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Relative Binding Energies of Sterically Demanding Tertiary Phosphine Ligands to the Cp*RuCl (Cp* = η^5-C_5Me_5) Moiety. Thermochemical Investigation of Coordinatively Unsaturated Organoruthenium Complexes

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The enthalpies of reaction of $(Cp^*RuCl)_4$ ($Cp^* = \eta^5$-C_5Me_5) with two sterically demanding monodentate tertiary phosphine ligands, leading to the formation of $Cp^*Ru(PR_3)Cl$ ($PR_3 = P(C_6H_{11})_3$ and P^iPr_3) complexes, 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 allow for a determination of relative ruthenium−phosphorus bond energy terms and, for the first time, enable a direct solution calorimetric measurement of the relative donating properties of large cone-angle phosphine ligands. Reaction of $Cp^*Ru(PR_3)Cl$ 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 thermochemical cycles, assuring the internal consistency of the thermochemical data. The ruthenium−phosphine bond energy in $Cp^*Ru(PCy_3)Cl$ was found to be 1.4 ± 0.5 kcal/mol more stable than in the $Cp^*Ru(P^iPr_3)Cl$ complex. Combining these and previously reported thermochemical data, a relative average $Ru-PR_3$ bond energy scale has been established: $P(OMe)_3 > PMe_3 > PPhMe_2 > P(OPh)_3 > PPh_2Me > PEt_3 > P^nBu_3 > PPh_3 > AsEt_3 > PCy_3 > P^iPr_3$. Comparisons with other organometallic systems and insight into factors influencing the $Ru-PR_3$ bond disruption enthalpies are discussed.

Introduction

Sterically demanding phosphine ligands have played an important role in organometallic chemistry in helping to stabilize very reactive species.[1] These ligands have also contributed to the existence of coordinative unsaturation about a metal center. The best known examples of such phosphine-assisted unsaturation are surely the $(PR_3)_2M(CO)_3$ ($R = C_6H_{11}$ and ^iPr; M = Cr, Mo, and W) complexes isolated by Kubas and Hoff.[2,3] Even though formal coordinative unsaturation is not entirely achieved in these systems (an intramolecular agostic interaction occupying the so-called "vacant site"), the phosphine ligand is at the origin of the very reactive nature of these complexes.[2]

$$(PR_3)_2W(CO)_3 + H_2 \rightarrow (PR_3)_2W(CO)_3(H_2) \qquad (1)$$

$$PR_3 = PCy_3,\ P^iPr_3$$

Recently, Grubbs and co-workers have reported the synthesis of ruthenium carbene complexes bearing sterically demanding phosphine ligands.[4a] The increase in steric demand and electronic donation caused by the phosphine is believed to be the reason behind the increased reactivity/stability of these ruthenium carbenes, which are capable of performing ring-opening metathesis and related reactions under surprisingly mild reaction conditions with remarkable functional group tolerance.[4b]

$$Cl_2(PPh_3)_2Ru({=}C{-}C{=}CPh_2) + 2PR_3 \rightarrow$$
$$Cl_2(PR_3)_2Ru({=}C{-}C{=}CPh_2) + 2PPh_3 \qquad (2)$$

$$PR_3 = PCy_3,\ P^iPr_3,\ P^iPr_2Ph$$

Tilley and co-workers have exploited the labile nature of $(Cp^*RuCl)_4$ (**1**) in the recent synthesis of unsaturated species bearing nitrogen-based ancillary ligands.[5]

$$(Cp^*RuCl)_4 + 4NaNHPh \rightarrow 2[Cp^*Ru(\mu\text{-}NHPh)]_2 \qquad (3)$$

Utilization of complex **1**, in reactions with large phosphine ligands, has led to the isolation of stable 16-electron species of the general composition $Cp^*Ru(PR_3)Cl$ ($Cp^* = C_5Me_5$; $PR_3 = P^iPr_3$ and PCy_3).[6]

$$(Cp^*RuCl)_4 + 4PCy_3 \rightarrow 4Cp^*Ru(PCy_3)Cl \qquad (4)$$

These researchers have then employed the coordinative

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unsaturation of a ruthenium complex in isolating a stable ruthenium silene complex.[7]

$$\mathrm{Cp^*Ru(PCy_3)Cl + ClMgCH_2SiHPh_2 \xrightarrow{-MgCl_2} Cp^*Ru(PCy_3)(H)(\eta^2\text{-}CH_2SiPh_2)} \quad (5)$$

Caulton and co-workers have utilized phosphine ligands in the isolation of $\mathrm{Cp^*Ru(PR_3)OR}$ complexes.[8] Here again the phosphines possess large cone angles ($\mathrm{PCy_3}$ and $\mathrm{P^iPr_2Ph}$). The unsaturated character of these complexes has been demonstrated by their reported ability to irreversibily bind one more donor ligand (e.g. CO, $\mathrm{C_2H_4}$)

$$\mathrm{Cp^*Ru(PCy_3)(OCH_2CF_3) + CO \rightarrow Cp^*Ru(PCy_3)(OCH_2CF_3)(CO)} \quad (6)$$

Although great progress is being made toward the isolation of coordinatively unsaturated organoruthenium species[9] (*vide supra*), no thermochemical data are presently available for these and their synthetic precursors. The area of organometallic thermochemistry is one of great potential insights into reactivity and bonding patterns.[10-13] In spite of this, the solution thermochemistry of certain sections of the periodic table remains uncharted.[14-17] In view of the remarkable versatility and chemistry revolving around the $\mathrm{(Cp^*RuCl)_4}$ (**1**)[18] complex, we have undertaken a number of solution calorimetric studies focusing on this and related systems in order to quantify the bond enthalpy terms associated with ruthenium–ligand interactions. In the present contribution, we report on the relative binding affinity of phosphine ligands to the Cp*RuCl fragment as a function of the phosphine cone angle, thereby clarifying the steric/electronic phosphine ligand contributions to the overall stability of saturated and unsaturated complexes.

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under inert atmospheres of argon or nitrogen using standard high vacuum or Schlenk tube techniques, or in a vacuum/atmospheres glovebox containing less than 1 ppm oxygen and water. Ligands were purchased from Strem Chemicals and used as received. Solvents were dried and distilled under dinitrogen before use, employing appropriate drying agents.[19] Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[20] or the enthalpy of solution of KCl in water.[21] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described[22] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. $\mathrm{(Cp^*RuCl)_4}$,[18c] $\mathrm{Cp^*Ru(PCy_3)Cl}$,[6] and $\mathrm{Cp^*Ru(P^iPr_3)Cl}$[6] were synthesized as reported in the literature.

NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organoruthenium complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF-d_8 was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^{1}H NMR spectroscopy and the reactions were found to be rapid, celan, 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 $\mathrm{(Cp^*RuCl)_4}$ (1) and $\mathrm{P^iPr_3}$ in THF. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox.

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Table 1. Enthalpies of Substitution (kcal/mol) and Relative Ru−PR$_3$ Bond Disruption Enthalpies (kcal/mol) in the following Reaction

$$(\mathrm{Cp^*RuCl})_{4\ \mathrm{s}} + n\mathrm{L}_{\mathrm{soln}} \xrightarrow[30\ °\mathrm{C}]{\mathrm{THF}} 4\mathrm{Cp^*Ru(L)}_{n/4}\mathrm{Cl}_{\mathrm{soln}}$$

L	complex	n	$-\Delta H_{\mathrm{exp}}$[a]	relative BDE[b]
P^iPr_3	Cp*Ru(P^{i}Pr$_3$)Cl	4	37.4(0.3)[c,d]	9.4(0.3)
PCy$_3$	Cp*Ru(PCy$_3$)Cl	4	41.9(0.2)[c,e]	10.5(0.2)
P^{n}Bu$_3$	Cp*Ru(P^{n}Bu$_3$)$_2$Cl	8	144.9(0.4)[e]	18.1(0.4)
PEt$_3$	Cp*Ru(PEt$_3$)$_2$Cl	8	147.5(0.6)[e]	18.4(0.6)
P(OMe)$_3$	Cp*Ru(P(OMe)$_3$)$_2$Cl	8	190.3(0.4)[e]	23.8(0.4)

[a] Enthalpy values are reported with 95% confidence limits. [b] Relative BDE values were derived by dividing the enthalpy value by the number of Ru−PR$_3$ formed during the reaction of interest. [c] Enthalpy refers to substitution of only one PR$_3$ ligand per Cp*RuCl fragment. [d] This work. [e] See ref 17c.

A 20−30 mg sample of recrystallized (Cp*RuCl)$_4$ was accurately weighted into the lower vessel and it was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of P^{i}Pr$_3$ [5 mL of P^{i}Pr$_3$ 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(P^{i}Pr$_3$)Cl (**2**) was found to be quantitative under these reaction conditions. The enthalpy of reaction, −37.4 ± 0.3 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(P^{i}Pr$_3$)Cl (2) in THF. In order to consider all species in solution, the enthalpy of solution of Cp*Ru(P^{i}Pr$_3$)Cl had to be directly measured. This was performed by using a similar procedure to the one described above, with the exception that no ligand was added to the reaction cell. The enthalpy of solution for complex **2** was performed in a THF solution containing the free ligand (P^{i}Pr$_3$) in a concentration similar to the one used in the enthalpy of reaction mentioned above. This enthalpy of solution represents the average of five individual determinations and is worth 4.4 ± 0.1 kcal/mol. A similar procedure was employed for measuring the enthalpy of solution of Cp*Ru(PCy$_3$)Cl (**3**).

Results

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.[6]

$$(\mathrm{Cp^*RuCl})_{4\ \mathrm{s}} + 4\mathrm{PR}_{3\ \mathrm{soln}} \xrightarrow[30\ °\mathrm{C}]{\mathrm{THF}} 4\mathrm{Cp^*Ru(PR_3)Cl}_{\mathrm{soln}} \quad (7)$$

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

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

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.[17c]

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

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

A compilation of enthalpies of reaction for all phosphines calorimetrically investigated to date can be found in Table 1.

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 9 and 10.

$$\mathrm{Cp^*Ru(PR_3)Cl}_{\mathrm{soln}} + 2\mathrm{PEt}_{3\ \mathrm{soln}} \xrightarrow[30\ °\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(PEt_3)_2Cl}_{\mathrm{soln}} + \mathrm{PR}_{3\ \mathrm{soln}} \quad (9)$$

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

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

$$\mathrm{Cp^*Ru(PR_3)Cl}_{\mathrm{soln}} + 2\mathrm{P(OMe)}_{3\ \mathrm{soln}} \xrightarrow[30\ °\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(P(OMe)_3)_2Cl}_{\mathrm{soln}} + \mathrm{PR}_{3\ \mathrm{soln}} \quad (10)$$

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

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

Discussion

Recent reports on the synthesis and high yield isolation of organoruthenium complexes have provided a thermodynamic entryway into the solution calorimetric studies of ligand substitution reactions in these systems.[18] 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.[18] It was also 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.[18c] Tilley and co-workers have also reported the use of **1** as a synthetic precursor to Cp*Ru(PR$_3$)Cl complexes. 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. On the basis of 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. Enthalpies of reaction associated with diene coordination to the Cp*RuCl fragment have recently been reported.[17c]

$$(\mathrm{Cp^*RuCl})_{4\ \mathrm{s}} + 4\mathrm{COD}_{\mathrm{soln}} \rightarrow 4\mathrm{Cp^*Ru(COD)Cl}_{\mathrm{soln}} \quad (11)$$

$$\Delta H_{\mathrm{rxn}} = -39.8 \pm 0.4\ \mathrm{kcal/mol}$$

Related calorimetric studies on tertiary phosphine substitution in the Cp*Ru(COD)Cl system have also been communicated.[17]

$$\mathrm{Cp^*Ru(COD)Cl_{soln} + 2PEt_{3\ soln} \rightarrow Cp^*Ru(PEt_3)_2Cl_{soln} + COD_{soln}} \quad (12)$$

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

In the course of these studies, the reaction enthalpy between **1** and PCy$_3$ was experimentally determined.[17c]

$$\mathrm{(Cp^*RuCl)_{4\ s} + 4PCy_{3\ soln} \xrightarrow[30\ ^\circ C]{THF} 4Cp^*Ru(PCy_3)Cl_{soln}} \quad (13)$$

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

The existence of a coordination unsaturated complex related to Cp*Ru(PCy$_3$)Cl allowed for enthalpy of reaction 14 to also be measured and is now reported below.

$$\mathrm{(Cp^*RuCl)_{4\ s} + 4P^iPr_{3\ soln} \xrightarrow[30\ ^\circ C]{THF} 4Cp^*Ru(P^iPr_3)Cl_{soln}} \quad (14)$$

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

The very reactive nature of the unsaturated complexes, **2** and **3**, can be exploited in order to thermodynamically link the Cp*Ru(PR$_3$)Cl to the Cp*Ru(PR$_3$)$_2$Cl systems. This is in fact possible since complex **3** was shown to react according to eq 15:

$$\underset{\mathbf{3}}{\mathrm{Cp^*Ru(PCy_3)Cl}} + \mathrm{2PMe_3 \rightarrow Cp^*Ru(PMe_3)_2Cl + PCy_3} \quad (15)$$

The Ru−PCy$_3$ bond in **3** appears quite labile and is therefore expected to be relative weak. Reaction 15 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^{n}Bu$_3$, P(OMe)$_3$), were the corresponding Cp*Ru(PR$_3$)$_2$Cl complexes.[23]

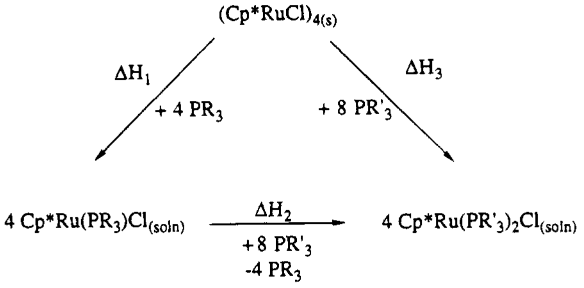
With the thermodynamic data on these organoruthenium complexes on hand, it is now possible to construct thermodynamic cycles to verify the internal consistency of the thermodynamic data. This is especially desirable in view of the highly reactive nature of **1**−**3**. Scheme 1 illustrates four separate thermochemical cycles verifying the internal consistency of the reported thermochemical information.

Subtracting reaction 14 from 13 leads to eq 16, which represents the phosphine exchange reaction between two complexes bearing sterically demanding phosphine ligands:

$$\mathrm{Cp^*Ru(P^iPr_3)Cl_{soln} + PCy_{3\ soln} \rightarrow Cp^*Ru(PCy_3)Cl_{soln} + P^iPr_{3\ soln}} \quad (16)$$

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

Scheme 1[a]



PR$_3$	PR$_3'$	-ΔH$_1$[a]	-ΔH$_2$[a]	-ΔH$_{3\ \mathrm{calcd}}$[a]	-ΔH$_{3\ \mathrm{exp}}$[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^{i}Pr$_3$	PEt$_3$	37.4 (0.3)	109.6 (1.2)	147.0 (1.5)	147.5 (0.6)
P^{i}Pr$_3$	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.

From the available thermodynamic data for the first section (ΔH_1) of the thermodynamic cycle, the Ru−PCy$_3$ bond is calculated to be 1.1 kcal/mol stronger than the Ru−P^{i}Pr$_3$ 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:

$$\mathrm{Cp^*Ru(P^iPr_3)Cl_{soln} + 2PEt_{3\ soln} \rightarrow Cp^*Ru(PEt_3)_2Cl_{soln} + P^iPr_{3\ soln}} \quad (17)$$

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

$$\mathrm{Cp^*Ru(PEt_3)_2Cl_{soln} + PCy_{3\ soln} \rightarrow Cp^*Ru(PCy_3)Cl_{soln} + 2PEt_{3\ soln}} \quad (18)$$

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

$$\mathrm{Cp^*Ru(P^iPr_3)Cl_{soln} + PCy_{3\ soln} \rightarrow Cp^*Ru(PCy_3)Cl_{soln} + P^iPr_{3\ soln}} \quad (16)$$

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

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^{i}Pr$_3$ 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 1). It should be specified here that the numbers obtained for the Ru−PR$_3$ in the Cp*Ru(PR$_3$)$_2$Cl 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,[24] in their study of

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[23] All complexes formed wre identified by comparing NMR spectroscopic data with that of independently synthesized samples reported in ref 17c.

enthalpies of ligand substitution in the $(C_6H_6)Mo(CO)_3$ system. In tetrahydrofuran solution, an enthalpy of reaction of −23.1 kcal/mol[25] was experimentally determined for reaction 19. Relying on a Mo−benzene BDE

$$(C_6H_6)Mo(CO)_3 + 2PCy_3 \rightarrow (PCy_3)_2Mo(CO)_3 + C_6H_6 \qquad (19)$$

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−

$$(C_6H_6)Mo(CO)_3 + 3P(OMe_3) \rightarrow (P(OMe)_3)_3Mo(CO)_3 + C_6H_6 \qquad (20)$$

$P(OMe)_3$ BDE value of 38.9 kcal/mol.[24] 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.

The relative bond enthalpy scale found in Table 1 also allows for an interpretation of the factors influencing the Ru−PR_3 bond whether it is found in a coordinatively unsaturated or saturated complex. It can readily be seen from these bond enthalpy estimates that the sterically demanding phosphines are the weakest binders, this resulting from a possible combination of steric and electronic factors. In order to quantify the relative role of sterics vs electronics in this phosphine system, a relationship first proposed by Tolman,[26] 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, were used:

$$-\Delta H = A_0 + A_1\theta + A_2\nu \qquad (21)$$

In order to gauge which of the two was predominant in this system, a direct correlation was attempted between the calculated BDE values and the electronic parameter determined by Tolman (Figure 1).[26] A poor correlation exists (R = 0.82) and is in keeping with similar data treatment for the enthalpies of phosphine substitution in the Cp*Ru(COD)Cl system.[17c] A strong correlation of steric factors was previously found to exist for the $Cp^*Ru(PR_3)_2Cl$ system. Since the steric factor has such a profound influence on the enthalpy of reaction in a related system, a direct relationship between the enthalpy of reaction and the phosphine cone angle was established (Figure 2) and the linear relationship (R = 0.98) emphasizes the major role played by steric effects in the present system. The importance of the phosphine steric factor has precedent in $(L)_3Mo(CO)_3$ complexes (L = PR_3), similarities which has been previously mentioned.[24]

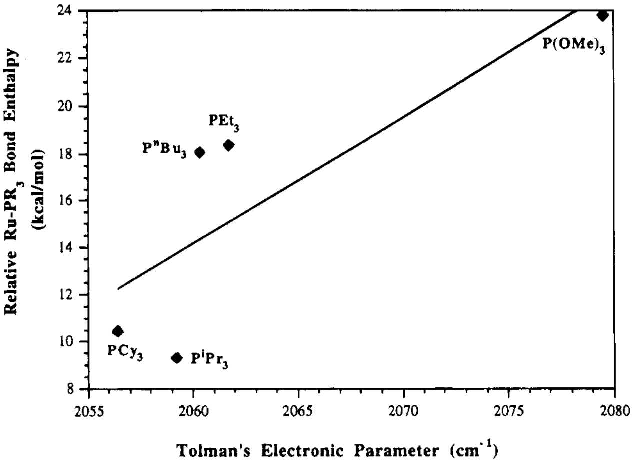

Figure 1. Relative Ru−PR_3 bond enthalpy (kcal/mol) vs Tolman's electronic parameter (cm^{-1}) for a series of tertiary phosphine ligands in the $Cp^*Ru(PR_3)_nCl$ (n = 1 or 2) system (slope = 0.54; R = 0.82).

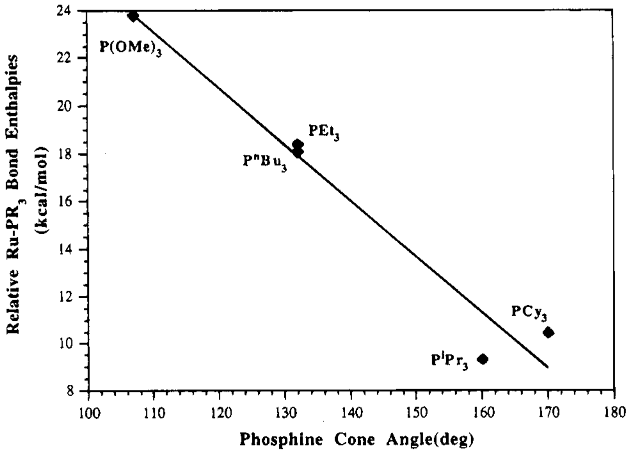

Figure 2. Relative Ru−PR_3 bond enthalpy (kcal/mol) vs phosphine cone angle (deg) for a series of tertiary phosphine ligands in the $Cp^*Ru(PR_3)_nCl$ (n = 1 or 2) system (slope = −0.24; R = 0.98).

Table 2. Relative Bond Disruption Enthalpies (kcal/mol) in the following Reaction

$$Cp^*RuCl_{soln} + nL_{soln} \rightarrow Cp^*Ru(L)_nCl_{soln}$$

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 two Ru−PR_3 bond energy values unless noted otherwise. [b] See the 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.

A relative bond enthalpy scale can be constructed including all ligands so far investigated in the Cp*RuCl system (Table 2). This can be achieved since a number of arsines/phosphines/phosphites have been linked through a thermodynamic cycle to reaction 11.[17c] This enables the determination of average bond enthalpy terms associated with the entire $Cp^*Ru(PR_3)_nCl$ (n = 1 and 2) series.[27]

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

[25] The exact product of this reaction in THF could possibly be the $(PCy_3)_2Mo(CO)_3(THF)$ adduct. The agostic interaction and THF binding to molybdenum are estimated to have a similar magnitude in this system; see ref 10b.

[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.

The relative weakness of the Ru–PCy_3 and Ru–P^iPr_3 bonds may not be entirely suprising when the observed chemistry is examined. However, the enthalpic data clearly illustrate the existence of an average Ru–$AsEt_3$ 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.

$$Cp^*Ru(PCy_3)Cl + 2AsEt_3 \rightarrow Cp^*Ru(AsEt_3)_2Cl + PCy_3 \quad (22)$$

$$\Delta H_{calcd} = -14.5 \pm 0.8 \text{ kcal/mol}$$

Even though entropic considerations do not favor this reaction by an estimated $T\Delta S \approx 5-10$ kcal/mol at 30 °C,[28] a dark blue solution of **3** rapidly changes to an orange color upon addition of the arsine ligand. The reaction was monitored by ^1H NMR spectroscopy and observed to proceed to completion with formation of a unique product, $Cp^*Ru(AsEt_3)_2Cl$.

Conclusion

A direct entryway into the thermochemistry of binding of large cone angle phosphines, leading to coordinatively unsaturated Ru(II) complexes, was successfully achieved with the P^iPr_3 and PCy_3 ligands. The PCy_3 ligand was found to be 1.4 ± 0.5 kcal/mol more strongly bound to ruthenium than the P^iPr_3 ligand. A relative enthalpy scale has been established for the binding of phosphines to the Cp*RuCl moiety, which incorporates phosphine ligands with both large and small cone angles. The enthalpy trend can be explained in terms of electronic and steric contribution to the enthalpy of reaction, with the steric constituent playing a major role. Four thermochemical cycles were constructed in order to confirm the internal consistency of these enthalpy data. A relative bond enthalpy scale was established and shows that the two sterically demanding phosphines exhibit the weakest Ru–PR_3 bond yet investigated. Furthermore, the weakness of these Ru–PR_3 bonds is such that a ruthenium–arsine bond was calculated to be stronger and experimentally tested to indeed have a stronger bond to ruthenium. Further thermochemical and mechanistic investigations focusing on coordinatively unsaturated and related systems are presently underway.

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(27) The average bond disruption enthalpy terms are calculated by taking the enthalpy of COD binding to $(Cp^*RuCl)_4$ (eq 11), adding it to 4 times the enthalpy of phosphine substitution from Cp*Ru(COD)-Cl (e.g. eq 12), and dividing by 8 (the total number of Ru-PR_3 bonds made in eq 8). This can be performed from measured or calculated enthalpies of reactions. For a complete thermodynamic cycle involving the Cp*Ru(COD)Cl complex, see ref 17c.

(28) (a) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805–6907. (b) Page, M. I. In *The Chemistry of Enzyme Action*; Page, M. I., Ed., Elsevier: New York, 1984; pp 1–54. (c) Page, M. I.; Jencks, W. F. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678–1683.