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Solution Thermochemical Study of Tertiary Phosphine Ligand Substitution Reactions in the RhCl(CO)(PR$_3$)$_2$ System

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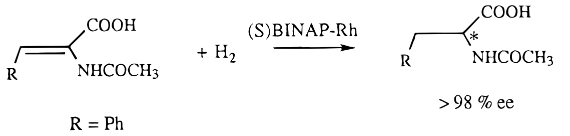
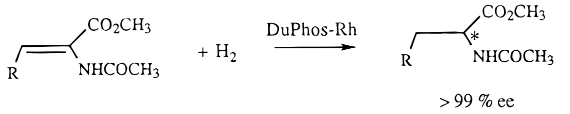
The enthalpies of reaction of $[Rh(CO)_2Cl]_2$ (**1**) with a series of monodentate tertiary phosphine ligands, leading to the formation of $RhCl(CO)(PR_3)_2$ complexes, have been measured by anaerobic solution calorimetry in CH_2Cl_2 at 30.0 °C. These reactions are rapid and quantitative. The measured reaction enthalpies span a range of 43 kcal/mol. The relative stability scale established is as follows: $P(NC_4H_4)_3 < P(NC_4H_4)_2(C_6H_5) < P(OPh)_3 < P(p\text{-}CF_3C_6H_4)_3 < P(NC_4H_4)(C_6H_5)_2 < P(p\text{-}ClC_6H_4)_3 < AsEt_3 < P(p\text{-}FC_6H_4)_3 < PPh_3 < P(p\text{-}CH_3C_6H_4)_3 < P(p\text{-}CH_3OC_6H_4)_3 < PPh_2Me < P(OMe)_3 < PPhMe_2 < PEt_3$. The relative importance of phosphine electronic ligand parameters is closely examined in terms of the presented quantitative thermochemical information. Comparisons with enthalpy data in related organometallic systems are also presented.

Introduction

The utilization of rhodium−phosphine complexes in homogeneous catalysis is widespread[1] and encompasses industrially important processes, hydroformylation[2] being one of the most widely known rhodium-mediated conversions. Phosphine ligands have shown great utility in organometallic chemistry and catalysis as a way to fine tune metal reactivity and selectivity.[3,4] A rapidly developing area of research is asymmetric catalysis involving metal centers bearing chiral phosphine ligands.[5]



(1)



(2)

A large number of kinetic and mechanistic studies have been performed on these catalytic systems to test substrate selectivities and reactivities. In spite of all this attention brought to rhodium−phosphine complexes, very little is known of the quantitative thermodynamic stability of these systems. It should be mentioned here that some thermochemical information is available on rhodium−phosphine systems. Pioneering work by Blake and co-workers[6] focused on the enthalpic driving force behind oxidative addition to square planar rhodium(I) systems.

$$RhX(CO)(PPh_3)_2 + I_2 \xrightarrow[C_6H_6]{} RhX(I)_2(CO)(PPh_3)_2 \quad (3)$$

$$X = \text{halide, NCS, } N_3$$

Drago has reported an estimate for the scission of the dimer $[RhCl(CO)_2]_2$ (**1**) to a monomeric species based on thermochemical treatment of enthalpies of reaction between **1** and nitrogen bases.[7] An E and C treatment of the data afforded a W term attributed to the strength of the dimer (20.8 ± 2.2 kcal/mol).

$$[RhCl(CO)_2]_2 \rightarrow 2RhCl(CO)_2 \quad (4)$$

$$\Delta H = 20.8 \pm 2.2 \text{ kcal/mol}$$

More recently, Goldman and co-workers determined the bond dissociation enthalpy for Rh−N$_2$, Rh−(H)$_2$, Rh−olefin, and Rh−acetylene complexes.[8]

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$$^{1}/_{2}[\mathrm{RhL_2Cl}]_2 + \mathrm{L'} \rightarrow 2\mathrm{RhL_2ClL'} \tag{5}$$

$$^{1}/_{2}[\mathrm{RhL_2Cl}]_2 + \mathrm{H_2} \rightarrow 2\mathrm{RhL_2Cl(H)_2} \tag{6}$$

$$\mathrm{L} = \mathrm{P^iPr_3};\ \mathrm{L'} = \mathrm{N_2},\ \mathrm{C_2H_4},\ \mathrm{PhCCPh}$$

Furthermore the enthalpy behind the observed decarbonylation of aldehydes by a coordinatively unsaturated rhodium system was experimentally determined.[9]

$$^{1}/_{2}[\mathrm{RhL_2Cl}]_2 + \mathrm{RC(O)H} \rightarrow 2\mathrm{RhL_2Cl(CO)} + \mathrm{RH} \tag{7}$$

$$\mathrm{L} = \mathrm{P^iPr_3};\ \mathrm{R} = \mathrm{alkyl}$$

We have been involved in mapping out the thermochemical surface of organo−ruthenium and −iron systems bearing phosphine and phosphite ligands. Researchers have been involved in recent years in describing metal−ligand systems in terms of stereoelectronic contributions, using a variety of methods.[10−12] We have been interested in clarifying the exact partitioning of steric and electronic ligand contributions present in tertiary phosphine-based systems by means of solution calorimetry.[13−15] We have achieved this in part for one iron- and two ruthenium-based organometallic systems using solution calorimetric techniques.

$$\mathrm{Cp^*Ru(COD)Cl(soln)} + 2\mathrm{PR_3(soln)} \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(PR_3)_2Cl(soln)} + \mathrm{COD(soln)} \tag{8}$$

$$\mathrm{CpRu(COD)Cl(soln)} + 2\mathrm{PR_3(soln)} \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{CpRu(PR_3)_2Cl(soln)} + \mathrm{COD(soln)} \tag{9}$$

$$\mathrm{(BDA)Fe(CO)_3(soln)} + 2\mathrm{PR_3(soln)} \xrightarrow[50\ ^\circ\mathrm{C}]{\mathrm{THF}} trans\text{-}\mathrm{(PR_3)_2Fe(CO)_3(soln)} + \mathrm{BDA(soln)} \tag{10}$$

$$\mathrm{Cp} = \mathrm{C_5H_5};\ \mathrm{Cp^*} = \mathrm{C_5Me_5};\ \mathrm{BDA} = \mathrm{PhCH{=}CHCOMe};\ \mathrm{PR_3} = \text{tertiary phosphine}$$

In the present contribution, our solution calorimetric work is extended to a fundamentally important organorhodium−phosphine system, $\mathrm{RhCl(CO)(PR_3)_2}$.

Experimental Section

General Considerations. All manipulations involving organorhodiun 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 or Aldrich and used as received or synthesized by the literature method.[16] Solvents were dried and distilled under dinitrogen before use by employing standard drying agents.[17] Only materials of high purity as indicated by IR and NMR spectroscopies 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[18] or the enthalpy of solution of KCl in water.[19] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[20] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. $\mathrm{[Rh(CO)_2Cl]_2}$ (**1**) was synthesized according to literature procedures.[21] The identity of all calorimetry products was determined by comparison with literature spectroscopic data.[22]

Infrared Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organorhodium complex was placed in a test tube fitted with a septum, and $\mathrm{CH_2Cl_2}$ was subse-

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

$$[Rh(CO)_2Cl]_2(soln) + 4PR_3(soln) \xrightarrow[30\ °C]{CH_2Cl_2} 2Rh(CO)(Cl)(PR_3)_2(soln) + 2CO$$

L	complex	ν_{CO} (cm^{-1})	$-\Delta H(rxn)$[a]
$P(NC_4H_4)_3$	$Rh(CO)(Cl)(P[NC_4H_4]_3)_2$	2024	34.4(0.2)
$P(NC_4H_4)_2(C_6H_5)$	$Rh(CO)(Cl)(P[NC_4H_4]_2[C_6H_5])_2$	2007	35.3(0.2)
$P(OPh)_3$	$Rh(CO)(Cl)(P[OPh]_3)_2$	2016	42.6(0.2)
$P(p\text{-}CF_3C_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}CF_3C_6H_4]_3)_2$	1990	43.8(0.2)
$P(NC_4H_4)(C_6H_5)_2$	$Rh(CO)(Cl)(P[NC_4H_4][C_6H_5]_2)_2$	1993	44.8(0.2)
$P(p\text{-}ClC_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}ClC_6H_4]_3)_2$	1984	47.8(0.3)
$AsEt_3$	$Rh(CO)(Cl)(AsEt_3)_2$	1952	49.2(0.3)
$P(p\text{-}FC_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}FC_6H_4]_3)_2$	1982	50.1(0.3)
PPh_3	$Rh(CO)(Cl)(PPh_3)_2$	1978	51.7(0.3)
$P(p\text{-}CH_3C_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}CH_3C_6H_4]_3)_2$	1975	56.1(0.2)
$P(p\text{-}CH_3OC_6H_5)_3$	$Rh(CO)(Cl)(P[p\text{-}CH_3OC_6H_4]_3)_2$	1973	58.7(0.3)
PPh_2Me	$Rh(CO)(Cl)(PPh_2Me)_2$	1974	61.7(0.3)
$P(OMe)_3$	$Rh(CO)(Cl)(P[OMe_3)_2$	2006	63.7(0.2)
$PPhMe_2$	$Rh(CO)(Cl)(PPhMe_2)_2$	1968	71.4(0.3)
PEt_3	$Rh(CO)(Cl)(PEt_3)_2$	1956	77.2(0.3)

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

quently 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 infrared spectroscopy, and the reactions were found to be rapid, clean, and quantitative under the experimental calorimetric (temperature and concentration) conditions necessary for accurate and meaningful calorimetric results. These conditions were satisfied for all organorhodium reactions investigated.

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 CD_2Cl_2 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 ^{31}P 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.

Solution Calorimetry. Calorimetric Measurement of Reaction between $[Rh(CO)_2Cl]_2$ (1) and $P(NC_4H_4)_3$. 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 25 mg sample of $[Rh(CO)_2Cl]_2$ was accurately weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A 4 mL volume of a stock solution of $P(NC_4H_4)_3$ [0.295 g of $P(NC_4H_4)_3$ in 20 mL of CH_2Cl_2] 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 organorhodium 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 and an infrared spectrum was immediately recorded. Conversion to $Rh(CO)(Cl)([P(NC_4H_4]_3)_2$ was found to be quantitative under these reaction conditions. Control reactions with Hg and no phosphine show no reaction. The enthalpy of reaction, −25.8 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations. The final enthalpy value listed in Table 1 (−34.4 ± 0.2 kcal/mol) represents the enthalpy of ligand substitution with all species in solution. The enthalpy of solution of **1** (8.6 ± 0.2 kcal/mol) has therefore been subtracted from the −25.8 kcal/mol value. This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study.

Enthalpy of Solution of $[Rh(CO)_2Cl]_2$ (1). In order to consider all species in solution, the enthalpy of solution of $[Rh(CO)_2Cl]_2$ (**1**) 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 enthalpy of solution, 8.6 ± 0.2 kcal/mol, represents the average of five individual determinations.

Results and Discussion

The use of $[RhCl(CO)_2]_2$ (**1**) as a versatile synthetic precursor has been reported.[3] Direct entry into the thermochemistry of $RhCl(CO)(PR_3)_2$ complexes is made possible by the rapid and quantitative reaction of $[RhCl(CO)_2]_2$ with stoichiometric amounts of phosphine ligands.[3]

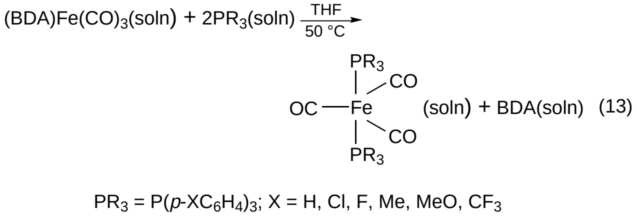
$$[RhCl(CO)_2]_2 + 4ER_3 \rightarrow 2RhCl(CO)(ER_3)_2 + 2CO \qquad (11)$$

$$ER_3 = \text{phosphine, phosphite, arsine}$$

This type of phosphine-binding reaction appears general and was found to be rapid and quantitative for all ligands calorimetrically investigated at 30.0 °C in methylene chloride. A compilation of phosphine ligands with their respective enthalpies of reaction, in solution, is presented in Table 1. These enthalpy values are reported on the basis of 1 mole of the rhodium dimer **1**. The strength of the dimeric form has been estimated by Drago (see eq 4), and this value could be added to the reported enthalpy values of Table 1, the sum divided by two to yield a relative stability scale (relative to the Rh−CO BDE). The correction for the bridge scission was not applied since this has no effect on the relative stability scale. The enthalpy data represents the sum of several bond disruption enthalpy (BDE) terms (Rh−Cl, Rh−CO, and Rh−P).

The donor properties of tertiary phosphine ligands can be modulated by electronic and steric parameter variation.[4] This is usually achieved by selective variation of the substituents bound to the phosphorus atom. The binding affinities of specific phosphine ligands are commonly explained in terms of electronic and /or steric effects, yet these two factors are not easily separated. A common approach in physical inorganic/organometallic chemistry is to examine such effects while maintaining one of the two factors constant. The most common approach used has been to examine a series of isosteric phosphines.[23]

$$CpRu(COD)Cl(soln) + 2PR_3(soln) \xrightarrow[30\ °C]{THF} CpRu(PR_3)_2Cl(soln) + COD(soln) \qquad (12)$$


(13)

$$(BDA)Fe(CO)_3(soln) + 2PR_3(soln) \xrightarrow[50\ °C]{THF} Fe(CO)_3(PR_3)_2(soln) + BDA(soln) \qquad (13)$$

$PR_3 = P(p\text{-}XC_6H_4)_3$; X = H, Cl, F, Me, MeO, CF_3

This can be achieved by specific substitution at the para

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(23) A specific example for the two ruthenium systems can be found in ref 13i. Other examples can be found in refs 1 and 4a.

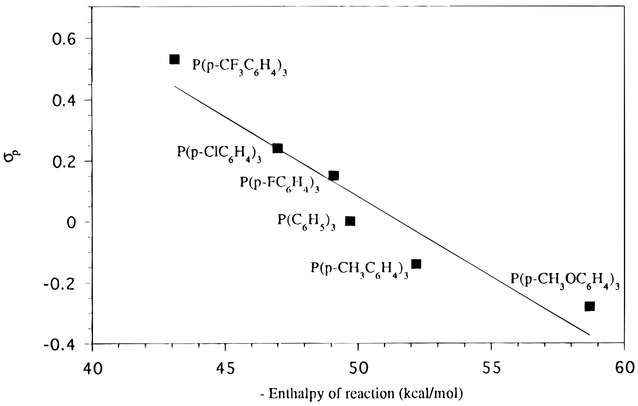
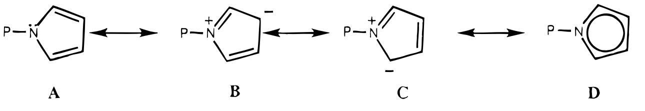


Figure 1. Hammett σ_p parameter vs enthalpies of reaction (kcal/mol) for the RhCl(CO)(PR$_3$)$_2$ system. Slope = −0.05; R = 0.95.

position of aryl grouping on a phosphorus center. We have recently reported on the thermochemical effects of such variations in both ruthenium and iron systems.[13i,14c]

In the present rhodium system, a linear relationship is present between the enthalpy of reaction and corresponding Hammett σ_p parameters, spanning some 15 kcal/mol. This is indicative of the important role played by phosphine electronic effects. A similar thermochemical relationship was found to exist in the *trans*-(PR$_3$)$_2$-Fe(CO)$_3$ system, where phosphine electronic effects were also determined to play a major contributing role to the enthalpy of reaction.[14c] The isosteric series can be expanded to include new ligands recently synthesized. Moloy and Petersen have reported on the synthesis and binding to rhodium systems of a novel class of *N*-pyrrolyl-substituted tertiary phosphine ligands which are isosteric with triphenylphosphine (and para-substituted triphenylphosphine ligands), with cone angle values of 145° (eq 4).[16] The *N*-pyrrolyl substituent was further shown to act as a potent electron withdrawing group, rendering the phosphine a poor σ donor and a good π acceptor. Pertinent resonance structures for the *N*-pyrrolyl phosphines can be drawn as follows:



Aromatic delocalization of the nitrogen lone pair into the pyrrole ring, as depicted in structures B and C, has the effect of placing a partial positive charge on the nitrogen. This would be expected to reduce the basicity of the adjacent phosphorus atom. Structure D suggests that *N*-pyrrolyl-substituted phosphines will be poorer donors than phenylphosphines since the more electronegative nitrogen replaces carbon. Moloy[16] has shown these ligands to undergo quantitative binding to the RhCl(CO) fragment:

$$[RhCl(CO)_2]_2 + 4PR_3 \rightarrow 2RhCl(CO)(PR_3)_2 + 2CO \qquad (14)$$

$$PR_3 = P(NC_4H_4)_3,\ P(NC_4H_4)_2Ph,\ P(NC_4H_4)Ph_2,\ P(NC_4H_8)_3$$

The pyrrolyl moiety, known for its π-involvement, should greatly affect the binding ability of the phosphine. This has been qualitatively demonstrated by infrared spectroscopy in the rhodium system. The thermochemical information supports quantitatively this poorer donor trend on increasing the number of pyrrolyl substituent on phosphorus. In addition, it was found that the following equilibrium lies far to the right, but was not analyzed quantitatively:

$$RhCl(CO)(P(NC_4H_4)_3)_2 + 2PPh_3 \rightleftharpoons RhCl(CO)(PPh_3)_2 + 2P(NC_4H_4)_3 \qquad (15)$$

We can estimate the enthalpy for this process from differences in enthalpies of reaction to be −8.7 kcal/mol.

The electronic parameter is observed to play the major role in dictating the magnitude of the enthalpy of reaction. Simple one-parameter relationships can be established with either the carbonyl stretching frequency (ν_{CO}) or Tolman's electronic parameter[4a] (χ). Both relationships illustrate a one-parameter relationship exhibiting a very good correlation. In Figure 2, it is interesting to note a magnitude effect on the infrared stretching frequency when comparing two L substituents in the RhCl(CO)L$_2$ system with one L in the Ni-(CO)$_3$L; the quantitative effect in the Rh system is twice that found in the Ni system. This type of relationship has also been observed in the *trans*-(PR$_3$)$_2$Fe(CO)$_3$

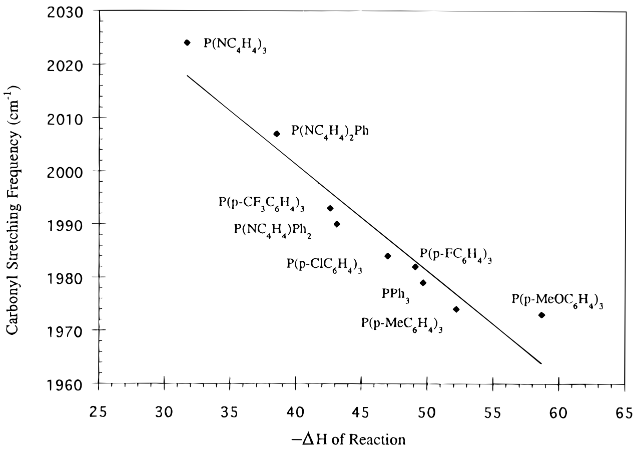


Figure 2. Carbonyl stretching frequency (cm^{-1}) vs enthalpies of reaction (kcal/mol) for the RhCl(CO)(PR$_3$)$_2$ system . Slope = −2.00; *R* = 0.96.

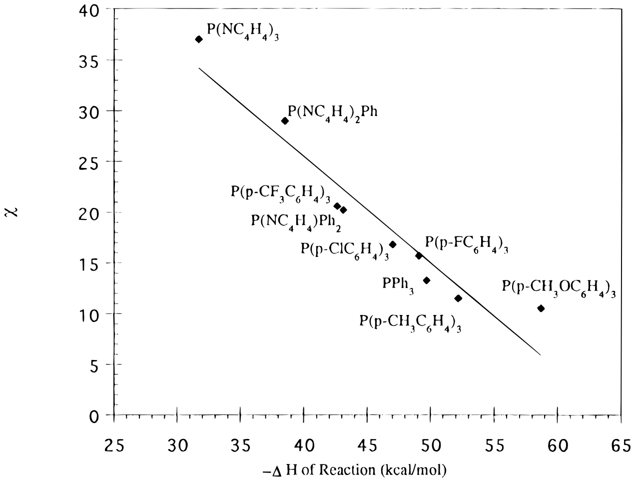


Figure 3. Electronic parameter (χ) vs enthalpies of reaction (kcal/mol) for the RhCl(CO)(PR$_3$)$_2$ system. Slope = −1.05; *R* = 0.96.

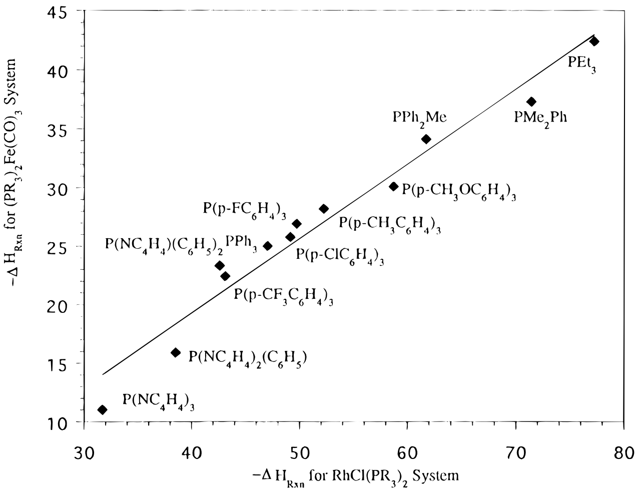


Figure 4. Enthalpies of reaction (kcal/mol) for the $RhCl(CO)(PR_3)$ system vs enthalpies of reaction (kcal/mol) for the $Fe(CO)_3(PR_3)_2$ system. Slope = 0.64; $R = 0.98$.

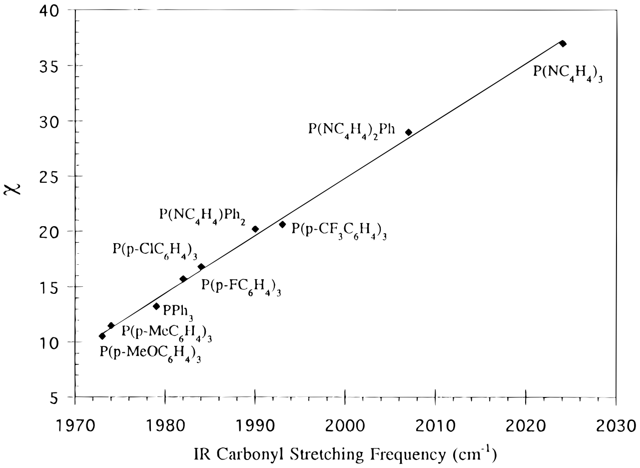


Figure 5. Carbonyl stretching frequency in the $RhCl(CO)(PR_3)$ system vs phosphine electronic parameter (χ). Slope = 0.52; $R = 1.00$.

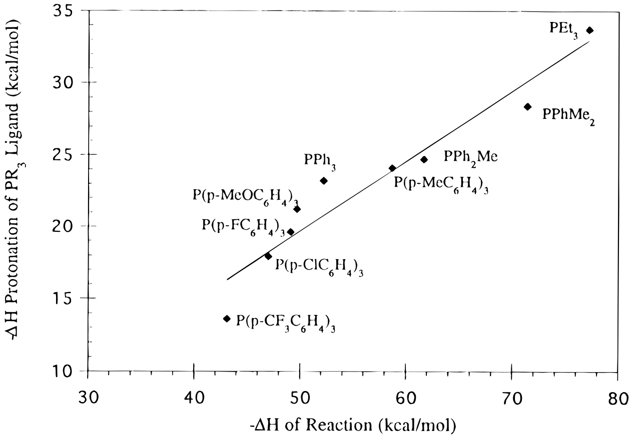


Figure 6. Enthalpies of reaction (kcal/mol) for the $RhCl(CO)(PR_3)$ system vs enthalpies of protonation (kcal/mol) of phosphine ligands. Slope = 0.49; $R = 0.96$.

system. In fact, a number of important similarities exist between the two systems. A relationship can be established between the two that shows that, when similar ligand electronic effects are at play, the relative stability scale established is fairly similar.

It must be pointed out that the carbonyl stretching frequency used in the above-mentioned relationships is not the one reported by Tolman for the Ni(CO)L system but the experimentally determined one for the rhodium system under investigation. To verify the correct usage of this carbonyl IR band in these relationships, these rhodium carbonyl data can be correlated to the χ values determined from the $Ni(CO)_3L$ system where ligand sterics are believed to play only a minor role. This relationship ($R = 1.00$) confirms the principal role of ligand electronic properties in the rhodium system.

Since it appears that phosphine electronic factors play a major role in determining the magnitude of the reaction enthalpy, a simple relationship linking the measured enthalpies of reaction in the rhodium system to the enthalpies of protonation of the free phosphine ligands[24] should provide a good correlation. The enthalpy of protonation is a direct measure of the donor ability of the phosphine ligand in the absence of any hindering/contributing steric factors.

Another subgrouping of interest is the $PPh_{3-x}Me_x$ series ($x = 0-3$). Here a regular increase in exothermicity is observed on going to an increasing number of methyl substituent, reflecting an increase in ligand basicity. The trend for the present rhodium system corresponds to an increase of ca. 2.5 kcal/mol (per Rh−P bond, if one wants to consider a per bond effect, keeping in mind again that the enthalpy data represents a change in a number of BDE terms) with each methyl substituent.[25]

Another interesting trend is the difference in enthalpy of reaction on going from triphenyl to trimethyl phosphite. The measured enthalpy difference between these two phosphorus-centered ligands is 5.3 kcal/mol (per Rh−P BDE). This is a relatively large enthalpy differences between these two phosphine but is in the same order of magnitude as in the $L_3Mo(CO)_3$ system investigated by Hoff[26] where the difference is 3.7 kcal/mol.

$$(C_6H_6)Mo(CO)_3 + 3P(OR)_3 \rightarrow (P(OR)_3)_3Mo(CO)_3 + C_6H_6 \quad (16)$$

$$R = \text{Me and Ph}$$

In the recently reported Cp′Ru(L)Cl (Cp′ = C_5H_5 and C_5Me_5) systems, this difference is 3.9 and 3.2 kcal/mol, respectively.[13b,f] In the nickel system investigated by Tolman and co-workers[27] this difference is 3 kcal/mol.

$$(COD)_2Ni + 4P(OR)_3 \rightarrow (P(OR)_3)_4Ni + COD \quad (17)$$

The molybdenum, ruthenium, and nickel systems exhibit a predominant phosphine steric factor contributing to the enthalpy of reaction. This steric factor would influence the M to P orbital overlap (by reducing the

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[24] Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51−60 and references cited therein.

[25] Attempts were made to investigate the enthalpy of reaction of the PMe_3 ligand with **1** in stoichiometric amounts. The results proved nonreproducible. The infrared analysis of the products showed that the reaction did not go to completion under these conditions or that other products were formed as judged by IR band positions.

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

[27] Tolman, C. A.; Reutter, D. W.; Seidel, W. C. *J. Organomet. Chem.* **1976**, *117*, C30−C33.

overlap in view of steric repulsion effects) and would be reflected by lower than expected enthalpies of reaction.

Thermochemical information was obtained for one arsine ligand, $AsEt_3$. The measured enthalpy of reaction, $-49.2(0.3)$ kcal/mol, is some 27 kcal/mol less exothermic than its phosphine congener, PEt_3. This trend of more weakly binding arsine vs phosphine ligation is a reoccurring one found in our previous work.[13,14] The interesting point here is the slight variation in the position of the carbonyl stretching band (4 cm^{-1}) as a function of ligand donor capability. This can be compared to an enthalpy change of 28 kcal/mol on going from $P(NC_4H_4)_3$ to $P(p\text{-}CH_3OC_6H_4)_3$ with a corresponding infrared shift of 50 cm^{-1}. This question of differences in bonding between metals and As and Sb donor ligands and P-donor ligands is still poorly understood, and it is hoped that such thermochemical data will help clarify and quantify the effects at play in such systems.

Conclusion

The labile nature of the chloro-bridged dimer $[RhCl(CO)_2]_2$ (**1**) was used to gain access into the thermochemistry of ligand substitution for tertiary phosphine ligands. The enthalpy trend can be explained in terms of overwhelming electronic contribution to the enthalpy of reaction. A quantitative relationship is established between phosphine electronic characteristics and measured enthalpies of reaction. Further thermochemical investigations focusing on sterically demanding ligands in this system are presently underway.

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