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Thermochemical Investigation of Phosphine Ligand Substitution Reactions Involving *trans*-$\mathrm{(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2}$ Complexes

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The enthalpies of reaction of $\mathrm{(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2}$ (**1**) with a series of tertiary phosphine ligands, leading to the formation of $\mathrm{(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2}$ complexes ($\mathrm{PR_3} = \mathrm{P^{\mathit{i}}Pr_3}$, $\mathrm{PBz_3}$, $\mathrm{PPh_2Cy}$, $\mathrm{PPhCy_2}$, $\mathrm{PCy_3}$, and $\mathrm{P^{\mathit{i}}Bu_3}$) have been measured by solution calorimetry in $\mathrm{CH_2Cl_2}$ at 30 °C. The range of reaction enthalpies spans some 6.5 kcal/mol and helps to establish a relative order of complex stability for these six ruthenium carbene complexes. The enthalpies of reaction for tertiary phosphine complexes, *trans*-$\mathrm{(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2}$, are as follows ($\mathrm{PR_3}$, kcal/mol): $\mathrm{PPh_3}$, 0; $\mathrm{PBz_3}$, −1.3 (0.2); $\mathrm{PCyPh_2}$, −1.8 (0.2); $\mathrm{PCy_2Ph}$, −3.8 (0.2); $\mathrm{P^{\mathit{i}}Bu_3}$, −3.8 (0.2); $\mathrm{P^{\mathit{i}}Pr_3}$, −5.2 (0.1); $\mathrm{PCy_3}$, −6.5 (0.3). The thermodynamics of the exchange of these sterically demanding tertiary phosphine ligands for $\mathrm{PPh_3}$ in **1** provides a measurement of the relative importance of phosphine steric and electronic properties/character to the enthalpy of reaction in this system. Correlations of various factors gauging the electron-donating properties of the phosphine ligands clearly show the electronic factor to be the overwhelming contributor to the enthalpy of reaction in this system.

Introduction

The field of organometallic thermochemistry has gained recognition as one of great relevance to catalysis.[1,2] Such valuable investigations have led to a better understanding of bonding and reactivity patterns in a number of organometallic systems.[3,4] These studies have also proven powerful tools in predicting the thermodynamic feasibility of given reactions or individual steps comprising catalytic cycles.[5]

Systems which could benefit from such thermochemical investigations are the ruthenium-based olefin metathesis catalysts. The utilization of neutral 16-electron ruthenium−carbene complexes in organic and polymer chemistry is now widespread.[6] Recent developments in the area of olefin metathesis have had a tremendous impact on both fields.[7,8] Continued efforts are directed toward improving catalyst activity, functional group tolerance, and versatility. Mechanistic investigations examining the activation and decomposition pathways of these catalytically active carbenes have generated important information which should guide the development of future generations of olefin metathesis cata-

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

$$Cl_2Ru(PPh_3)_2({=}CH{-}CH{=}CPh_2)_{(soln)} + 2PR_{3(soln)} \xrightarrow{CH_2Cl_2,\ 30\ °C} Cl_2Ru(PR_3)_2({=}CH{-}CH{=}CPh_2)_{(soln)} + 2PPh_{3(soln)}$$

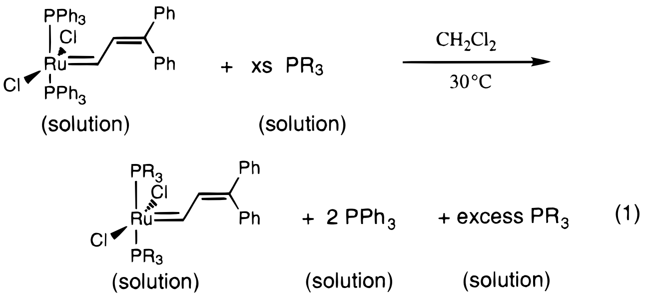
L	θ[a]	complex	χ[b]	$-\Delta H_{rxn}$[c]
PPh_3	145	$Cl_2Ru(PPh_3)_2({=}CH{-}CH{=}CPh_2)$	13.45	0
PBz_3	165	$Cl_2Ru(PBz_3)_2({=}CH{-}CH{=}CPh_2)$	10.3	1.3 (0.2)
$PCyPh_2$	153	$Cl_2Ru(PCyPh_2)_2({=}CH{-}CH{=}CPh_2)$	9.4	1.8 (0.2)
PCy_2Ph	162	$Cl_2Ru(PCy_2Ph)_2({=}CH{-}CH{=}CPh_2)$	5.35	3.8 (0.2)
P^iBu_3	143	$Cl_2Ru(P^iBu_3)_2({=}CH{-}CH{=}CPh_2)$	5.7	3.8 (0.2)
P^iPr_3	160	$Cl_2Ru(P^iPr_3)_2({=}CH{-}CH{=}CPh_2)$	3.45	5.2 (0.1)
PCy_3	170	$Cl_2Ru(PCy_3)_2({=}CH{-}CH{=}CPh_2)$	1.4	6.5 (0.3)

[a] Taken from ref 11. [b] Taken from ref 15b. [c] Enthalpy values are reported with 95% confidence limits.

lysts.[9] One important feature of this class of catalyst precursor is the mandatory presence of a bulky tertiary phosphine as part of the supporting ligation. One crucial role of this bulky electron donor ligand is to stabilize the reactive intermediate and/or inhibit carbene bimolecular decomposition.[9a] The role of this ligand in terms of stereoelectronic effect on catalyst activity and decomposition is now better understood. Yet, this understanding is based principally on kinetic studies[9] and observed reactivity patterns. We have had a longstanding interest in the thermochemistry of organogroup VIII metal centers.[10] To gain a more detailed insight into their reactivity patterns, this report presents the first thermochemical study of ligand exchange in a metathesis active metal carbene system.

Results and Discussion

Calorimetric Results. The $(PPh_3)_2Cl_2Ru({=}C{-}C{=}CPh_2)$ (**1**) complex was selected as the entryway into the thermochemistry of the ruthenium−carbene system in view of the labile nature of the PPh_3 ligands. In the present study, PPh_3 replacement by a series of sterically demanding tertiary phosphine ligands was investigated by batch solution calorimetry (eq 1). Excess phosphine is required to drive the reactions to completion.



(1)

All reactions investigated rapidly and cleanly led to formation of product under the calorimetric conditions as determined by NMR spectroscopy (vide infra). A list of all reaction enthalpies is provided in Table 1.

Correlation of Reaction Enthalpies with Tolman Electronic Parameter. Using a relationship first proposed by Tolman (eq 2),[11] one of us has recently[12] interpreted enthalpies of ligand substitution in terms of phosphine steric and electronic parameters. This

$$-\Delta H_{rxn} = A_0 + A_1\theta + A_2\nu \qquad (2)$$

relationship permits the correlation of reaction enthalpies (ΔH) to the steric (θ, cone angle) and electronic (ν, carbonyl stretching frequency in $Ni(CO)_3L$ (L = tertiary phosphine)) properties of the incoming ligand. An excellent correlation is found to exist with the present ruthenium data ($R = 0.995$; $A_0 = 946.1$; $A_1 = 0.036$; $A_2 = -0.460$). The A_1/A_2 ratio can be taken as a measure of the relative importance of steric versus electronic factors.[13] It would be expected that steric factors play only a minor role in this ruthenium system in view of the trans arrangement of ligands. This has also been observed in *trans*-$Rh(CO)(Cl)(PR_3)_2$.[14] A value of 0.08 was calculated for the A_1/A_2 ratio, illustrating the predominant influence of electronic factors. The triviality of the steric effect within this series is also evident in that a plot correlating the reaction enthalpies in Table 1 with the corresponding Tolman electronic factor (ν) was found to give a very good fit (Figure 1).

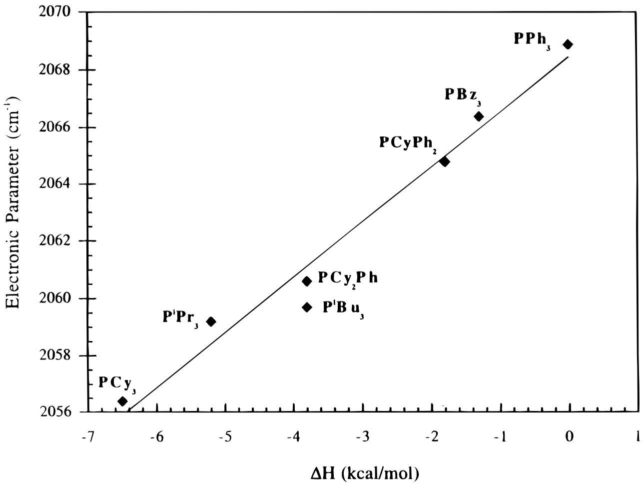


Figure 1. Enthalpy of phosphine exchange reaction (kcal/mol) vs Tolman electronic parameter (ν) (cm^{-1}) for *trans*-$(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ complexes. Slope = 1.93, R = 0.98.

Correlation of Reaction Enthalpies with Phosphine Electronic Factors. Giering and co-workers have developed a model to extract information about the stereoelectronic factors which influence the thermodynamics and kinetics of chemical reactions.[15] This quantitative analysis of ligand effects (QALE) model attempts to separate steric and electronic ligand characteristics into independent parameters. Correlations obtained using the QALE approach often are linear and

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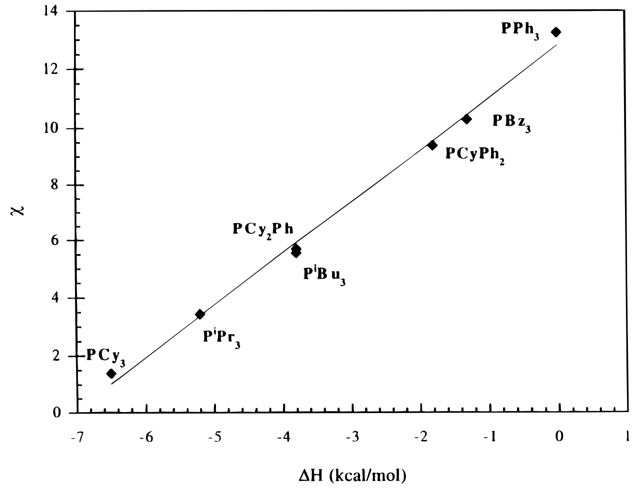


Figure 2. Enthalpy of phosphine exchange reaction (kcal/mol) vs χ for *trans*-$(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ complexes. Slope = 1.813, R = 0.997.

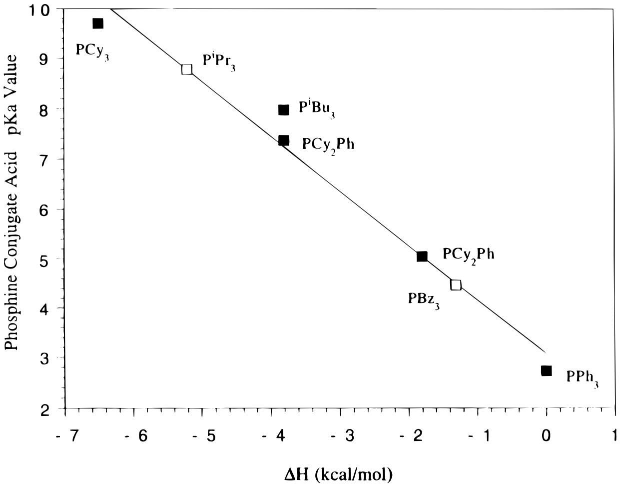


Figure 3. Enthalpy of phosphine exchange reaction (kcal/mol) vs pK_a of HPR_3^+ for *trans*-$(PR_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ complexes. Slope = −1.092, R = 0.983. Solid: literature value taken from ref 16. Hollow: predicted value.

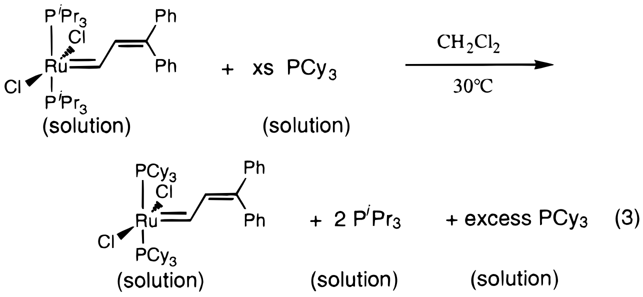
can offer insights into structure and reactivity patterns. Such a treatment was performed for the present thermochemical data using only the QALE electronic parameter, and the result is illustrated in Figure 2.

From the excellent correlation between χ^{16} and ΔH, the electronic parameter can be taken as the origin of any variations in measured enthalpies of reaction. Enthalpies of reaction correlate in a linear fashion with the ligand electronic parameter (χ). The apparent lack of interaction between phosphine ligands and Cl or carbene fragments as demonstated by structural work performed on the $(PR_3)_2Cl_2Ru({=}C(H){-}R)$ complexes[8a,c] is entirely in line with the illustrated correlation.

Correlation of Reaction Enthalpies with pK_a of HPR_3^+. The pK_a value of the conjugated acid of a trialkylphosphine, HPR_3^+, can be used as a rough estimate of the σ-donor ability of the phosphine.[17] The reaction enthalpies from Table 1 also correlate well with these values (Figure 3), again suggesting that σ-donation plays an important role in dictating the magnitude of the reaction enthalpy.

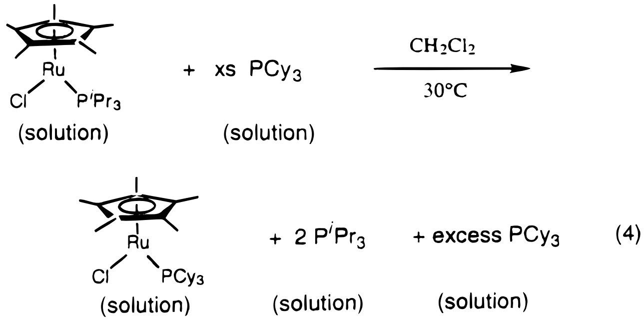
Since this relationship is so linear, it has been used to estimate the yet to be determined pK_a values of two phosphines, P^iPr_3 (8.8) and PBz_3 (4.6).

Predicting Enthalpy of Other Ligand Exchange Processes. In the present system, the enthalpy associated with any ligand exchange process can be calculated by simply subtracting appropriate enthalpy values taken from Table 1. For example, substitution of PCy_3 for P^iPr_3 can be calculated to be exothermic by some 1.3 kcal/mol (eq 3). This enthalpy value may be



$$\Delta H(P^iPr_3\text{-}PCy_3) = \Delta H(PPh_3\text{-}PCy_3) - \Delta H(PPh_3\text{-}P^iPr_3) = -6.5 + 3.2 = -1.3 \pm 0.3 \text{ kcal/mol}$$

indicative of a stronger $Ru{-}PCy_3$ bond compared to $Ru{-}P^iPr_3$ interaction (by some 0.7 kcal/mol), but we favor an interpretation of the enthalpy representing the overall enthalpic driving force for the exchange instead of assigning the enthalpy to individual bonds. An example of the complications involved in the latter approach has recently been reported.[18] This small enthalpy difference can be directly compared with a similar calculated exchange in a recently investigated organoruthenium system.[19] In that system, only two ligands were investigated and exchange enthalpies can be calculated as illustrated in eq 4



$$\Delta H(P^iPr_3\text{-}PCy_3) = -1.5 \pm 0.5 \text{ kcal/mol}$$

where the enthalpy difference is 1.5 kcal/mol. We can see that within experimental error the two differences are the same. In both systems, the $Ru{-}PCy_3$ interaction is stronger which is a trend in accord with the better donating properties of PCy_3.

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[16] These electronic values are taken from either ref 11 or from the following: Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29−41.

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Conclusion

The reported solution calorimetric investigation represents the first detailed thermochemical study of ligand substitution reactions involving a catalytically active transition-metal carbene system. The data obtained can be used to quantitatively evaluate electronic effects of the ancillary phosphine ligands in the present ruthenium system. Excellent correlations are established with the phosphine electronic parameters as first proposed by Tolman and modified by Giering. In assessing the donor properties of the phosphine ligand, even a simple pK_a model describes fairly well the influence of phosphine electronics. Our results clearly show the importance of σ-donation as a major contributor to enthalpy of ligand substitution reactions in this system. After having stated the influence of electronic effects within this system, it should be emphasized that first and foremost the synthetic feasibility of and access to the 16-electron ruthenium carbene complexes described in this study has a fundamental steric component. Phosphines smaller than PPh_3 do not allow for isolation of monomeric ruthenium carbene 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 of oxygen and water. Methylene chloride (CH_2Cl_2) was dried over CaH_2 and then vacuum-transferred into flame-dried glassware immediately before use. NMR spectra were recorded using a GE-300 Plus (300.10 MHz ^{1}H) 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. The organoruthenium complex $(PPh_3)_2(Cl)_2Ru({=}C{-}C{=}CPh_2)$ (**1**) was synthesized according to literature procedures.[8a] All other carbene complexes have been reported.[8,9] Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. All ligands were purchased from Strem Chemicals (Newburyport, MA) or Organometallics, Inc. (East Hampstead, NH) and purified by standard techniques[23] prior to use.

NMR Titrations. Prior to every set of calorimetric experiments involving a new phosphine 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 CD_2Cl_2 was subsequently added. The solution was titrated with a solution of the PR_3 of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^{31}P and ^{1}H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organometallic reactions investigated.

Calorimetric Measurement for Reaction Involving $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ and PCy_3. The following procedure describes a typical experiment. 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 $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**1**) was transferred into a 2 mL volumetric flask and accurately weighed on a high-precision balance. Enough dry CH_2Cl_2 was added to make a 2 mL solution, and the resulting green liquid was then syringed into the inner compartment of the calorimetric cell. Next, 1.0 g of the PCy_3 ligand was dissolved in enough CH_2Cl_2 to make 10 mL of stock solution, 2 mL of which was then syringed into the outer compartment of the cell. The vessel was closed, taken out of the glovebox, and loaded in the calorimeter. The reference vessel was charged in an identical manner except that the inner compartment contained neat CH_2Cl_2 (2 mL). After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the reaction was initiated by inverting the calorimeter. At the end of the reaction (1−2 h), the vessels were removed from the calorimeter and taken into the glovebox. There the cell was opened, the solvent removed in vacuo, and a ^{1}H and ^{31}P NMR spectra were recorded in CD_2Cl_2 solution. The conversion to the $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ product was shown to be quantitative. The enthalpy of reaction, -6.5 ± 0.3 kcal/mol, represents the average of five individual calorimetric determinations.

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