regarding these processes. This is fundamental information lacking to the overall understanding of these systems.

Our present research efforts mainly focus on experimentally measuring the enthalpies of reaction associated with Group 8–ligand bond-making/bond-breaking processes and quantifying the enthalpy variations associated with these bonds as a function of the ancillary ligation. This will provide quantitative thermodynamic explanations of the driving forces behind known stoichiometric and catalytic reactions and allow for rational catalyst modifications. Moreover, as a rarely used tool in organometallic chemistry, the experimentally determined metal–ligand bond disruption enthalpies can be used to predict the feasibility of new reactions. The thermodynamic data necessary to perform these enthalpic predictions for iron and ruthenium systems are almost non-existent (*vide supra*). This fact is difficult to believe in view of the large volume of Group 8-based chemistry published every year and the involvement of Group 8 complexes in important areas of modern chemistry. The ligand substitution process is one of vital importance to catalysis.[9] Metal–ligand bonds are cleaved in the course of homogeneous catalytic processes leaving a coordinatively unsaturated species which can then react with incoming substrates. In the following sections the thermochemistry of a series of exchange reactions will be presented in order to gauge the influence of ancillary ligation on the metal–ligand bond disruption enthalpy. Available solution phase thermodynamic information is presented including some of our own ruthenium calorimetric work centering on the Cp*Ru-, Cp*(CO)$_2$Ru- and Cp′(Cl)Ru- (Cp′ = Cp and Cp*) systems.

B. ORGANORUTHENIUM THERMOCHEMISTRY

The synthetic entryway into ruthenium chemistry was greatly facilitated by the recent discovery of the useful (Cp*RuCl)$_4$ compound.[17]

$$4\ \mathrm{RuCl_3 \cdot x\ H_2O} + 4\ \mathrm{HC_5Me_5} \xrightarrow[\text{(2) LiHBEt}_3]{\text{(1) MeOH, }\Delta} \underset{\mathbf{1}}{(\mathrm{Cp^*RuCl})_4} \qquad (9)$$

Using this complex, a large number of related compounds can be isolated in multigram quantities. As previously mentioned, substitution reactions are the main focus of our investigations.

1. Enthalpies of Reaction of Cp'Ru(diene)Cl Complexes (Cp' = Cp or Cp) with Dienes and Monodentate Ligands*

The $(\mathrm{Cp^*RuCl})_4$ (**1**) complex offers a useful entryway into the thermochemistry of Ru–diene complexes. Fagan and co-workers have used **1** to isolate a series of Cp*Ru(diene)Cl complexes.[17a]

$$(Cp^*RuCl)_{4(s)} + 4\ CHD_{(soln)} \xrightarrow[30^\circ C]{THF} 4\ Cp^*Ru(CHD)Cl_{(soln)}$$

$$\mathrm{CHD = Cyclohexadiene} \qquad \Delta H_{rxn} = -39.3 \pm 0.5\ \mathrm{kcal/mol} \qquad (10)$$

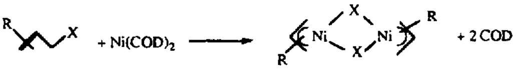
This type of diene binding reaction appears to be general, and it was found to be rapid and quantitative for a number of dienes calorimetrically investigated at 30°C in tetrahydrofuran.

With the diene information in hand, the Cp*Ru(COD)Cl (**2**) complex was found to have the diene ligand more weakly bound to the metal center. The labile nature of the Ru–COD bond was exploited in reaction (11).

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

$$\Delta H_{rxn} = -27.2 \pm 0.2\ \mathrm{kcal/mol} \qquad (11)$$

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 $\mathrm{Ni(COD)_2}$ complex readily loses cyclooctadiene ligands to form nickel allyl complexes in the presence of allylic halides[18] (Eq. (12)):



(12)

These nickel allyl complexes have found great utilization in organic chemistry in the formation of C–C bonds.[18] 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.

In the present ruthenium system, based on 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. So 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 (13) did not proceed quantitatively under calorimetric conditions when norbornadiene was the diene bound to ruthenium.

$$\mathrm{Cp^*Ru(NBD)Cl} + 2\,\mathrm{PPh_3} \not\longrightarrow \mathrm{Cp^*Ru(PPh_3)_2Cl} + \mathrm{NBD} \qquad (13)$$

Reaction (13) 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.[1b]

Two possible factors can account for this different behavior exhibited by the mentioned 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. (15) is subtracted from Eq. (14) leading directly to the enthalpy of the diene exchange.

$$\begin{array}{lcllr}
 & & & \underline{\Delta H_{rxn}\ (\text{kcal/mol})} & \\
(Cp^*RuCl)_{4(s)} + 4\ NBD_{(soln)} & \rightarrow & 4\ Cp^*Ru(NBD)Cl_{(soln)} & -52.1 \pm 0.2 & (14) \\
(Cp^*RuCl)_{4(s)} + 4\ COD_{(soln)} & \rightarrow & 4\ Cp^*Ru(COD)Cl_{(soln)} & -39.8 \pm 0.4 & (15) \\
\hline
4\ Cp^*Ru(COD)Cl_{(soln)} & \rightarrow & 4\ Cp^*Ru(NBD)Cl_{(soln)} & -12.3 \pm 0.4 & (16) \\
+ 4\ NBD_{(soln)} & & + 4\ COD_{(soln)} & &
\end{array}$$

The calculated enthalpy of reaction (16) corresponds to the exchange of four COD for four NBD ligands. Equation (17) provides a view of the diene exchange process on a per mole basis.

$$Cp^*Ru(COD)Cl_{(soln)} + NBD_{(soln)}$$

$$\rightarrow Cp^*Ru(NBD)Cl_{(soln)} + COD_{(soln)} \qquad (17)$$

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

Reaction (17) is calculated to be exothermic by some 3.1 kcal/mol. This relative increased thermodynamic stability might not entirely explain the fact that reaction (13) does not proceed extensively at 30°C. An enthalpy of reaction can be estimated from the present data.

$$\begin{array}{rcllr}
 & & & \underline{\Delta H_{rxn}\ (\text{kcal/mol})^{a}} & \\
1/4(Cp^*RuCl)_{4(s)} + 2\ P(OMe)_3 & \rightarrow & Cp^*Ru(P(OMe)_3)_2Cl & -47.6 \pm 0.2 & (18) \\
Cp^*Ru(NBD)Cl & \rightarrow & 1/4(Cp^*RuCl)_{4(s)} + NBD & 13.0 \pm 0.2 & (19) \\
Cp^*Ru(P(OMe)_3)_2Cl + COD & \rightarrow & Cp^*Ru(COD)Cl + 2\ P(OMe)_3 & 37.5 \pm 0.4 & (20) \\
Cp^*Ru(COD)Cl + 2\ PPh_3 & \rightarrow & Cp^*Ru(PPh_3)_2Cl + COD & -18.1 \pm 0.2 & (21) \\
\hline
Cp^*Ru(NBD)Cl + 2\ PPh_3 & \rightarrow & Cp^*Ru(PPh_3)_2Cl + NBD & -15.2 \pm 0.3 & (22)
\end{array}$$

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

This exothermic value clearly indicates reaction (22) to be enthalpically favored. It appears then that the dominating factor behind our inability to observe Eq. (13) must then not be a thermodynamic one but a kinetic one.

Furthermore, the enthalpy difference between reactions (21) and (22) (−2.9 kcal/mol) is the same within experimental error as the previously determined value for Eq. (17) (−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.[19]

$$\text{(COD)Mo(CO)}_{4(\text{soln})} + \text{NBD}_{(\text{soln})} \rightarrow \text{(NBD)Mo(CO)}_{4(\text{soln})} + \text{COD}_{(\text{soln})} \quad (23)$$

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

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,20]

Taking advantage of the labile nature of the COD ligand in **2**, reactions involving the displacement of the COD ligand by two equivalents of monodentate ligands were investigated by solution calorimetry at 30°C.

$$\text{Cp*(Ru(COD)Cl}_{(\text{soln})} + 2\ \text{AsEt}_{3(\text{soln})} \xrightarrow[30^\circ\text{C}]{\text{THF}} \text{Cp*Ru(AsEt}_3)_2\text{Cl}_{(\text{soln})} + \text{COD}_{(\text{soln})} \quad (24)$$

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

Arsine and phosphine ligands were investigated in view of their importance as catalyst modifiers.[9a] All enthalpies of reaction for monodentate ligands are reported in Table I. 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$_3$)$_2$Fe(CO)$_3$[16b,c] and (AsEt$_3$)$_2$Mo(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.

TABLE I

Enthalpies of substitution (kcal/mol) in the reaction:

$$\mathbf{Cp'Ru(COD)Cl_{(soln)} + 2\,L_{(soln)} \xrightarrow[30°C]{THF} Cp'Ru(L)_2Cl_{(soln)} + COD_{(soln)}}$$

$$\mathbf{Cp' = C_5H_5\ (Cp)\ and\ C_5Me_5\ (Cp^*)}$$

L	Complex	$-\Delta H_{rxn}Cp^{*a}$	$-\Delta H_{rxn}Cp^{a}$
$AsEt_3$	$Cp'Ru(AsEt_3)_2Cl$	15.0 (0.2)	19.4 (0.2)
PPh_3	$Cp'Ru(PPh_3)_2Cl$	18.1 (0.2)	22.9 (0.4)
PPh_2Me	$Cp'Ru(PPh_2Me)_2Cl$	29.4 (0.2)	32.8 (0.2)
$P(OPh)_3$	$Cp'Ru(P(OPh)_3)_2Cl$	31.2 (0.2)	34.1 (0.4)
PEt_3	$Cp'Ru(PEt_3)_2Cl$	27.2 (0.2)	34.5 (0.2)
P^nBu_3	$Cp'Ru(P^nBu_3)_2Cl$	26.0 (0.2)	35.4 (0.2)
$PPhMe_2$	$Cp'Ru(PPhMe_2)_2Cl$	31.8 (0.3)	35.9 (0.2)
PMe_3	$Cp'Ru(PMe_3)_2Cl$	32.2 (0.4)	38.4 (0.4)
$P(OMe)_3$	$Cp'Ru(P(OMe)_3)_2Cl$	37.5 (0.4)	41.8 (0.2)

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

$$Cp^*Ru(AsEt_3)_2Cl_{(soln)} + 2\ PEt_{3(soln)}$$

$$\rightarrow Cp^*Ru(PEt_3)_2C_{(soln)} + 2\ AsEt_{3(soln)} \qquad (25)$$

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

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[19] (L = arsine and phosphine ligands). A recent study of the diaxial–$(L)_2Fe(CO)_3$ system[16b,c] 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) worth −5.4 kcal/mol, the difference in enthalpies of binding of $AsEt_3$ vs PEt_3 is calculated 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.

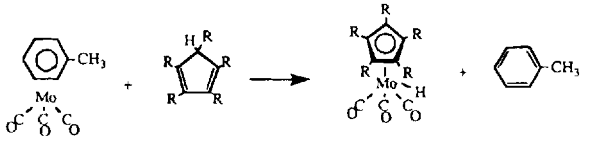
The monodentate phosphine ligand data can be examined in terms of steric and electronic contributions to the enthalpy of reaction, the relative importance of which can be quantified in terms of the respective A_1/A_2 ratios obtained in a treatment first proposed by Tolman[21] where enthalpies of reaction are correlated to steric (θ, cone angle) and electronic (ν, A_1 carbonyl stretching frequency in $Ni(CO)_3L$, L = tertiary phosphine) factors.

$$-\Delta H^{\circ} = A_o + A_1\theta + A_2\nu \tag{26}$$

A correlation factor (R) of 0.95 is obtained when enthalpic data is fitted to Eq. (26). The obtained A_1/A_2 ratio 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[22] which exhibits a considerable influence of steric factor when compared to the data for the parent $(L)_2Mo(CO)_4$ system (A_1/A_2 = 0.81).[19] 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.[16] In that instance, the A_1/A_2 ratio is only 0.008, and as might be expected the steric factor play a minor role since the phosphine ligands have adopted a mutually trans arrangement. Since the steric factor has such a profound influence on the enthalpy of reaction, a direct relationship between the enthalpy of reaction and the phosphine cone angle was established, and the linear relationship found to exist emphasizes the major role played by steric effects in this system.[23]

It appears from the experimental enthalpy data that trimethylphosphite leads to the formation of the most stable organoruthenium complex. This is not obvious even though similar high binding affinities of this ligand for transition metals have previously been observed.[22] This fact can possibly be explained in terms of backdonation from the metal into orbitals on the phosphite ligand (phosphorus–oxygen σ^* orbitals).

In view of the limited number of thermochemical studies for Group 8 metal centers (*vide infra*), it is not too surprising that investigations addressing the influence of ancillary ligand modification on the enthalpy of ligand substitution for such systems are virtually non-existent. In fact, very little thermochemical information is available concerning the effects of ligand variation on enthalpies of reaction. Hoff and co-workers have probed ancillary ligand variation and thermodynamic effects in organomolybdenum complexes examining enthalpies associated with the substitution/oxidative addition and ligand addition reactions illustrated below.[1b,24]



(27)

R = H or Me

$$[Cp'Mo(CO)_2]_2 + 2\ CO \rightarrow [Cp'Mo(CO)_3]_2 \qquad (28)$$

$$Cp' = C_5H_5,\ C_5Me_5,\ C_9H_7$$

Sowa and Angelici have investigated the effects of ancillary ligand modification on the enthalpy of protonation of organoiridium complexes in order to gauge the basicity of the metal center.[25]

$$Cp'Ir(1{,}5\ COD) + CF_3SO_3H$$
$$\rightarrow CP'Ir(1{,}5\ COD)H^+\ CF_3SO_3^- \qquad (29)$$

$$Cp' = C_5Me_xH_{x-5},\ X = 0,\ 1,\ 3\text{–}5$$

Lastly, Tilset and Parker have investigated the absolute metal–hydride bond dissociation enthalpy for transition metal hydrides, with little observed variation in M–H BDE associated with modifications of the ancillary ligation.[13]

As in the case of the Cp*Ru(COD)Cl complex,[23] the related CpRu(COD)Cl (**3**) complex was found to have a diene ligand that is weakly bound to the metal center. The labile nature of this diene ligand leads to the CpRu(COD)Cl complex being an efficient catalyst precursor; this emerging catalytic chemistry has recently been reviewed.[26] The labile nature of the Ru–COD bond was exploited in reaction (30) and investigated by solution calorimetry.

$$\begin{aligned} &\mathrm{CpRu(COD)Cl_{(soln)} + 2\ PEt_{3(soln)}} \\ &\qquad \xrightarrow[30^\circ C]{\mathrm{THF}} \mathrm{CpRu(PEt_3)_2Cl_{(soln)} + COD_{(soln)}} \qquad (30) \\ &\qquad \Delta H_{rxn} = -34.5 \pm 0.2\ \mathrm{kcal/mol} \end{aligned}$$

As in the case of related Cp* system, arsine and phosphine ligands were investigated in view of their importance as catalyst modifiers.[9a,27] As might be expected, in view of its steric bulk and weak electronic donating ability, the $AsEt_3$ ligand is the most weakly bound ligand studied. A similar trend has been observed for $(AsEt_3)_2Fe(CO)_3$[16c] 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 reactions listed in Table I. The reaction involving the phosphine ligand, PEt_3, displays an enthalpy 15.1 kcal/mol more exothermic than its arsenic relative.

$$\begin{aligned} &\mathrm{CpRu(AsEt_3)_2Cl_{(soln)} + 2\ PEt_{3(soln)}} \\ &\qquad \rightarrow \mathrm{CpRu(PEt_3)_2Cl_{(soln)} + 2\ AsEt_{3(soln)}} \qquad (31) \\ &\qquad \Delta H_{calcd} = -15.1 \pm 0.4\ \mathrm{kcal/mol} \end{aligned}$$

This compares to an enthalpy difference of 12.2 kcal/mol for the $Cp^*Ru(L)_2Cl$ system.[23] Similar enthalpy differences (12.4 ± 0.3 kcal/mol) have been observed in the cis-$(L)_2Mo(CO)_4$ complexes[19] (L = arsine and phosphine ligands). A recent study of the diaxial-$(L)_2Fe(CO)_3$ system[16b,c] also shows important similarities as far as the binding of arsenic *versus* phosphorus donors. Taking into consideration the estimated enthalpy of isomerization (axial-equatorial to diaxial) worth −5.4 kcal/mol, the difference in enthalpies of binding of $AsEt_3$ vs PEt_3 is calculated to be 12.5 kcal/mol in the iron system.

From the experimental data, it is now clear why the triphenylphosphine complex acts as a useful synthon in the isolation of bis(phosphine) complexes.[28] These reactions are enthalpically driven; for a typical example see Eq. (32).

$$\begin{aligned} &\mathrm{CpRu(PPh_3)_2Cl_{(soln)} + 2\ PMe_{3(soln)}} \\ &\qquad \rightarrow \mathrm{CpRu(PMe_3)_2Cl_{(soln)} + 2\ PPh_{3(soln)}} \qquad (32) \\ &\qquad \Delta H_{calcd} = -14.5 \pm 0.6\ \mathrm{kcal/mol} \end{aligned}$$

The ruthenium–PPh_3 is the weakest Ru–P interaction found in the present study. Metal–PPh_3 interactions renowned for their thermodynamic weakness have found great use in catalysis. In this instance, we can estimate the difference in average Ru–P bond energy between the PMe_3 and PPh_3 to be on the order of 7.3 kcal/mol in tetrahydrofuran solution.

The thermodynamic data can be examined in terms of steric and electronic contributions to the enthalpy of reaction (*vide infra*). In view of the cis arrangement of phosphine ligands, steric factors might be expected, as in the related Cp* system[23] to represent the predominant factor influencing the magnitude of the enthalpy of reaction. Since the steric factor has such a profound influence on the enthalpy of reaction, a direct relationship between the enthalpy of reaction and the phosphine cone angle was established, and the linear relationship emphasizes the major role played by steric effects in the present system.

Important insights are offered by a comparison between the present data and that of the $Cp^*Ru(PR_3)_2Cl$ system. In both Cp and Cp* systems the role of the phosphine steric factor is most important. Yet the difference in enthalpies of reaction between the two systems is based on differences in electronic features at the metal, resulting from a change of ancillary ligation (Cp vs Cp*). Since Cp is less electron donating than Cp*, the Cp system will be able to accommodate greater electron density from the incoming two electron donor (higher electrophilicity), therefore leading to more exothermic enthalpies of ligand substitution. The electronic origin of this difference in enthalpy of reaction between the present Cp- and Cp*-based systems can be further illustrated upon examination of χ factors, used by Geiring and co-workers,[29] which express the donicity of the phosphine ligand. The ligand donicity remains constant while the accepting properties of the metal have been modified by the change in ancillary ligation (Cp to Cp*). Here lies the electronic difference between the two systems.

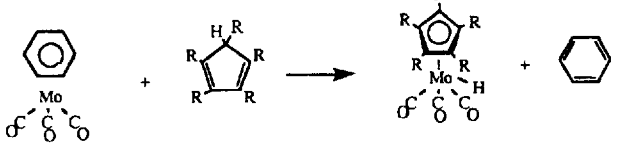
$$Cp^*Ru(COD)Cl_{(soln)} + 2\ PPh_{3(soln)} \xrightarrow[30^\circ C]{THF} Cp^*Ru(PPh_3)_2Cl_{(soln)} + COD_{(soln)} \qquad (33)$$

$$\Delta H_{rxn} = -18.1 \pm 0.2 \text{ kcal/mol}$$

$$\mathrm{CpRu(COD)Cl_{(soln)}} + 2\ \mathrm{PPh_{3(soln)}} \xrightarrow[30^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{CpRu(PPh_3)_2Cl_{(soln)}} + \mathrm{COD_{(soln)}} \qquad (34)$$

$$\Delta H_{rxn} = -22.9 \pm 0.4\ \mathrm{kcal/mol}$$

This difference in electronic properties at the metal center measures the change in metal basicity. Sowa and Angelici have investigated a series of iridium complexes and have observed a difference in enthalpies of protonation of 5.7 kcal/mol between CpIr(COD) and Cp*Ir(COD) complexes.[25] In these experiments, H^+ proved to be more strongly bound to M–Cp* by ca. 5 kcal/mol. This is in view of the increased electron density imparted by the better Cp* donor. In the present ruthenium systems electron donating phosphine groups are more strongly bound in the CpRu system. Both sets of experiments, although using different approaches, relate information concerning the same fundamental characteristic, namely metal basicity. Hoff and co-workers have first demonstrated this difference in metal basicity between Cp and Cp* in their thermochemical investigations of organomolybdenum complexes.[24,30]



(35)

$$R = H;\ \Delta H_{rxn} = -12.8\ \mathrm{kcal/mol}$$

$$R = Me;\ \Delta H_{rxn} = -10.5\ \mathrm{kcal/mol}$$

The enthalpy difference between ligand substitution reactions, -2.3 kcal/mol, reflects the difference of metal basicity accompanying a change of the ancillary ligation. This difference is of the same order of magnitude as Angelici's enthalpies of protonation and the average difference in enthalpy of ligand substitution in the Cp versus Cp* organoruthenium systems. Rottink and Angelici have also measured metal basicity differences in a related $\mathrm{Cp'Ru(PPh_3)_2H}$ system (Cp = Cp and Cp*) and found protonation to be 5.5 kcal/mol favoring the $\mathrm{Cp^*Ru(PPh_3)_2H}$ complex.[31] These researchers have also found differences in the related chloro complexes, $Cp'Ru(PMe_3)_2Cl$, on the order of 9.0 kcal/mol. This result can be directly compared with the present difference in enthalpies of ligand substitution in these two $Cp'Ru(PR_3)_2Cl$ systems for PMe_3 (6.2 ± 0.5 kcal/mol).

Differences in Ru–E distances can be qualitatively understood in terms of binding energy. The Ru–As interaction being the weakest of the series examined will possess the longest Ru–E bond distance (no corrections were applied for differences in atomic radii). Three other $CpRu(PR_3)_2Cl$ (PR_3 = PMe_3, $P(OMe)_3$ and PPh_3) complexes have previously been structurally characterized.[32] A comparison involving all five complexes in terms of bond distances and bond angles suggests a linear relationship between bond enthalpy data and ruthenium–phosphine/arsine bond length information ($R = 0.94$).

A comparison between Cp- and Cp*-based ruthenium complexes bearing similar arsine or phosphine ligands offers further insights into the bond strength/bond length relationship. In the present system, the average Ru–As and Ru–P bond length cited above can be compared with distances of 2.445 and 2.321 Å for the related Cp* complexes.[33] There appears to exist a correlation between bond length and magnitude of the enthalpies of substitution in both systems. Further structural studies are in progress in order to examine to what extent this relationship remains valid for these ruthenium systems.[33]

Trost and co-workers have recently reported on the catalytic role of $CpRu(PPh_3)_2Cl$ as an efficient catalyst precursor in the ruthenium-catalyzed addition of allyl alcohols and acetylenes leading, in a simple synthetic route, to unsaturated ketones.[34] They have since reported that complex **3** can very easily perform such a transformation, although using a different mechanistic route.[34] The utility of the ruthenium–COD complex (**3**) as a catalyst precursor can be understood in terms of relative bond dissociation enthalpies. The $Ru–PPh_3$ bond is on average 11.5 kcal/mol stronger than the Ru–olefin bond present in **3**.

2. *Enthalpies of Reaction of Cp′Ru(diene)Cl Complexes (Cp′ = Cp or Cp*) with Chelating Diphosphine Ligands*

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.[9a]

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.[9b,35] 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. We have recently reported on the thermochemistry of two related organoruthenium systems bearing chelating diphosphine ligations:

$$\mathrm{Cp'Ru(COD)Cl_{(soln)}} + \overset{\frown}{\mathrm{P\,P}}_{\mathrm{(soln)}} \xrightarrow[30^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{Cp'Ru(\overset{\frown}{P\,P})Cl_{(soln)}} + \mathrm{COD_{(soln)}} \qquad (36)$$

$\overset{\frown}{\mathrm{P\,P}}$ = chelating diphosphine, Cp′ = C_5H_5 and C_5Me_5

A compilation of diphosphine ligands and their respective enthalpies of reaction is listed in Table II.

An apparent trend in examining Table II is that reactions involving alkyl substituted phosphines (more basic phosphines) prove to be more exothermic, resulting in more thermodynamically stable complexes. This trend is also present in the related Cp* system.[23,36]

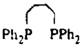
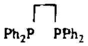
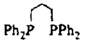
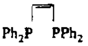
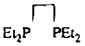
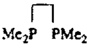
The strain energies in cyclic organic compounds have been extensively investigated. Ring strain estimates for four-, five- and six-membered rings are on the order of 26, 6 and 0 kcal/mol, respectively.[37] Incorporation of a metal center into the chelate structures produces four- to seven-membered metallacyclic rings with enthalpies of reaction as shown in Table II. The five-, six- and seven-membered ring complexes based on 1,2-(diphenylphosphinoethane) (dppe), 1,2-(diphenylphosphinopropane) (dppp) and 1,2-(diphenylphosphinobutane) (dppb) are most stable, their enthalpies of reaction being of the same order of magnitude as two equivalents of PPh_2Me. The least stable of the metallacycles investigated is the four-membered ring where ring strain is estimated as 13 kcal/mol. This 13

TABLE II

Enthalpies of substitution (kcal/mol) in the reaction:

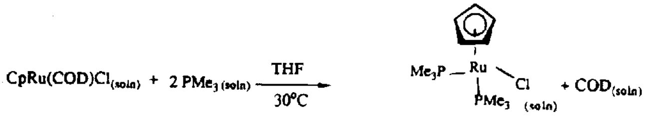
$$\mathrm{Cp'Ru(COD)Cl_{(soln)}} + \overset{\frown}{\mathrm{P\,P}} \xrightarrow[30^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{Cp'Ru(\overset{\frown}{P\,P})Cl_{(soln)}} + \mathrm{COD_{(soln)}}$$

$$\mathrm{Cp'} = \mathrm{C_5H_5\ (Cp)\ and\ C_5Me_5}$$

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

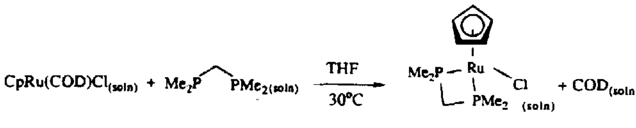
[a]Enthalpies of reaction are reported with 95% confidence limits.

kcal/mol strain energy is on the same order of magnitude as strain energy estimates for a thorium metallacyclobutane complex (10 kcal/mol).[38] This energy is also in relatively good agreement with more closely related four-membered organomolybdenum, $\mathrm{(Ph_2PCH_2PPh_2)Mo(CO)_4}$ (8.3 kcal/mol),[22] organoiron, $\mathrm{(Ph_2PCH_2PPh_2)Fe(CO)_3}$ (12.6 kcal/mol)[16c] as well as $\mathrm{Cp^*Ru(Ph_2PCH_2PPh_2)Cl}$ (10 kcal/mol)[36] 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 (37).



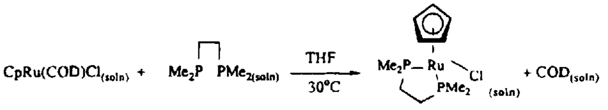
(37)

ΔH_{rxn} = -38.4 ± 0.4 kcal/mol



(38)

ΔH_{rxn} = -26.2 ± 0.2 kcal/mol



(39)

ΔH_{rxn} = -39.7 ± 0.3 kcal/mol

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. Similar results are obtained with the Cp*-based system[36] (Fig. 1).

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 focussed on the (PP)Mo(CO)$_4$ system.[22] When the relative enthalpy data for a series of ligands common to the two systems are compared, a poor linear fit (R = 0.84) 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 exhibits a remarkable fit (R = 0.96) 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

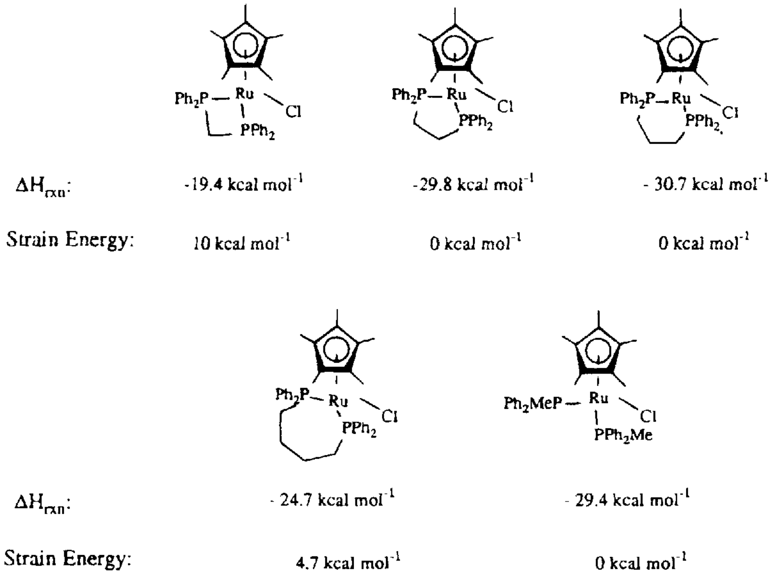


FIGURE 1

between the present system and the recently investigated Cp*Ru(PP)Cl system. Direct comparison of these enthalpies of reaction 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$_3$)$_2$Cl system[39] 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 P–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. Both steric and electronic factors appear to play important roles in determining the overall thermodynamic stability of these and other metallacyclic complexes. 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.

3. *Thermochemistry of 16 Electron Cp*Ru(PR$_3$)Cl Complexes*

A facile entryway into the thermochemistry of Cp*Ru(PR$_3$)Cl complexes is made possible by the rapid and quantitative reaction of (Cp*RuCl)$_4$ (**1**) with the phosphine ligand.[40,41]

$$(\mathrm{Cp^*RuCl})_{4(s)} + 4\ \mathrm{PR}_{3(soln)} \xrightarrow[30^\circ C]{\mathrm{THF}} 4\ \mathrm{Cp^*Ru(PR_3)Cl}_{(soln)} \qquad (40)$$

$$\mathrm{PR_3} = \mathrm{PCy_3};\ \Delta H_{rxn} = -41.9 \pm 0.2\ \mathrm{kcal/mol}$$

$$\mathrm{PR_3} = \mathrm{P^iPr_3};\ \Delta H_{rxn} = -37.4 \pm 0.3\ \mathrm{kcal/mol}$$

This type of phosphine binding reaction appears general for the two sterically demanding ligands investigated. Furthermore, we previously reported that complex **1** could also allow access into the thermochemistry of 18-electron complexes of formulation Cp*Ru(PR$_3$)$_2$Cl, where PR$_3$ is a phosphine possessing a smaller size cone angle.[23]

$$(\mathrm{Cp^*RuCl})_{4(s)} + 8\ \mathrm{PEt}_{3(soln)} \xrightarrow[30^\circ C]{\mathrm{THF}} 4\ \mathrm{Cp^*Ru(PEt_3)_2Cl}_{(soln)} \qquad (41)$$

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

The 16-electron complexes have been found to react with smaller cone angle phosphine ligands to produce complexes with filled coordination spheres, according to Eqs. (42) and (43).

$$\mathrm{Cp^*Ru(PR_3)Cl}_{(soln)} + 2\ \mathrm{PEt}_{3(soln)} \xrightarrow[30^\circ C]{\mathrm{THF}} \mathrm{Cp^*Ru(PEt_3)_2Cl}_{(soln)} + \mathrm{PR}_{3(soln)} \qquad (42)$$

$$PR_3 = PCy_3;\ \Delta H_{rxn} = -25.9 \pm 0.4\ \text{kcal/mol}$$

$$PR_3 = P^iPr_3;\ \Delta H_{rxn} = -27.4 \pm 0.3\ \text{kcal/mol}$$

$$Cp^*Ru(PR_3)Cl_{(soln)} + 2\ P(OMe)_{3(soln)} \xrightarrow[30^\circ C]{THF} Cp^*Ru(P(OMe)_3)_2Cl_{(soln)} + PR_{3(soln)} \quad (43)$$

$$PR_3 = PCy_3;\ \Delta H_{rxn} = -36.7 \pm 0.3\ \text{kcal/mol}$$

$$PR_3 = P^iPr_3;\ \Delta H_{rxn} = -38.4 \pm 0.4\ \text{kcal/mol}$$

Tilley and co-workers have also reported the use of **1** as a synthetic precursor to Cp*Ru(PR$_3$)Cl complexes.[40] A combination of these two recent synthetic contributions offers an opportunity to probe the thermochemistry and factors influencing the strength of ruthenium–phosphine bonds in these related systems. Based on these recent observations concerning the reactivity of the (Cp*RuCl)$_4$ complex (**1**), thermochemical studies were undertaken in order to quantify the enthalpic driving forces behind the chemistry. Related calorimetric studies on tertiary phosphine substitution in the Cp*Ru(COD)Cl system have also been communicated.[23]

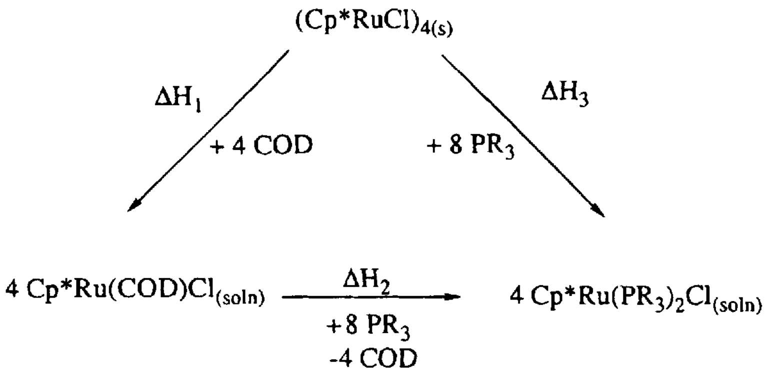
$$Cp^*Ru(COD)Cl_{(soln)} + 2\ PEt_{3(soln)} \rightarrow Cp^*Ru(PEt_3)_2Cl_{(soln)} + COD_{(soln)} \quad (44)$$

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

In the course of these studies, the reaction enthalpy between **1** and PCy$_3$ was experimentally determined[23] (Eq.(45)) and allowed for a thermochemical cycle to be constructed in order to gauge the internal consistency of the data (Scheme 1).

$$(Cp^*RuCl)_{4(s)} + 4\ PCy_{3(soln)} \xrightarrow[30^\circ C]{THF} 4\ Cp^*Ru(PCy_3)Cl_{(soln)} \quad (45)$$

$$\Delta H_{rxn} = -41.9 \pm 0.2\ \text{kcal/mol}$$



PR_3	$-\Delta H_1$[a]	$-\Delta H_2$[a]	$-\Delta H_{3\,calcd}$	$-\Delta H_{3\,exp}$[a]
P^nBu_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)**

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[a] All enthalpy values are reported with 95% confidence limits.

SCHEME 1

The existence of a coordinatively unsaturated complex related to $Cp^*Ru(PCy_3)Cl$ allowed for enthalpy of reaction (46) to also be measured and is now reported below.

$$(Cp^*RuCl)_{4(s)} + 4\ P^iPr_{3(soln)} \xrightarrow[30°C]{THF} \underset{\mathbf{4}}{4\ Cp^*Ru(P^iPr_3)Cl_{(soln)}} \qquad (46)$$

$$\Delta H_{rxn} = -37.4 \pm 0.3\ \text{kcal/mol}$$

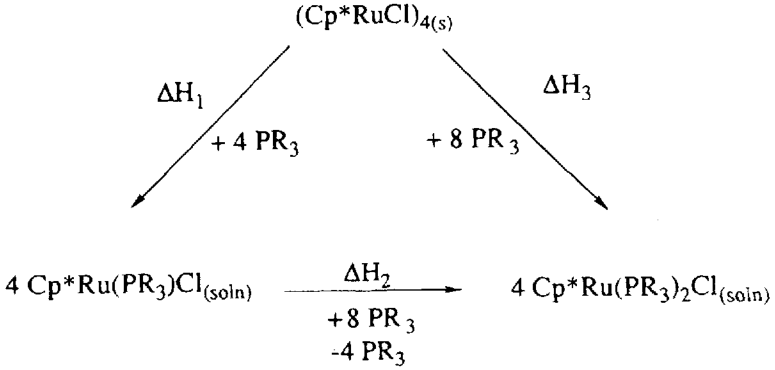
The very reactive nature of the unsaturated complexes, **4** and **5**, can be exploited in order to thermodynamically link the $Cp^*Ru(PR_3)Cl$ to the $Cp^*Ru(PR_3)_2Cl$ systems. This is in fact possible since complex **1** was shown to react according to eq. (47).

$$\underset{\mathbf{5}}{Cp^*Ru(PCy_3)Cl} + 2\ PMe_3 \rightarrow Cp^*Ru(PMe_3)_2Cl + PCy_3 \qquad (47)$$

The Ru–PCy_3 bond in **5** appears quite labile and is therefore expected to be relatively weak. Reaction (48) was tested for a number of different phosphines and phosphites. The only products detected by ^{1}H NMR spectroscopy, in the presence of excess PR_3 (PR_3 = PEt_3, P^nBu_3, $P(OMe)_3$), were the corresponding $Cp^*Ru(PR_3)_2Cl$ complexes.[23]

With the thermodynamic data on these organoruthenium complexes on hand, it is now possible to construct thermodynamic cycles to verify the internal consistency of the thermodynamic data. This is especially desirable in view of the highly reactive nature of **1**, **4** and **5**. Scheme 2 illustrates four separate thermochemical cycles verifying the internal consistency of the reported thermochemical information.

Subtracting reaction (46) from (44) leads to Eq. 48, which represents the phosphine exchange reaction between two complexes bearing sterically demanding phosphine ligands.



PR_3	PR_3	$-\Delta H_1$[a]	$-\Delta H_2$[a]	$-\Delta H_{3\,calcd}$[a]	$-\Delta H_{3\,exp}$[a]
PCy_3	PEt_3	41.9 (0.2)	103.6 (2.4)	145.5 (2.6)	147.5 (0.6)
PCy_3	$P(OMe)_3$	41.9 (0.2)	146.8 (2.4)	188.7 (2.6)	190.3 (0.2)
P^iPr_3	PEt_3	37.4 (0.3)	109.6 (1.2)	147.0 (1.5)	147.5 (0.6)
P^iPr_3	$P(OMe)_3$	37.4 (0.3)	153.6 (1.2)	191.0(1.5)	190.3 (0.2)

---

[a] All enthalpy values are reported with 95% confidence limits.

SCHEME 2

$$\mathrm{Cp^*Ru(P^iPr_3)Cl_{(soln)} + PCy_{3(soln)} \rightarrow Cp^*Ru(PCy_3)Cl_{(soln)} + P^iPr_{3(soln)}} \quad (48)$$

$$\Delta H_{calcd} = -1.1 \pm 0.4 \text{ kcal/mol}$$

From the available thermodynamic data for the first section in Scheme 2 (ΔH_1) of the thermodynamic cycle, the Ru–PCy_3 bond is calculated to be 1.1 kcal/mol stronger than the Ru–P^iPr_3 bond. This compares very closely to the value obtained using data for the PEt_3 reactions in the second portion (ΔH_2) of the thermodynamic cycle:

$$\mathrm{Cp^*Ru(P^iPr_3)Cl_{(soln)} + 2\,PEt_{3(soln)} \rightarrow Cp^*Ru(PEt_3)_2Cl_{(soln)} + P^iPr_{3(soln)}} \quad (49)$$

$$\Delta H_{rxn} = -27.4 \pm 0.3 \text{ kcal/mol}$$

$$\mathrm{Cp^*Ru(PEt_3)_2Cl_{(soln)} + PCy_{3(soln)} \rightarrow Cp^*Ru(PCy_3)Cl_{(soln)} + 2\,PEt_{3(soln)}} \quad (50)$$

$$\Delta H_{rxn} = 25.9 \pm 0.4 \text{ kcal/mol}$$

$$\mathrm{Cp^*Ru(P^iPr_3)Cl_{(soln)} + PCy_{3(soln)} \rightarrow Cp^*Ru(PCy_3)Cl_{(soln)} + P^iPr_{3(soln)}} \quad (48)$$

$$\Delta H_{calcd} = -1.5 \pm 0.5 \text{ kcal/mol}$$

A value of -1.7 ± 0.5 kcal/mol is obtained when the $P(OMe)_3$ values are considered. Within experimental error, all these values are in agreement, and a value of -1.4 ± 0.5 kcal/mol is taken to represent the difference between the Ru–PCy_3 and Ru–P^iPr_3 bonds.

The third section of the cycle (ΔH_3) presents, when combined with the first (ΔH_1), a unique opportunity to compare the various Ru–PR_3 bond energies so far investigated, on a relative scale. When measured enthalpies of reaction are divided by the number of Ru–PR_3 bonds formed in the course of the reaction, a relative energetic contribution per Ru–PR_3 bond can be estimated (see Table III). It should be specified here that the numbers obtained for the Ru–PR_3 in the $Cp^*Ru(PR_3)_2Cl$ system represent an average of the two ruthenium–phosphine bond energies.

The only enthalpy of reaction for sterically demanding phosphine ligand available for comparison is found in the work of Hoff and co-workers,[22] in their study of enthalpies of ligand substitution in the $(C_6H_6)Mo(CO)_3$ system. In tetrahydrofuran solution, an enthalpy

TABLE III

Relative bond disruption enthalpies (kcal/mol) in the reaction:

$$\mathrm{Cp^*RuCl_{(soln)} + n\ L_{(soln)} \longrightarrow Cp^*Ru(L)_nCl_{(soln)}}$$

L	n	Complex	Relative BDE[a,b]
P^iPr_3	1	$Cp^*Ru(P^iPr_3)Cl$	9.4 (0.3)[c]
PCy_3	1	$Cp^*Ru(PCy_3)Cl$	10.5 (0.2)[c]
$AsEt_3$	2	$Cp^*Ru(AsEt_3)_2Cl$	12.5 (0.6)
PPh_3	2	$Cp^*Ru(PPh_3)_2Cl$	14.0 (0.6)
P^nBu_3	2	$Cp^*Ru(P^nBu_3)_2Cl$	18.0 (0.4)
PEt_3	2	$Cp^*Ru(PEt_3)_2Cl$	18.4 (0.6)
PPh_2Me	2	$Cp^*Ru(PPh_2Me)_2Cl$	19.7 (0.7)
$P(OPh)_3$	2	$Cp^*Ru(P(OPh)_3)_2Cl$	20.6 (0.6)
$PPhMe_2$	2	$Cp^*Ru(PPhMe_2)_2Cl$	20.9 (0.7)
PMe_3	2	$Cp^*Ru(PMe_3)_2Cl$	21.1 (0.8)
$P(OMe)_3$	2	$Cp^*Ru(P(OMe)_3)_2Cl$	23.8 (0.4)

[a] Relative BDE values refer to the average of the 2 Ru–PR_3 bond energy values unless noted otherwise.

[b] See text for an explanation on the calculation of relative Ru–PR_3 BDE values.

[c] Refers to the relative disruption enthalpy of one Ru–PR_3 bond.

of reaction of −23.1 kcal/mol was experimentally determined for reaction (51).

$$\mathrm{(C_6H_6)Mo(CO)_3 + 2\ PCy_3 \rightarrow (PCy_3)_2Mo(CO)_3 + C_6H_6} \qquad (51)$$

Relying on a Mo–benzene BDE value of 63.2 kcal/mol, an average bond energy estimate can be calculated for Mo–PCy_3 (28.7 kcal/mol). A similar treatment of reaction (20) affords an average Mo–$P(OMe)_3$ BDE value of 38.9 kcal/mol.[23]

$$\mathrm{(C_6H_6)Mo(CO)_3 + 3\ P(OMe)_3 \rightarrow (P(OMe)_3)_3Mo(CO)_3 + C_6H_6} \qquad (52)$$

The enthalpy difference between the two Mo–PR_3 bonds, 10.2 kcal/mol, is similar to the one which can be calculated for the Ru–PR_3 bond energy difference between Ru–PCy_3 and Ru–$P(OMe)_3$, 13.3 kcal/mol.

A relative bond enthalpy scale can be constructed including all ligands so far investigated in the Cp*RuCl system. This can be achieved since a number of arsines/phosphines/phosphites have been linked through a thermodynamic cycle to reaction (53).[23]

$$(\mathrm{Cp^*RuCl})_{4(s)} + 4\ \mathrm{COD}_{(soln)} \rightarrow 4\ \mathrm{Cp^*Ru(COD)Cl}_{(soln)} \qquad (53)$$
$$\Delta H_{rxn} = -39.8 \pm 0.4\ \mathrm{kcal/mol}$$

This enables the determination of average bond enthalpy terms associated with the entire $\mathrm{Cp^*Ru(PR_3)_nCl}$ (n = land 2) series (see Table III).

The relative weakness of the Ru–$\mathrm{PCy_3}$ and Ru–$\mathrm{P^iPr_3}$ bonds may not be entirely surprising when the observed chemistry is examined. However, the enthalpic data clearly illustrate the existence of an average Ru–$\mathrm{AsEt_3}$ bond enthalpy which is in fact *stronger* than either of the ruthenium–large cone angle phosphine bonds. To our knowledge, this represents the first observation of this type. In this context, the enthalpy of reaction can be calculated for the ligand exchange process which illustrates the relative strength of the ruthenium–arsine bond.

$$\mathrm{Cp^*Ru(PCy_3)Cl} + 2\ \mathrm{AsEt_3} \rightarrow \mathrm{Cp^*Ru(AsEt_3)_2Cl} + \mathrm{PCy_3} \qquad (54)$$
$$\Delta H_{calcd} = -14.5 \pm 0.8\ \mathrm{kcal/mol}$$

Even though entropic considerations do not favor this reaction by an estimated $T\Delta S = 5–10$ kcal/mol at 30°C,[42] a dark blue solution of **3** rapidly changes to an orange color upon addition of the arsine ligand. The reaction was monitored by ^{1}H NMR spectroscopy and observed to proceed to completion with formation of a unique product, $\mathrm{Cp^*Ru(AsEt_3)_2Cl}$.

4. *Enthalpy of Arene Binding to the $Cp^*Ru(CH_3CN)_3OTf$ System*

One series of ruthenium compounds of particular interest to us contains the $\mathrm{Cp'Ru^+}$ ($\mathrm{Cp'} = \eta^5$ - $\mathrm{C_5H_5}$, η^5 - $\mathrm{C_5Me_5}$) fragment which has

has been shown to effectively bind arenes.[17] Fagan and co-workers have recently reported on the synthesis and utilization of $Cp^*Ru(CH_3CN)_3{}^+OTf^-$ ($OTf^- = O_3SCF_3^-$; $Cp^* = \eta^5$ - C_5Me_5) as a versatile organometallic building block and precursor leading to the isolation of $Cp^*Ru(arene)^+OTf^-$ complexes,[17] illustrated in Eq. (55).

$$\begin{aligned} Cp^*Ru(CH_3CN)_3OTf + \text{Arene} &\xrightarrow{\text{THF}} Cp^*Ru(\text{arene})OTf \\ &+ 3\ CH_3CN + \Delta H_{rxn} \qquad (55) \end{aligned}$$

Reaction (55) offers a direct entryway into the thermochemistry of the Cp*Ru(arene)OTf system. A variety of arenes can be substituted for the three acetonitrile molecules bound to the ruthenium center. Valuable information concerning the enthalpy of arene exchange can be obtained by simply subtracting reaction (56) from reaction (55):

$$Cp^*Ru(CH_3CN)_3OTf + \text{Arene} \xrightarrow{\text{THF}} Cp^*Ru(\text{arene})OTf + 3\ CH_3CN + \Delta H_{rxn} \qquad (55)$$

$$Cp^*Ru(CH_3CN)_3OTf + \text{Arene}' \xrightarrow{\text{THF}} Cp^*Ru(\text{arene}')OTf + 3\ CH_3CN + \Delta H_{rxn} \qquad (56)$$

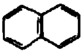
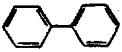
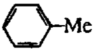
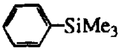
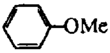
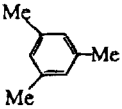
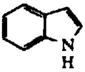
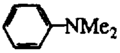
$$Cp^*Ru(\text{arene}')OTf + \text{Arene} \xrightarrow{\text{THF}} Cp^*Ru(\text{arene})OTf + \text{Arene}' + \Delta H_{rxn} \qquad (57)$$

This solution calorimetric investigation was performed in order to assess the magnitude and scope of steric and electronic effects on the ruthenium–arene bond enthalpies. Enthalpy values for the corresponding arenes are listed in Table IV. The order of stability ranges from the least stable naphthalene complex, with an enthalpy of substitution of only −1.7 (0.1) kcal/mol, to the most stable [bis(dimethylamino)benzene], with its enthalpy of reaction of −8.3 (0.2) kcal/mol. This small enthalpy scale, spanning only some 6 kcal/mol, illustrates the small enthalpic contribution to the overall energetics of arene binding. In other systems, namely $(\text{arene})Mo(CO)_3$, entropic factors have been estimated as 12.5 kcal/mol. The entropic contribution in the present system favors formation of the arene complexes by some 12.5 kcal/mol without even considering enthalpic forces. This factor explains the possible isolation of ruthenium–arene complexes where the arene displays an electron withdrawing character.[43]

TABLE IV

Enthalpies of arene substitution (kcal/mol) in the reaction:

$$\mathrm{Cp^*Ru(CH_3CN)_3OTf_{(soln)} + Arene_{(soln)} \xrightarrow[30°C]{THF} Cp^*Ru(arene)OTf_{(soln)}}$$
$$\mathrm{+\ 3\ CH_3CN_{(soln)}}$$

Arene		$-\Delta H_{Rxn}$
Naphtalene		1.7 ± 0.1
Benzene		3.4 ± 0.1
Biphenyl		3.6 ± 0.1
Toluene		4.3 ± 0.2
p-Xylene		4.6 ± 0.2
Trimethylsilylbenzene		5.0 ± 0.2
Anisole		5.4 ± 0.2
Mesitylene		5.5 ± 0.1
Indole		7.3 ± 0.2
Dimethylaniline		7.5 ± 0.1
p-bis(dimethylamino) benzene		8.3 ± 0.2

C. CONCLUSION

The thermochemistry related to some important Group 8 organometallic compounds is presented in this contribution. Such information is fundamental to the complete understanding of chemical behavior exhibited by these complexes and will continue to prove of great utility to the chemical community. This paucity of organogroup 8 thermochemical data observed in the literature is slowly being corrected, and emerging from such fundamental studies are factors influencing the binding of organic and main group fragments to these metal centers. Our continued efforts in the field of organometallic thermochemistry will hopefully provide insights into factors leading to improved catalyst design and activity.

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