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Ruthenium(II) chemistry of phosphorus-based ligands, $Ph_2PN(R)PPh_2$ (R = Me or Ph) and $Ph_2PN(Ph)P(E)$ Ph_2 (E = S or Se). Solution thermochemical study of ligand substitution reactions in the Cp′RuCl(COD) (Cp′ = Cp, Cp*; COD = cyclooctadiene) system

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Dedicated to Professor S.S. Krishnamurthy on the occasion of his 60th birthday.

Abstract

The enthalpies of reactions of Cp′RuCl(COD) (Cp′ = Cp, Cp*; COD = cyclooctadiene) with bis(phosphino)amines of the type $Ph_2PN(R)PPh_2$(R = Me **1** or R = Ph **2**) and the monochalcogen derivatives $Ph_2PN(Ph)P(E)Ph_2$(E = S **3** or Se **4**) leading to the formation of Cp′RuCl(PNP) and Cp′RuCl{PNP(E)} complexes, respectively, have been measured by anaerobic solution calorimetry in THF at 30°C. These reactions are clean and quantitative. The synthesis and characterization of new organoruthenium complexes is reported. Comparisons with enthalpy data in this two related organoruthenium systems and other similar organometallic systems are also presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Thermochemistry; Bis(phosphino)amines; Ruthenium(II) complexes; Enthalpy; Mononuclear

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1. Introduction

The use of chelating bis(phosphine) ligands is widespread in organometallic chemistry and in homogeneous catalysis [1] as these ligands can be used to fine tune the metal reactivity and selectivity. The ruthenium complexes incorporating this ligand type are of considerable interest because of their potential use in processes such as reductive elimination and oxidative addition for making and breaking C–H bonds [2–8], formation and cleavage of N–H and O–H bonds [9]. Also their extensive use in classical catalytic processes such as hydrogenation, isomerisation, decarbonylation, etc. [10–14] cannot be ignored. In this context, bis(phosphino)amines display their versatility by exhibiting different coordination behavior when the donor–acceptor properties are altered by incorporating different substituents at both the phosphorus centers and at the bridging nitrogen center [15].

In homogeneous catalytic processes, the factors playing a major role in understanding the exact ligand effect at the metal sites are: (i) the entropy of the system and (ii) the metal–ligand bond disruption enthalpy value. This bond disruption enthalpy (BDE) value is a net effect of the stabilizing metal–phosphorus interaction and the destabilizing strain energy caused by the formation of metallacyclic fragment in chelating systems. Solution calorimetric studies have been useful in providing bonding and reactivity pattern information [16–18] that gives insight to design new catalysts for various organic transformations. Nolan and co-workers have previously examined, using solution calorimetric

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techniques, the enthalpy of reaction associated with ligand displacement in related organoruthenium systems [19].

In the present study, we report a thermochemical study used to examine quantitatively the binding ability of the ligands **1**–**4** in two related organoruthenium systems. Furthermore, the synthesis and characterization of new organoruthenium complexes **5**–**13** are presented.

2. Experimental

2.1. General considerations

All experimental manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. Solvents, including deuterated solvents for NMR analysis, were dried by standard methods and vacuum transferred before use. Multinuclear NMR spectra were recorded using VXR 300S or Varian Unity 400 MHz spectrometers operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. $CDCl_3$ was used as both solvent and internal lock. Positive shifts are downfield in all cases. Microanalyses were carried out in the Department of Chemistry, IIT, Bombay. 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]. This calorimeter has been previously described [22] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

2.2. NMR titrations

Prior to every set of calorimetric experiments involving each new ligand, a precisely measured amount ($+0.1$ mg) of CpRuCl(COD) or Cp*RuCl(COD) was placed in an NMR tube along with THF-d_8 and >1.2 equivalents of ligand. Both ^{1}H- and ^{31}P{^{1}H}-NMR spectra were measured within 1.5 h of mixing; both indicated the reactions were clean and quantitative. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all reactions investigated.

2.3. Solution calorimetry

The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120°C, and then taken into the glove box. For the reactions forming **5**, **6**, **7**, **9**, **10**, and **11** a representative experimental trial involved weighing a sample of Cp*RuCl(COD) (17.3 mg, 45.5 μmol) into the lower vessel, which was closed and sealed with 1.5 ml of mercury. A solution of $Ph_2PN(Me)PPh_2$ (108.0 mg, 270.4 μmol) in THF (4 ml) was added, and the remainder of the cell was assembled, removed from the glove box, and inserted into the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organometallic complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30°C (ca. 2 h), it was inverted, thereby allowing the reactants to mix. The reaction was considered complete after the calorimeter had once again reached thermal equilibrium (ca. 2.5 h). Control reactions with Hg and phosphine show no reaction enthalpy contribution. The enthalpy of ligand substitution ($-19.9+0.2$ kcal mol^{-1}) listed in Table 2 represents the average of at least three individual calorimetric determinations with all species in solution. All calorimetric results (in solution) are presented in Table 2. These values include the enthalpy of solution of CpRuCl(COD) ($+3.9+0.1$ kcal mol^{-1}) or Cp*RuCl(COD) ($+4.9+0.1$ kcal mol^{-1}) in THF.

Reactions with $Ph_2PN(Ph)P(Se)Ph_2$ showed reactivity with Hg and an alternative calorimetric method was utilized. For reactions forming **8** and **12**, the mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120°C, and then taken into the glove box. A sample of Cp*RuCl(COD) (20.5 mg, 54.0 μmol) was dissolved in THF (2 ml) and syringed into the inner vessel. A solution of $Ph_2PN(Ph)P(Se)Ph_2$ (61.8 mg, 114.4 μmol) was dissolved in THF (2 ml) was added to the outer vessel, and the remainder of the cell was assembled, removed from the glove box, and inserted into the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organometallic complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30°C (ca. 2 h), it was inverted, thereby allowing the reactants to mix. The reaction was considered complete after the calorimeter had once again reached thermal equilibrium (ca. 2.5 h).

2.4. Syntheses

The ligands **1**–**4** [23–25] and the compounds $CpRuCl(PPh_3)_2$ [26], CpRuCl(COD) [27] and Cp*RuCl(COD) [28] were synthesized according to literature procedures. Experimental details leading to the isolation of complexes **5**–**12** are reported below.

*2.5. [CpRuCl{η^2-$Ph_2PN(R)PPh_2$}] (R = Me **5**, R = Ph **6**)*

A solution of $Ph_2PN(R)PPh_2$ (0.028 g, 0.069 mmol R = Me **1**; 0.032 g, 0.069 mmol R = Ph **2**) in toluene (8 ml) was added to a solution of $CpRuCl(PPh_3)_2$ (0.05 g, 0.069 mmol) also in toluene (8 ml) and the reaction mixture was stirred at room temperature (r.t.) for 3 h. During that period a yellow crystalline product was separated from the reaction mixture. The solution was cooled to r.t. and the product was isolated by filtration and dried under vacuum.

When the above reaction was carried out in toluene at 60°C for 6 h, the analytically pure cationic product [CpRuPPh$_3${η^2-Ph$_2$PN(R)PPh$_2$}]Cl (R = Me **13**, R = Ph **14**) precipitated as yellow microcrystalline material.

Complex **5**, light yellow crystals, yield 93% (0.038 g), m.p. > 250°C (decomposes). Anal. Found: C, 60.16; H, 4.91; N, 2.20. Calc. for $C_{30}H_{28}NP_2ClRu$: C, 59.94; H, 4.69; N, 2.33%. ^{1}H-NMR (CDCl$_3$): δ 7.08–7.41 (m, 20H, Ph), δ 4.66 (s, 5H, Cp), δ 3.00 (t, $^3J_{P-H} = 9.89$ Hz, 3H, N–Me).

Complex **6**, light yellow crystals, yield 86% (0.039 g), m.p. 220°C (decomposes). Anal. Found: C, 63.17; H, 4.43; N, 1.99. Calc. for $C_{35}H_{30}NP_2ClRu$: C, 63.30; H, 4.56; N, 2.11%. ^{1}H-NMR (CDCl$_3$): δ 7.32–7.50 (m, 25H, Ph), δ 4.41 (s, 5H, Cp).

*2.6. [CpRuCl{η^2-Ph$_2$PN(R)P(E)Ph$_2$}] (E = S **7**, E = Se **8**)*

A solution of Ph$_2$PN(R)P(E)Ph$_2$ (0.021 g, 0.041 mmol E = S **3**; 0.023 g, 0.041 mmol E = Se **4**) in THF (8 ml) was added to a solution of CpRuCl(PPh$_3$)$_2$ (0.030 g, 0.041 mmol) also in THF (8 ml) and the reaction mixture was stirred at r.t. for 24 h. During that period a clear red solution was obtained to which 3 ml of *n*-hexane was added. A red product was isolated by filtration and dried under vacuum.

Complex **7**, red crystals, yield 72% (0.021 g), m.p. 218°C (decomposes). Anal. Found: C, 60.23; H, 4.18; N, 2.21. Calc. for $C_{35}H_{30}SNP_2ClRu$: C, 60.46; H, 4.35; N, 2.02%. ^{1}H-NMR (CDCl$_3$): δ 7.19–7.75 (m, 25H, Ph), δ 4.39 (s, 5H, Cp).

Complex **8**, red crystals, yield 68% (0.021 g), m.p. 240°C (decomposes). Anal. Found: C, 56.61; H, 4.12; N, 1.78. Calc. for $C_{35}H_{30}SeNP_2ClRu$: C, 56.64; H, 4.07; N, 1.89%. ^{1}H-NMR (CDCl$_3$): δ 7.21–7.41 (m, 25H, Ph), δ 4.41 (s, 5H, Cp).

*2.7. [Cp*RuCl{η^2-Ph$_2$PN(R)PPh$_2$}] (R = Me **9**, R = Ph **10**)*

A solution of Ph$_2$PN(R)PPh$_2$ (0.038 g, 0.095 mmol R = Me **1**; 0.044 g, 0.095 mmol R = Ph **2**) in THF (8 ml) was added to a solution of Cp*RuCl(COD) (0.036 g, 0.095 mmol) also in THF (8 ml) and the reaction mixture was stirred at r.t. for 3 h. During that period an orange–red solution was obtained. The solvent and volatile were removed under vacuum and 8 ml solvent mixture hexane and THF (2:6) was vacuum transferred to the cooled (− 78°C) solid product. This solution was warmed to r.t., stirred for 15 min and filtered. The filtrate was kept at low temperature to get orange crystals, which were isolated by filtration and dried under vacuum.

Complex **9**, orange crystals, yield 90% (0.057 g), m.p. 160°C (decomposes). Anal. Found: C, 62.69; H, 5.79; N, 1.89. Calc. for $C_{35}H_{38}NP_2ClRu$: C, 62.63; H, 5.71; N, 2.08%. ^{1}H-NMR (CDCl$_3$): δ 7.24–7.75 (m, 20H, Ph), δ 1.49 (s, 15H, Cp*), δ 2.73 (t, $^3J_{P-H} = 8.99$ Hz, 3H, N–Me).

Complex **10**, orange crystals, yield 97% (0.067 g), m.p. 168°C (decomposes). Anal. Found: C, 65.29; H, 5.47; N, 1.79. Calc. for $C_{40}H_{40}NP_2ClRu$: C, 65.51; H, 5.50; N, 1.91%. ^{1}H-NMR (CDCl$_3$): δ 7.21–7.41 (m, 25H, Ph), δ 1.50 (s, 15H, Cp*).

*2.8. [Cp*RuCl{η^2-Ph$_2$PN(R)P(E)Ph$_2$}] (E = S **11**, E = Se **12**)*

A solution of Ph$_2$PN(R)P(E)Ph$_2$ (0.047 g, 0.095 mmol E = S **3**; 0.051 g, 0.095 mmol E = Se **4**) in THF (8 ml) was added to a solution of Cp*RuCl(COD)(0.036 g, 0.095 mmol) also in THF (8 ml) and the reaction mixture was stirred at r.t. for 3 h. During that period a brick-red solution was obtained. The solvent and volatile were removed under vacuum and 5 ml of THF was added to the solid product, stirred for 15 min, filtered and 2 ml of hexane was added to the filtrate. A brick-red crystalline product was precipitated at low temperature, which was isolated by filtration and dried under vacuum.

Complex **11**, brick-red crystals, yield 87% (0.063 g), m.p. 146°C (decomposes). Anal. Found: C, 62.82; H, 5.39; N, 1.92. Calc. for $C_{40}H_{40}SNP_2ClRu$: C, 62.77; H, 5.27; N, 1.83%. ^{1}H-NMR (CDCl$_3$): δ 7.13–7.58 (m, 25H, Ph), δ 1.39 (s, 15H, Cp*).

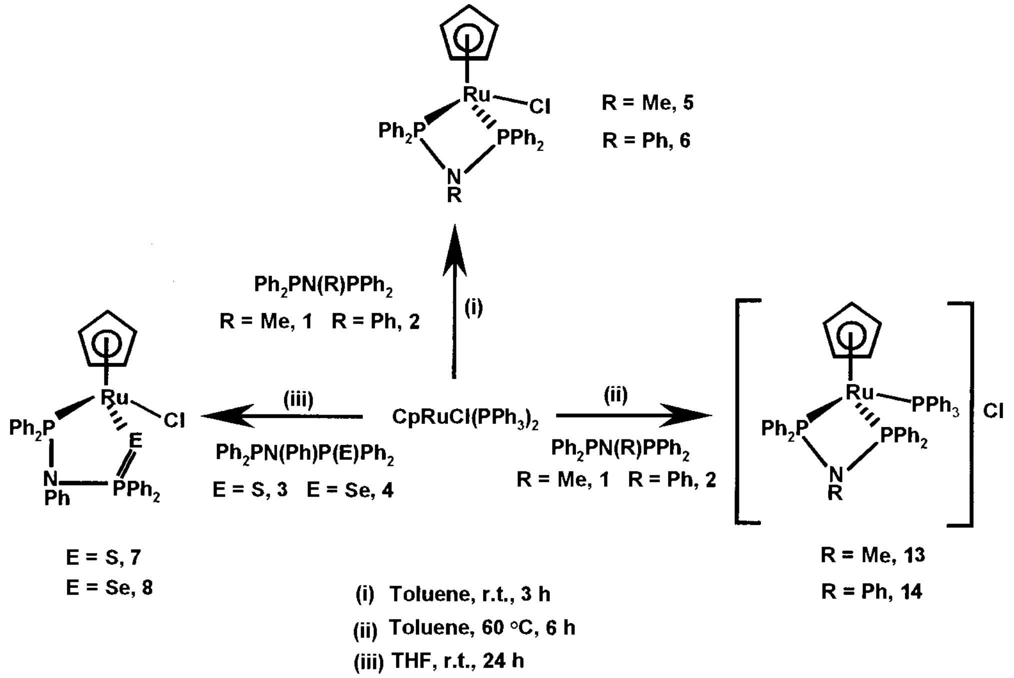
Complex **12**, brick-red crystals, yield 89% (0.069 g), m.p. 140°C (decomposes). Anal. Found: C, 59.01; H, 4.83; N, 1.69. Calc. for $C_{40}H_{40}SeNP_2ClRu$: C, 59.15; H, 4.96; N, 1.72%. ^{1}H-NMR (CDCl$_3$): δ 7.21–7.41 (m, 25H, Ph), δ 1.42 (s, 15H, Cp*).

3. Results and discussion

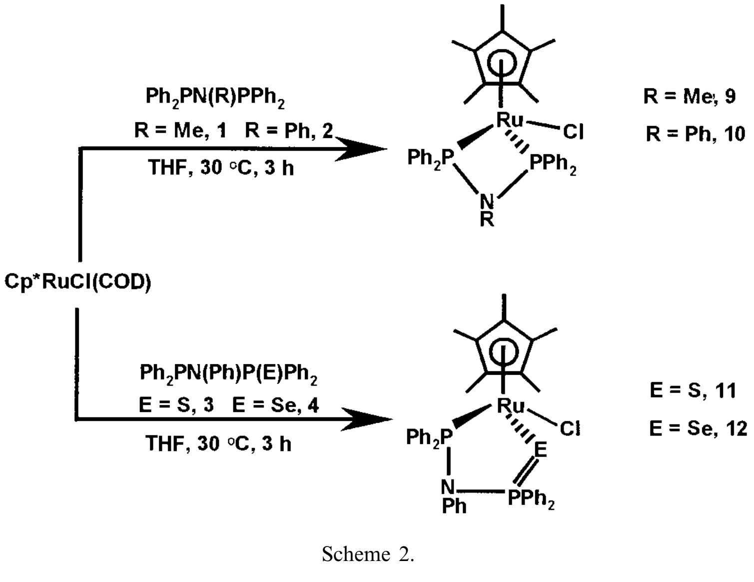
Following our previous studies [15d, 29], we prepared a series of ruthenium complexes **5**–**12** either via the displacement of COD or 2 moles of PPh$_3$, respectively from Cp*RuCl(COD) and CpRuCl(PPh$_3$)$_2$ with the chelate ligands **1**–**4** as shown in Schemes 1 and 2.

The synthesis and the spectroscopic characterization of the above compounds are provided in Section 2. The ^{31}P{^{1}H}-NMR spectroscopic data are listed in Table 1.

Reactions of CpRuCl(PPh$_3$)$_2$ with Ph$_2$PN(R)-PPh$_2$(R = Me **1**, R = Ph **2**) in toluene in a ratio of 1:1 at r.t. for 3 h gave a yellow insoluble micro crystalline precipitate of neutral complexes **5** and **6**, respectively. The $^{31}P\{^{1}H\}$-NMR spectrum shows single peaks at 54.0 ppm for **5** and 49.0 ppm for **6**, respectively indicating that both PPh_3 ligands are replaced by $Ph_2PN(R)PPh_2$, which is acting as a bidentate chelating ligand. The same reactions when carried out at 60°C for 6 h gave cationic complexes **13** and **14** [29] as the major products. The $^{31}P\{^{1}H\}$-NMR spectrum of the product **13** shows a doublet at 80.5 ppm for chelating $Ph_2PN(R)PPh_2$ and a triplet at 45.2 ppm for PPh_3 with a $^{2}J_{\mathrm{P-P}}$ value of 34.9 Hz. The reaction of $Ph_2PN(R)PPh_2$($R = Me$ **1**, $R = Ph$ **2**) with Cp*RuCl(COD) afforded only the neutral complexes **9** and **10**, respectively in good yield even in the presence of an excess of bis(phosphino)amine ligand. The $^{31}P\{^{1}H\}$-NMR spectra of the complexes **9** and **10** show singlets at 87.9 and 90.8 ppm, respectively indicating that the diene (COD) has been replaced by the bidentate chelating bis(phosphino)amines. The reactions of **3** and **4** with Cp*RuCl(COD) in equimolar quantities afforded the mononuclear neutral complexes **11** and **12**, respectively. The $^{31}P\{^{1}H\}$-NMR spectrum of **11** shows two sharp doublets as expected [25] at 117.9 ppm and 76.2 ppm, respectively, for P^{III} and P^{V} centers with a $^{2}J_{\mathrm{P}}^{\mathrm{MI}}$ value of 70.0 Hz. The $^{31}P\{^{1}H\}$-NMR spectrum of **12** also shows two sharp doublets at 121.8 and 62.5 ppm with a $^{2}J_{\mathrm{P}}^{\mathrm{MI}}$ coupling of 80.9 Hz with the latter (P^{V}



Scheme 1.



Scheme 2.

Table 1
$^{31}P\{^1H\}$-NMR [a] spectroscopic data for ligands **1**–**4** and their complexes **5**–**13**

Compounds	Chemical shifts		J (Hz)
	$\delta(P^{III})$	$\delta(P^{V})$	
$Ph_2PN(Me)PPh_2$(**1**)	73.6		
$Ph_2PN(Ph)PPh_2$(**2**)	69.1		
$Ph_2PN(Ph)P(S)Ph_2$(**3**)	54.5d	72.4d	$^2J_{P-P} = 104.6$
$Ph_2PN(Ph)P(Se)Ph_2$(**4**)	55.1d	72.1d	$^2J_{P-P} = 104.6$ $^1J_{P-Se} = 766.5$
$[CpRuCl\{\eta^2\text{-}Ph_2PN(Me)PPh_2\}]$(**5**)	54.0		
$[CpRuCl\{\eta^2\text{-}Ph_2PN(Ph)PPh_2\}]$(**6**)	49.0		
$[CpRuCl\{\eta^2\text{-}Ph_2PN(Ph)P(S)Ph_2\}]$(**7**)	125.9d	46.0d	$^2J_{P-P} = 46.0$
$[CpRuCl\{\eta^2\text{-}Ph_2PN(Ph)P(Se)Ph_2\}]$(**8**)	126.0d	42.9d	$^2J_{P-P} = 47.2$ $^1J_{P-Se} = 710.2$
$[Cp^*RuCl\{\eta^2\text{-}Ph_2PN(Me)PPh_2\}]$(**9**)	87.9		
$[Cp^*RuCl\{\eta^2\text{-}Ph_2PN(Ph)P(Ph_2\}]$(**10**)	90.8		
$Cp^*RuCl\{\eta^2\text{-}Ph_2PN(Ph)P(S)Ph_2\}]$(**11**)	117.9d	76.2d	$^2J_{P-P} = 70.0$
$[Cp^*RuCl\{\eta^2Ph_2PN(Ph)P(Se)Ph_2\}]$(**12**)	121.8d	62.5d	$^2J_{P-P} = 80.9$ $^1J_{P-Se} = 682.0$
$[CpRu(PPh_3)\{\eta^2Ph_2PN(Me)PPh_2\}]Cl$**(13)**	80.0d 45.2t		$^2J_{P-P} = 34.9$

[a] All spectra in $CDCl_3$; δ in ppm vs 85% H_3PO_4; d = doublet; t = triplet.

center) also showing $^1J_{Pse}$ coupling of 682.0 Hz. The heterodifunctional ligands **3** and **4** also react with $CpRuCl(PPh_3)_2$ to give the chelates **7** and **8**, respectively.$^{31}P\{^1H\}$-NMR data for these compounds (Table 1) are consistent with the proposed chelated structures.

The use of (Cp′RuCl(COD) (Cp′ = Cp; Cp*; COD = cyclooctadiene) system in this synthesis and solution calorimetry study of the complexes **5**–**12** has been possible by the rapid substitution of COD with the chelate ligands. This type of bis(phosphino)amine binding reaction appears general and quantitative for all ligands investigated by solution calorimetry at 30°C in THF. A tabulation of the enthalpies ($-\Delta H_{rxn}$) for the reaction of Cp′RuCl(COD) with chelate ligands **1**–**4** to give complexes **5**–**12** is presented in Table 2. These values include the enthalpy of solution of Cp*RuCl(COD) ($+4.9 \pm 0.1$ kcal mol^{-1}) or CpRuCl(COD) ($+3.9 \pm 0.1$ kcal mol^{-1}) in THF.

The labile nature and relative thermodynamic stability of a number of metal–diene complexes are well known [30]. In the case of Cp′RuCl(COD), the diene ligand has been shown to be weakly bound to the metal center. This reaction type was investigated by solution calorimetry involving 2 moles of monodentate phosphines or with chelating bis(phosphine) ligands [19]. The labile nature of the Ru–COD bond has also been exploited in the present thermochemical study of bis(phosphino)amine substitution reactions. This exchange reaction has been quite efficient in leading to quantitative conversion of Cp′RuCl(COD) to complexes **5**–**12.** From the experimental data of the solution calorimetry, important insights are offered by a comparison between the present data and that of the $Cp^*RuCl(\eta^2\text{-}PP)$ (PP = bisphosphines with PCP backbone) system [19e–g]. The magnitude of the enthalpy of reaction can be examined in terms of the basicity of the donor atoms and that of the metal centers.

The reactions involving the ligands **1** and **2** prove to be more exothermic where the donor atoms are phosphorus centers. However, the substitutions of the mixed ligands **3** and **4** are ca. 10 kcal mol^{-1} less exothermic than those for **1** and **2,** resulting in less thermodynamically stable complexes. In the latter case the donor atom other than the phosphorus center is sulfur or selenium, which is less basic, rendering the M–L bond weaker and hence the low enthalpy of reaction. A similar trend [19e] is observed in the reactions involving alkyl-substituted phosphines and mixed phosphine–ar-

Table 2
Enthalpies of substitution (kcal mol^{-1}) in the reaction

$$Cp'RuCl(COD)(soln) + L\sim L(soln) \xrightarrow[30°C]{THF} Cp'Ru(L\sim L)Cl(soln)$$
$$(C\acute{p} = Cp, Cp^*)$$
$$+ COD_{(soln)}$$

Complex [a]	Ligands (L ~ L)	ΔH_{rnx} [b] (kcal mol^{-1})
5	$Ph_2PN(Me)PPh_2$	−23.1(4)
6	$Ph_2PN(Ph)PPh_2$	−25.6(4)
7	$Ph_2PN(Ph)P(S)Ph_2$	−13.1(2)
8	$Ph_2PN(Ph)P(Se)Ph_2$	−13.4(3)
9	$Ph_2PN(Me)PPh_2$	−19.9(2)
10	$Ph_2PN(Ph)PPh_2$	−19.8(2)
11	$Ph_2PN(Ph)P(S)Ph_2$	−9.3(3)
12	$Ph_2PN(Ph)P(Se)Ph_2$	−9.7(2)

[a] 5–8 $CpRu(\eta^2\text{-}L\sim L)Cl$; 9–12 $Cp^*Ru(\eta^2\text{-}L\sim L)Cl$.

[b] Enthalpy values are provided with 95% confidence limit.

sine ligands (arphos). The measured enthalpy of reaction is 6.1 kcal mol^{-1} less exothermic for arphos than for the symmetrical diphosphine dppe(bis(diphenylphosphino)ethane). In the substitution involving the monodentate ligands [19f] $AsEt_3$ and PEt_3, this trend of arsenic-based ligands being weaker donors has also been observed. A difference of 3.1 kcal mol^{-1} is observed in the above case.

Further, the thermochemical data exhibit a difference in enthalpies of reaction between the Cp and Cp* systems. For two sets of ligands, **1** and **2** having two phosphorus centers (symmetrical) and **3** and **4** having one phosphorus and one sulfur or selenium, significant enthalpy differences are observed. In both Cp and Cp* systems, we can compare (Cp vs. Cp*) the magnitude of enthalpy of reaction on the basis of the effect of electronic properties of the ancillary ligand as it contributes to the change in metal basicity [30]. Since Cp* is more electron donating than Cp, it renders the metal center more basic and hence less electrophilic. As a consequence the metal center will not be able to accommodate greater electron density from the incoming ligand, resulting in lower enthalpy of ligand substitution. Angelici and co-workers [31] have also investigated a series of iridium complexes and have observed a difference, in enthalpies of protonation, of 5.7 kcal mol^{-1} between CpIr(COD) and Cp*Ir(COD) complexes. Hoff and co-workers [32] first demonstrated this difference in metal basicity between Cp and Cp* in their thermochemical investigation of organomolybdenum complexes. In the present study the enthalpy difference of 4 kcal mol^{-1} between the ligand substitution reactions reflects the difference of metal basicity due to the change in ancillary ligand. 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 system.

4. Conclusions

The enthalpy of ligand substitution reactions in the case of heterodifunctional ligands has clearly indicated that they have weaker M–E (E = S, Se) bonds. Although these heterodifunctional ligands form stable five-membered metallacycles, the M–E bonds can be easily cleaved. This feature can be exploited in utilizing this class of ligands bound to suitable metals for designing a variety of heterodinuclear or polynuclear complexes and in a variety of metal-mediated organic transformations. Research in this direction is in progress.

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