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Relative Binding Energies of Tertiary Phosphine Ligands to the $Cp^*RuOCH_2CF_3$ ($Cp^* = \eta^5$-C_5Me_5) Moiety

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The enthalpies of reaction of $(Cp^*RuOR_f)_2$ (**1**; $Cp^* = \eta^5$-C_5Me_5, $OR_f = OCH_2CF_3$) with $PR_3 = PCy_3$ (**2**) and P^iPr_3 (**3**) have been measured by solution calorimetry in THF at 30 °C. In order to test the internal consistency of the approach, a thermochemical cycle was constructed involving reactions of $Cp^*Ru(PR_3)OR_f$ with tertiary phosphine and phosphite ligands (L) leading to the formation of $Cp^*Ru(L)_2OR_f$ complexes. The range of these reaction enthalpies spans some 11 kcal/mol. Furthermore, complex **1** reacts directly with smaller cone angle phosphines to quantitatively yield $Cp^*Ru(L)_2OR_f$ complexes. To allow for full comparison of the present thermochemical information with that of the parent $Cp^*Ru(L)_2Cl$ ($L= PR_3$) system, synthetic efforts were directed toward the isolation of a $Cp^*Ru(COD)OR_f$ (COD = cyclooctadiene) complex. Surprisingly, the straightforward reaction of **1** with COD leads to the isolation of a tetramethylfulvene complex, $C_5Me_4CH_2Ru(COD)$ (**4**), resulting from an alcohol elimination reaction. A single-crystal X-ray diffraction study of **4** has been performed. Thermochemical comparisons with the $Cp^*Ru(L)_2Cl$ system are also presented.

Introduction

A significant role of sterically demanding phosphine ligands in organometallic chemistry has been in stabilizing very reactive species.[1] These ligands have thereby contributed to the existence of coordinative unsaturation about a metal center. The best known examples of such phosphine-assisted unsaturation are surely the $(PR_3)_2M(CO)_3$ ($R = C_6H_{11}$, ^iPr; M = Cr, Mo, 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]

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

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

Utilization of the complex $(Cp^*RuCl)_4$, in reactions with large phosphine ligands, has led to the isolation of stable 16-electron species of the general composition $Cp^*Ru(PR_3)Cl$ ($Cp^* = C_5Me_5$; $PR_3 = P^iPr_3$, PCy_3).[4]

$$(Cp^*RuCl)_4 + 4PCy_3 \rightarrow 4Cp^*Ru(PCy_3)Cl \qquad (2)$$

Tilley has then employed the coordinative unsaturation of a ruthenium complex in isolating a stable ruthenium silene complex.[5]

$$Cp^*Ru(PCy_3)Cl + ClMgCH_2SiHPh_2 \xrightarrow{-MgCl_2} Cp^*Ru(PCy_3)(H)(\eta^2\text{-}CH_2SiPh_2) \qquad (3)$$

In view of the remarkable versatility and chemistry revolving around the $(Cp^*RuCl)_4$[6] complex, we have undertaken a number of solution calorimetric studies focusing on this and related systems[7] in order to quantify the bond enthalpy terms associated with ruthenium−ligand interactions.

$$(Cp^*RuCl)_4(s) + 4COD(soln) \xrightarrow[30\ °C]{THF} 4Cp^*Ru(COD)Cl(soln) \qquad (4)$$

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

$$(Cp^*RuCl)_4(s) + 8PEt_3(soln) \xrightarrow[30\ °C]{THF} 4Cp^*Ru(PEt_3)_2Cl(soln) \qquad (5)$$

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

Although great progress is being made toward the isolation of coordinatively unsaturated organoruthe-

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nium species[8] (*vide supra*), little thermochemical data are presently available for these unusual complexes. In an effort to obtain bond disruption enthalpy terms associated with organoruthenium complexes, we recently reported on the thermochemistry of the 16-electron species $Cp^*Ru(PR_3)Cl$[7] ($PR_3 = PCy_3$, P^iPr_3).

$$(Cp^*RuCl)_4(s) + 4PR_3(soln) \xrightarrow[30\ °C]{THF} 4Cp^*Ru(PR_3)Cl(soln) \quad (6)$$

Caulton and co-workers have utilized phosphine ligands in the isolation of $Cp^*Ru(PR_3)OR_f$ complexes.[9]

$$(Cp^*Ru(OCH_2CF_3))_2 + 2PR_3 \rightarrow 2Cp^*Ru(PR_3)OCH_2CF_3 \quad (7)$$

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

Here again the phosphines possess large cone angles (PCy_3 and P^iPr_3). The unsaturated character of these complexes has been demonstrated by their reported ability to irreversibly bind one more donor ligand (e.g. CO, C_2H_4).

$$Cp^*Ru(PCy_3)(OCH_2CF_3) + CO \rightarrow Cp^*Ru(PCy_3)(OCH_2CF_3)(CO) \quad (8)$$

The area of organometallic thermochemistry is one of great potential insights into reactivity and bonding patterns.[10-13] In the present contribution, we report on the relative binding affinity of phosphine ligands to the $Cp^*RuOCH_2CF_3$ fragment as a function of phosphine ligand variation, thereby clarifying the steric/electronic phosphine ligand contributions to the overall stability of saturated and unsaturated complexes and allowing for a comparison with the related thermochemical study of the Cp^*RuCl fragment.

Experimental Section

General Considerations. All manipulations involving organometallic 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. Solvents, including deuterium solvents for NMR analysis, were dried and distilled under dinitrogen before use by employing the standard drying agents.[14] For example, tetrahydrofuran was stored over sodium wire, distilled from sodium benzophenone ketyl, stored over Na/K alloy, and vacuum-transferred into flame-dried glassware prior to use. Phosphine and phosphite ligands were purchased from Strem Chemicals and used as received. 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 or Oxford 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[15] or the enthalpy of solution of KCl in water.[16] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[17] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organometallic 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 organometallic reactions investigated.

Synthesis. $[Cp^*Ru(OCH_2CF_3)]_2$ (**1**), $Cp^*Ru(P^iPr_3)(OCH_2CF_3)$ (**2**), and $Cp^*Ru(PCy_3)(OCH_2CF_3)$ (**3**) were synthesized according to the literature procedures.[9] The identities of all calorimetry products were determined by comparison with materials independently synthesized. Other organoruthenium complexes were synthesized according to the following procedures.

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$C_5Me_4CH_2Ru(C_8H_{12})$ (4). In a 100 mL round-bottom flask of a high-vacuum frit assembly was charged 505 mg (0.753 mmol) of **1**, 0.26 mL (2.12 mmol) of COD, and 35 mL of THF. The solution was stirred for 24 h. The solvent was then evacuated and the residue washed with a small amount of pentane. Filtration afforded 450 mg of a yellow microcrystalline solid, a yield of 87%. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 3.50 (s, 2H, $-CH_2-$), 2.67 (m, 4H, COD), 2.14 (m, 6H, COD), 2.04 (m, 2H, COD), 1.90 (s, 6H, $-CH_3$), 1.21 (s, 6H, $-CH_3$). Anal. Calcd for $C_{18}H_{26}Ru$: C, 62.94; H, 7.63. Found: C, 63.23; H, 7.65.

$Cp^*Ru(PEt_3)_2(OCH_2CF_3)$ (5). In a 100 mL round-bottom flask of a high-vacuum frit assembly was charged 200 mg (0.298 mmol) of **1**, 145 mg (1.227 mmol) of PEt_3, and 25 mL of THF. The solution was stirred for 24 h. No color change was observed. The solvent and the volatiles were then removed in vacuo. The orange-brown microcrystalline material was washed with pentane to afford 300 mg of the product (88% yield). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 3.91 (q, 2H, $-CH_2CF_3$), 1.75 (m, 6H, $-CH_2Me$), 1.60 (m, 6H, $-CH_2Me$), 1.50 (s, 15H, Cp*), 0.97 (m, 18H, $-CH_3$). Anal. Calcd for $C_{24}H_{47}F_3OP_2Ru$: C, 50.43; H, 8.29. Found: C, 50.23; H, 8.58.

$Cp^*Ru(P(OMe)_3)_2(OCH_2CF_3)$ (6). In a 100 mL round-bottom flask of a high-vacuum frit assembly was charged 150 mg (0.224 mmol) of **1**, 111 mg (0.895 mmol) of $P(OMe)_3$, and 25 mL of THF. The solution was stirred for 4 h at room temperature. An obvious color change from orange to bright yellow was observed. The volatiles were removed in vacuo. Collection of the yellow microcrystalline solid afforded 160 mg of the product, a 61% yield. ^1H NMR (300 MHz, C_6D_6, 25 °C): 4.04 ppm (q, 2H, CH_2CF_3), 3.50 (t, 18H, $-OCH_3$), 1.65 (s, 15 H, Cp*). Anal. Calcd for $C_{18}H_{35}F_3O_7P_2Ru$: C, 37.12; H, 5.88; Found: C, 37.15; H, 6.05.

Solution Calorimetry. Calorimetric Measurement for Reactions of $[Cp^*Ru(OCH_2CF_3)]_2$ with Triisopropylphosphine. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20−30 mg sample of recrystallized $[Cp^*Ru(OCH_2CF_3)]_2$ was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. A 4 mL amount of a stock solution of the phosphine ligand (1 mL of triisopropylphosphine in 20 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 organoiron complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 1 h), the reaction was initiated by inverting the calorimeter. Conversion to a coordinatively unsaturated 16-electron complex, $Cp^*Ru(P^iPr_3)(OCH_2CF_3)$, was found to be quantitative under these reaction conditions through the examination with ^1H NMR spectroscopy. The enthalpy of reaction, −13.3 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations. This methodology represents a typical procedure involving all reactions of $[Cp^*Ru(OCH_2CF_3)]_2$ with other monodentate phosphines or phosphites investigated in this study.

Calorimetric Measurement for Reactions of $Cp^*Ru(P^iPr_3)(OCH_2CF_3)$ with Triethylphosphine. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20−30 mg sample of recrystallized $Cp^*Ru(P^iPr_3)(OCH_2CF_3)$ was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. A 4 mL amount of a stock solution of triethylphosphine (2 mL of triethylphosphine in 20 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 organoiron complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 1 h), the reaction was initiated by inverting the calorimeter. Conversion from coordinatively unsaturated to saturated complex, $Cp^*Ru(PEt_3)_2(OCH_2CF_3)$, was found to be quantitative under these reaction conditions through the ^1H NMR spectroscopy. The enthalpy of reaction, −17.2 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations. This methodology represents a typical procedure involving the reactions of $Cp^*Ru(P^iPr_3)(OCH_2CF_3)$ with $P(OMe)_3$ and $Cp^*Ru(PCy_3)(OCH_2CF_3)$ with PEt_3 and $P(OMe)_3$.

Calorimetric Measurement of the Enthalpy of Solution of $(Cp^*RuOR_f)_2$, $Cp^*Ru(P^iPr_3)(OCH_2CF_3)$ (2), and $Cp^*Ru(PCy_3)(OCH_2CF_3)$ (3) in THF. In order to consider all species in solution, the enthalpies of solution of $(Cp^*RuOR_f)_2$ (**1**), $Cp^*Ru(P^iPr_3)(OCH_2CF_3)$ (**2**), and $Cp^*Ru(PCy_3)(OCH_2CF_3)$ (**3**) 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. The enthalpies of solution, 5.6 ± 0.2, 4.6 ± 0.3, and 5.2 ± 0.1 kcal/mol, represent the average of five individual determinations respectively for **1**−**3**.

Structure Determination of $C_5Me_4CH_2Ru(C_8H_{12})$ (4). A trapezoidal block, grown by slow cooling of a saturated hexane solution, having approximate dimensions 0.36 × 0.23 × 0.49 mm was selected and mounted on the end of a glass fiber in a random orientation. This selected crystal was mounted on a Syntex R3 diffractometer, and data were collected using Mo Kα radiation at 100 K under a stream of cold nitrogen gas. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with $4.3° < 2\theta < 55°$. The structure was solved using direct methods (SHELX) and refined by full-matrix least-squares techniques.

Results

A facile entryway into the thermochemistry of $Cp^*Ru(PR_3)OR_f$ ($OR_f = OCH_2CF_3$) complexes is made possible by the rapid and quantitative reaction of $(Cp^*RuOR_f)_2$ (**1**) with the phosphine ligand.[9]

$$(Cp^*RuOR_f)_2(soln) + 2PR_3(soln) \xrightarrow[30\ °C]{THF} 2Cp^*Ru(PR_3)OR_f(soln) \quad (9)$$

$$PR_3 = PCy_3;\ \Delta H_{reacn} = -18.9 \pm 0.3\ kcal/mol$$

$$PR_3 = P^iPr_3;\ \Delta H_{reacn} = -18.6 \pm 0.2\ kcal/mol$$

This type of phosphine binding reaction appears general for the two sterically demanding ligands investigated. We now report that complex **1** can also allow access into the thermochemistry of 18-electron complexes of formulation $Cp^*Ru(PR_3)_2OR_f$, where PR_3 is a phosphine possessing a smaller size cone angle.

$$(Cp^*RuOR_f)_2(soln) + 4PEt_3(soln) \xrightarrow[30\ °C]{THF} 2Cp^*Ru(PEt_3)_2OR_f(soln) \quad (10)$$

$$\Delta H_{reacn} = -60.1 \pm 0.5\ kcal/mol$$

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

The 16-electron complexes have been found to react with smaller cone angle phosphine ligands to produce

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

$$\mathrm{Cp^*Ru(PR_3)X + 2PR'_3 \xrightarrow[30\ °C]{THF} Cp^*Ru(PR'_3)_2X + PR_3}$$

X	PR_3	PR'_3	$-\Delta H_{reacn}$[a]
Cl	P^iPr_3	PEt_3	27.4(0.3)[b]
Cl	PCy_3	PEt_3	25.9(0.5)[b]
Cl	P^iPr_3	$P(OMe)_3$	38.4(0.3)[b]
Cl	PCy_3	$P(OMe)_3$	36.7(0.5)[b]
OCH_2CF_3	P^iPr_3	PEt_3	21.8(0.4)[c]
OCH_2CF_3	PCy_3	PEt_3	20.8(0.3)[c]
OCH_2CF_3	P^iPr_3	$P(OMe)_3$	33.5(0.5)[c]
OCH_2CF_3	PCy_3	$P(OMe)_3$	32.9(0.4)[c]

[a] Enthalpy values are reported with 95% confidence limits. [b] Taken from ref 7e. [c] This work.

Table 2. Summary of Crystallographic Data for (1-Methylene-2,3,4,5-tetramethylcyclopentadienyl)-(cyclooctadiene)ruthenium (4)

empirical formula	$C_{18}H_{26}Ru$
space group	$P2_1/c$ (No.14)
unit cell dimens	
a, Å	8.342(1)
b, Å	13.807(2)
c, Å	13.468(2)
α, deg	90
β, deg	101.00(1)
γ, deg	90
V, Å^3	1522.7
Z	4
density (calcd), g/cm^3	1.498
μ(Mo), cm^{-1}	39.62
monochromator	highly ordered graphite crystal
temp, K	173
abs cor	empirical (ψ-scan method)
diffractometer	Syntex R3
scan type	θ−2θ
data collected	$10 \le h \le 10, -17 \le k \le 0, 0 \le l \le 17$
2θ range, deg	4.3−55.0
no. of collected rflns	3784
no. of indep rflns	2913
no. of obsd rflns	3058
R_F (obsd data), %	1.9
R_{wF}, %	2.2
goodness of fit	1.0
no. of variables	276

complexes with filled coordination spheres, according to eqs 11 and 12. All enthalpy data are summarized in

$$\mathrm{Cp^*Ru(PR_3)OR_f(soln) + 2PEt_3(soln) \xrightarrow[30\ °C]{THF} Cp^*Ru(PEt_3)_2OR_f(soln) + PR_3(soln)} \quad (11)$$

$$\mathrm{PR_3 = PCy_3;\ \Delta \mathit{H}_{reacn} = -20.8 \pm 0.3\ kcal/mol}$$

$$\mathrm{PR_3 = P^iPr_3;\ \Delta \mathit{H}_{reacn} = -21.8 \pm 0.4\ kcal/mol}$$

$$\mathrm{Cp^*Ru(PR_3)OR_f(soln) + 2P(OMe)_3(soln) \xrightarrow[30\ °C]{THF} Cp^*Ru(P(OMe)_3)_2OR_f(soln) + PR_3(soln)} \quad (12)$$

$$\mathrm{PR_3 = PCy_3;\ \Delta \mathit{H}_{reacn} = -32.9 \pm 0.4\ kcal/mol}$$

$$\mathrm{PR_3 = P^iPr_3;\ \Delta \mathit{H}_{reacn} = -33.6 \pm 0.4\ kcal/mol}$$

Table 1 and Scheme 1. A single-crystal diffraction study was performed on $C_5Me_4CH_2Ru(COD)$ (**4**) in order to confirm the structure determined by NMR. Crystal data for **4** are summarized in Table 2, and selected bond distances and angles are listed in Tables 3. Positional and equivalent isotropic thermal parameters are presented in the Supporting Information. An ORTEP drawing of this molecule is given in Figure 1.

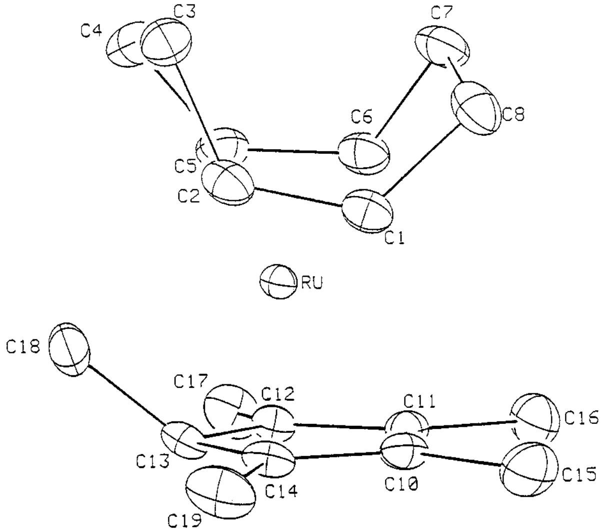


Figure 1. ORTEP drawing of $C_5Me_4CH_2Ru(COD)$ (**4**) with ellipsoids drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $C_5Me_4CH_2Ru(COD)$ (4)

Bond Lengths			
Ru−C(1)	2.134(2)	C(1)−C(2)	1.420(3)
Ru−C(2)	2.148(2)	C(1)−C(8)	1.519(2)
Ru−C(5)	2.139(2)	C(2)−C(3)	1.531(3)
Ru−C(6)	2.153(2)	C(3)−C(4)	1.538(3)
Ru−C(10)	2.320(2)	C(4)−C(5)	1.521(3)
Ru−C(11)	2.327(2)	C(5)−C(6)	1.418(3)
Ru−C(12)	2.179(2)	C(6)−C(7)	1.525(3)
Ru−C(13)	2.073(1)	C(7)−C(8)	1.522(3)
Ru−C(14)	2.187(2)	C(10)−C(11)	1.433(2)
Ru−C(18)	2.301(2)	C(10)−C(14)	1.422(2)
C(11)−C(12)	1.418(2)	C(10)−C(15)	1.496(2)
C(11)−C(16)	1.491(2)	C(13)−C(14)	1.458(2)
C(12)−C(13)	1.463(2)	C(13)−C(18)	1.420(2)
C(12)−C(17)	1.496(2)	C(14)−C(19)	1.500(2)
Cp(c)−Ru	1.856 (2)		
Bond Angles			
Ru−C(1)−C(2)	71.2(1)	C(14)−C(10)−C(15)	125.9(2)
Ru−C(1)−C(8)	113.3(1)	C(10)−C(11)−C(12)	108.8(1)
Ru−C(2)−C(1)	70.1(1)	C(10)−C(11)−C(16)	125.1(2)
Ru−C(2)−C(3)	113.9(1)	C(12)−C(11)−C(16)	126.0(2)
Ru−C(5)−C(4)	111.7(1)	C(11)−C(12)−C(13)	107.3(1)
Ru−C(5)−C(6)	71.3(1)	C(12)−C(13)−C(18)	118.7(2)
Ru−C(6)−C(5)	70.2(1)	C(14)−C(13)−C(18)	117.5(2)
Ru−C(6)−C(7)	115.2(1)	Ru−C(18)−H(18)	114(1)
Ru−C(10)−C(11)	72.30(9)	Ru−C(18)−H(18′)	117(1)
Ru−C(10)−C(14)	66.6(1)	H(18)−C(18)−H(18′)	113(2)
Ru−C(13)−C(18)	80.0(1)	C(13)−C(18)−H(18)	120(1)
Ru−C(14)−C(19)	125.7(1)	C(13)−C(18)−H(18′)	121(1)
Ru−C(18)−C(13)	62.5(1)		

Discussion

We have recently reported on the thermochemistry of ligand binding to the Cp*RuCl moiety[7b] using as an entryway reaction 13. Solution calorimetric studies

$$\mathrm{Cp^*Ru(COD)Cl(soln) + 2PEt_3(soln) \rightarrow Cp^*Ru(PEt_3)_2Cl(soln) + COD(soln)} \quad (13)$$

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

have been performed on a number of tertiary phosphine ligands, and the approach proved general as long as the phosphine of interest did not possess a large cone angle.[7b] In these instances, an alternative route was employed which made use of the synthetic precursor of Cp*Ru(COD)Cl, namely the tetrameric species (Cp*RuCl)$_4$.[7e]

$$(\mathrm{Cp^*RuCl})_4(\mathrm{s}) + 4\mathrm{PCy_3}(\mathrm{soln}) \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} 4\mathrm{Cp^*Ru(PCy_3)Cl}(\mathrm{soln}) \quad (14)$$

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

Finally, two other approaches were used in this series of investigations to establish a thermodynamic cycle in order to verify the internal consistency of the results.[7e]

$$(\mathrm{Cp^*RuCl})_4(\mathrm{s}) + 4\mathrm{COD}(\mathrm{soln}) \rightarrow 4\mathrm{Cp^*Ru(COD)Cl}(\mathrm{soln}) \quad (15)$$

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

$$\mathrm{Cp^*Ru(PR_3)Cl} + 2\mathrm{PEt_3} \rightarrow \mathrm{Cp^*Ru(PR_3)_2Cl} + \mathrm{PCy_3} \quad (16)$$

This cycle also allowed for a relative ruthenium−ligand bond enthalpy scale to be established.

Having these results on hand, we thought it necessary to examine how these relative bond disruption enthalpy values might vary as a function of ancillary ligation. We have previously reported on such thermodynamic effects in a comparison between the CpRu(PR$_3$)$_2$Cl and Cp*Ru(PR$_3$)$_2$Cl systems.[7f]

$$\mathrm{Cp^*Ru(COD)Cl}(\mathrm{soln}) + 2\mathrm{PPh_3}(\mathrm{soln}) \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(PPh_3)_2Cl}(\mathrm{soln}) + \mathrm{COD}(\mathrm{soln}) \quad (17)$$

$$\Delta H_{\mathrm{reacn}} = -18.1 \pm 0.2\ \mathrm{kcal/mol}$$

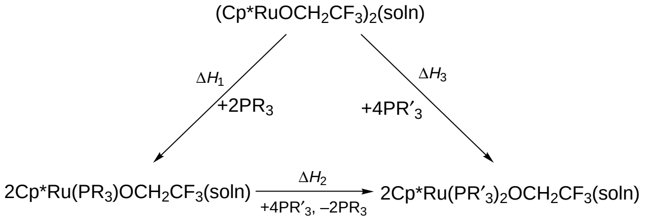
$$\mathrm{CpRu(COD)Cl}(\mathrm{soln}) + 2\mathrm{PPh_3}(\mathrm{soln}) \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{CpRu(PPh_3)_2Cl}(\mathrm{soln}) + \mathrm{COD}(\mathrm{soln}) \quad (18)$$

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

The enthalpy difference between these two systems (ca. 5 kcal/mol) results from the better donor properties of Cp* vs Cp. Thermodynamic studies examining ancillary ligand effects remain scarce. Having examined how modulation of the Cp-type ligation affects ruthenium−phosphine bond disruption enthalpy values, we focused our efforts on Ru−X variation enthalpic effects.

Alkoxide ligations have been utilized in organoruthenium chemistry to support a number of important metal-mediated reactions.[8,9,18] The recent report by Caulton and co-workers of the [Cp*RuOR$_f$]$_2$ (OR$_f$ = OCH$_2$CF$_3$) (**1**) complex[9,19] affords an entryway into the thermochemistry of ligand binding to the Cp*RuOR$_f$ moiety by the rapid and quantitative nature of reaction 19, where the phosphine ligands initially used were sterically demanding ones (P^{i}Pr$_3$ and PCy$_3$), analogous complex to those reported by Tilley [4] in the Cp*Ru(PR$_3$)Cl series.

Scheme 1 [a]



PR$_3$	Pr′$_3$	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$(calcd)	$-\Delta H_3$(exptl)
PCy$_3$	PEt$_3$	18.9(0.3)	41.6(0.6)	60.5(0.9)	60.1(0.5)
PCy$_3$	P(OMe)$_3$	18.9(0.3)	65.8(0.8)	84.7(1.1)	83.8(0.8)
P^{i}Pr$_3$	PEt$_3$	18.6(0.2)	43.6(0.8)	62.2(1.0)	60.1(0.5)
P^{i}Pr$_3$	P(OMe)$_3$	18.6(0.2)	67.2(0.8)	85.8(1.2)	83.8(0.8)

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

$$(\mathrm{Cp^*RuOR_f})_2(\mathrm{soln}) + 2\mathrm{PR_3}(\mathrm{soln}) \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} 2\mathrm{Cp^*Ru(PR_3)OR_f}(\mathrm{soln}) \quad (19)$$

We have further explored the reactivity of **1** with smaller cone angle phosphine and phosphite ligands and found that the reaction of type 20 was sufficiently well-behaved to afford meaningful thermochemical information. Measured enthalpies of reaction are reported in Table 1. Being able to perform these two types of reactions allows for the construction of a thermodynamic cycle to check on the internal consistency of the data. Thermochemical measurements were carried out on reactions exemplified by eq 21. This made possible the construction of the thermochemical cycle presented in Scheme 1. Within experimental error, all experimental and calculated enthalpy values are similar.

$$(\mathrm{Cp^*RuOR_f})_2(\mathrm{soln}) + 4\mathrm{PR_3}(\mathrm{soln}) \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} 2\mathrm{Cp^*Ru(PR_3)_2OR_f}(\mathrm{soln}) \quad (20)$$

$$\mathrm{Cp^*Ru(PR_3)OR_f}(\mathrm{soln}) + 2\mathrm{PEt_3}(\mathrm{soln}) \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(PEt_3)_2OR_f}(\mathrm{soln}) + \mathrm{PR_3}(\mathrm{soln}) \quad (21)$$

Our previous experience with the Cp*RuCl system, and more specifically the reactivity of the tetrameric (Cp*RuCl)$_4$ species with dienes,[6,7b,7f] suggested that a COD complex, used as an entryway into the Cp*Ru(PR$_3$)$_2$Cl series, might prove useful in completing a different thermochemical cycle and offer a broader range of ligand for study. Reaction between **1** and excess cyclooctadiene (COD) leads, however, to the isolation of a sole ruthenium-containing product, the tuck-in complex **4**. One of the driving forces behind this reaction is the formation of the free alcohol (BDE(O−H) = 105 kcal/mol). This alcohol elimination process has previously been observed by Caulton in reactions of **1** with

$$\underset{\mathbf{1}}{(\mathrm{Cp^*RuOR_f})_2} + 2\mathrm{COD} \rightarrow \underset{\mathbf{4}}{2\mathrm{C_5Me_4}\overline{\mathrm{CH_2Ru}}(\mathrm{COD})} + 2\mathrm{HOR_f} \quad (22)$$

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(18) Halcrow, M. A.; Urbanos, F.; Chaudret, B. *Organometallics* **1993**, *12*, 955−957.

(19) Complex **1** is structurally similar to (Cp*RuOMe)$_2$, reported by Kölle; see: (a) Kölle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549−551. (b) Kölle, U.; Kossakowski, J.; Boese, R. *J. Organomet. Chem.* **1989**, *378*, 449−455.

dihydrogen.[9b] A single-crystal diffraction study was carried out on a crystal of **4**, and an ORTEP drawing of the structure is presented in Figure 1. Crystallographic information is summarized in Table 2. Selected bond distances and angles are presented in Table 3. Of specific interest in this complex, besides the obvious tilting of the Cp methylene group (Ru−C(13)−C(18) angle of 80.0 (1)° vs Ru−C(10)−C(15) of 129.5 (0.1)°), is the apparent displacement of the ruthenium center toward the methylene group and the fact that the ruthenium center does not lie in the exact center of the C_5 ring. This is reminiscent of the trimethylenemethane ligand situation[20] or a cross between a four-electron donor and a six-electron ligand. Maitlis and co-workers[21] have reported on the related (tetramethylfulvene)ruthenium complex $[(\eta^6\text{-}C_5Me_4CH_2)RuX_2]_2$, produced via ring-methyl activation in (pentamethylcyclopentadienyl)ruthenium species. This structure also shows strong tilting of the methylene grouping toward the metal center. Kölle and Kang, in their reactivity studies of $[Cp^*RuOMe]_2$, have encountered and characterized a complex similar to **4**.[22] Testing of the reactivity of our tuck-in complex is ongoing.

Relative Ru−PR_3 bond enthalpies can be established using the measured enthalpies of reaction

$$\mathrm{Cp^*Ru(P^iPr_3)OR_f(soln) + 2PEt_3(soln) \rightarrow Cp^*Ru(PEt_3)_2OR_f(soln) + P^iPr_3(soln)} \quad (23)$$

$$\Delta H_{\mathrm{reacn}} = -21.8 \pm 0.4\ \mathrm{kcal/mol}$$

$$\mathrm{Cp^*Ru(PEt_3)_2OR_f(soln) + PCy_3(soln) \rightarrow Cp^*Ru(PCy_3)OR_f(soln) + 2PEt_3(soln)} \quad (24)$$

$$\Delta H_{\mathrm{reacn}} = 20.8 \pm 0.3\ \mathrm{kcal/mol}$$

$$\mathrm{Cp^*Ru(P^iPr_3)OR_f(soln) + PCy_3(soln) \rightarrow Cp^*Ru(PCy_3)OR_f(soln) + P^iPr_3(soln)} \quad (25)$$

$$\Delta H_{\mathrm{calcd}} = -1.0 \pm 0.5\ \mathrm{kcal/mol}$$

This difference compares to a difference in binding strength between the P^iPr_3 and PCy_3 ligands in the $Cp^*Ru(PR_3)Cl$ system of −1.5 ± 0.5 kcal/mol.[7e]

$$\mathrm{Cp^*Ru(P^iPr_3)Cl(soln) + PCy_3(soln) \rightarrow Cp^*Ru(PCy_3)Cl(soln) + P^iPr_3(soln)} \quad (26)$$

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

The only enthalpy of reaction for sterically demanding phosphine ligand available for comparison is found in the work of Hoff and co-workers,[23] in their study of 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[24] was experimentally determined for reaction 27. From a Mo−benzene BDE value

$$\mathrm{(C_6H_6)Mo(CO)_3 + 2PCy_3 \rightarrow (PCy_3)_2Mo(CO)_3 + C_6H_6} \quad (27)$$

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 28 affords an average Mo−$P(OMe)_3$ BDE value of 38.9 kcal/mol.[24] The enthalpy

$$\mathrm{(C_6H_6)Mo(CO)_3 + 3P(OMe)_3 \rightarrow (P(OMe)_3)_3Mo(CO)_3 + C_6H_6} \quad (28)$$

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 for the X = Cl[7e] and 13.5 kcal/mol for the X= OR_f systems.

These sterically demanding phosphine ligands, just as in the $Cp^*Ru(PR_3)Cl$ system, are the most weakly bound ligands investigated and it can be seen that, within experimental error, the enthalpy of ligand exchange for these ligands in both systems are the same. With the available thermochemical data in this system a relative enthalpy/stability scale for all ligands investigated can be constructed and is presented in Table 4. This analysis compares average Ru−PR_3 BDE terms. Important comparisons can be made between the Cp^*RuCl and the Cp^*RuOR_f systems in order to gauge the relative donor strength of the X (Cl vs OR_f) ligands. Examination of data in Table 1 readily shows that enthalpies of reaction involving similar phosphine ligands are more exothermic for the Cp^*RuCl moiety.

$$\mathrm{Cp^*Ru(P^iPr_3)OR_f(soln) + 2PEt_3(soln) \rightarrow Cp^*Ru(PEt_3)_2OR_f(soln) + P^iPr_3(soln)} \quad (29)$$

$$\Delta H_{\mathrm{reacn}} = -21.8 \pm 0.4\ \mathrm{kcal/mol}$$

$$\mathrm{Cp^*Ru(P^iPr_3)Cl(soln) + 2PEt_3(soln) \rightarrow Cp^*Ru(PEt_3)_2Cl(soln) + P^iPr_3(soln)} \quad (30)$$

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

This trend (4−6 kcal/mol more exothermic for the X = Cl system) is understood to reflect the increased electron donation residing on the metal when the ancillary ligand X is OR_f. This would lead to a tendency of the Cp^*RuOR_f moiety to be able to accept less electron density from the incoming donor ligands, resulting in a lower exothermic value for the enthalpy of reaction. This has qualitatively been shown to be the case, as indicated by the carbonyl stretching frequency of the respective CO adducts $Cp^*Ru(PR_3)(CO)X$ ($PR_3 = P^iPr_2Ph$; X = OR_f (1914 cm^{-1}) and Cl (1925 cm^{-1})).[9a] Fundamentally, this

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(20) (a) Meyer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651−2660. (b) Bazan, G. C.; Rodriguez, G.; Cleary, B. P. *J. Am. Chem. Soc.* **1994**, *116*, 2177−2178. (c) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 10155−10156.

(21) Fan, L.; Wei, C.; Aigbirhio, F. I.; Turner, M. L.; Gusev, O. V.; Morozova, L. N.; Knowles, D. R. T.; Maitlis, P. T. *Organometallics* **1996**, *15*, 98−104.

(22) For other examples of transition-metal−tetramethylfulvene complexes see: (a) Kölle, U.; Kang, B.-S. *J. Organomet. Chem.* **1990**, *386*, 267−273. (b) Schock, L. E.; Marks, T. J. *Organometallics* **1987**, *6*, 232−241.

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

(24) 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 similar magnitudes in this system.[10b]

Table 4. Enthalpies of Substitution (kcal/mol) and Relative Ru−PR$_3$ Bond Disruption Enthalpies (kcal/mol) in the Reaction

$$(\mathrm{Cp^*RuOR_f})_2(\mathrm{s}) + n\mathrm{L}(\mathrm{soln}) \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} 2\mathrm{Cp^*Ru(L)}_{n/2}\mathrm{OR_f}(\mathrm{soln})$$

L	complex	n	$-\Delta H_{\mathrm{exptl}}$[a]	rel BDE[b]
P^{i}Pr$_3$	Cp*Ru(P^{i}Pr$_3$)OR$_f$	2	13.0(0.3)	6.5(0.3)
PCy$_3$	Cp*Ru(PCy$_3$)OR$_f$	2	13.3(0.3)	6.7(0.3)
PEt$_3$	Cp*Ru(PEt$_3$)$_2$OR$_f$	4	57.3(0.5)	14.3(0.5)
P(OMe)$_3$	Cp*Ru(P(OMe)$_3$)$_2$OR$_f$	4	81.0(0.8)	20.2(0.8)

[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$_3$ bonds formed during the reaction of interest.

Table 5. Relative Average Ru−PR$_3$ Bond Disruption Enthalpies (kcal/mol) in the Reaction

$$\mathrm{Cp^*RuX} + \mathrm{L} \rightarrow \mathrm{Cp^*Ru(L)X}$$

L	complex	X = OR$_f$	X = Cl[b]
P^{i}Pr$_3$	Cp*Ru(P^{i}PR$_3$)X	6.5(0.3)	9.4(0.3)
PCy$_3$	Cp*Ru(PCy$_3$)X	6.7(0.3)	10.5(0.2)
PEt$_3$	Cp*Ru(PEt$_3$)$_2$X	14.3(0.5)	18.4(0.6)
P(OMe)$_3$	Cp*Ru(P(OMe)$_3$)$_2$X	20.2(0.8)	23.8(0.4)

[a] Enthalpy values are reported with 95% confidence limits. [b] Taken from ref 7e.

increased electron-donating character of the OR$_f$ ligand might explain why a dimeric species is favored for **1** rather than a tetrameric one, isostructural with (Cp*RuCl)$_4$.

A qualitative examination of enthalpies of reaction in both Cp*Ru(PR$_3$)X (X = Cl, OR$_f$) is offered in Table 5. The enthalpies are calculated on the basis of the number of bonds made in the course of the reaction. Enthalpies associated with breaking either the tetrameric or dimeric structures of the precursors is unknown. These two relative scales, however, can be used to establish that a similar enthalpy scale exists between the two systems and that differences between ligand stability appear constant between the two systems. It appears that a change in ligation X results in a fairly constant effect on the enthalpy of reaction.

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^{i}Pr$_3$ and PCy$_3$ ligands. The PCy$_3$ ligand was found to be 1.0 ± 0.5 kcal/mol more strongly bound to ruthenium than the P^{i}Pr$_3$ ligand. A relative enthalpy scale has been established for the binding of phosphines to the Cp*RuOR$_f$ moiety, which incorporates phosphine ligands with both large and small cone angles. The enthalpy trend parallels the one previously established for the Cp*RuCl system, which was explained in terms of electronic and steric contribution to the enthalpy of reaction, with the steric constituent playing a major role. A thermochemical cycle was 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 investigated. Further thermochemical and mechanistic investigations focusing on coordinatively unsaturated and related systems are presently underway.

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Supporting Information Available: Tables of atomic coordinates, selected distances and angles, anisotropic thermal displacement parameters, and intramolecular nonbonded distances for **4** (4 pages). Ordering information is given on any current masthead page.

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