Solution Thermochemical Study of Tertiary Phosphine Ligand Substitution Reactions in the Rh(acac)(CO)(PR_3) System

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The enthalpies of reaction of Rh(acac)$(CO)_2$ (**1**) with a series monodentate tertiary phosphine ligands, leading to the formation of Rh(acac)(CO)(PR_3) 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 12 kcal/mol. The relative stability scale established is as follows: PPh_2(*o*-Tol) < P(*p*-$CF_3C_6H_4)_3 \approx$ P(*p*-$ClC_6H_4)_3$ < P(*p*-$FC_6H_4)_3$ < P$(NC_4H_4)_3$ < P$(NC_4H_4)_2(C_6H_5)$ < P(*m*−$CH_3OC_6H_4)_3$ < P$(NC_4H_4)(C_6H_5)_2$ < P$(OPh)_3 \approx PPh_2$(*p*-Tol) ≈ P(*m*-Tol)$_3$ < P(*p*−$CH_3C_6H_4)_3$ < PPh_3 < P(*p*−$CH_3OC_6H_4)_3$ < PCy_3 < PPh_2Me < P^iPr_3 < $PPhMe_2$. The relative importance of the phosphine stereoelectronic ligand parameters are 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 such as hydroformylation.[2] Phosphine ligands have shown great utility in organometallic chemistry and catalysis as a way to fine tune metal reactivity and selectivity.[3,4] Despite the importance of rhodium−phosphine complexes, very little is known about the quantitative thermodynamic stability of these systems. Pioneering work by Blake and co-workers[5] represents a notable exception. These studies dealt with the enthalpic driving force behind oxidative addition to square planar rhodium(I) systems eq 1.

$$RhX(CO)(PPh_3)_2 + I_2 \xrightarrow[C_6H_6]{} RhX(I)_2(CO)(PPh_3)_2 \quad (1)$$

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

More recently, Goldman and co-workers determined the bond-dissociation enthalpy for Rh−N_2, Rh−$(H)_2$, Rh−olefin, and Rh−acetylene complexes, eq 2 and 3.[6] Furthermore the enthalpy behind the observed

$$^1/_2[RhL_2Cl]_2 + L' \rightarrow 2RhL_2ClL' \quad (2)$$

$$^1/_2[RhL_2Cl]_2 + H_2 \rightarrow 2RhL_2Cl(H)_2 \quad (3)$$

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

decarbonylation of aldehydes by a coordinatively unsaturated rhodium system was experimentally determined.[7]

$$^1/_2[RhL_2Cl]_2 + RC(O)H \rightarrow 2RhL_2Cl(CO) + RH \quad (4)$$

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

We have been involved in mapping out the thermochemical surface of organometallic 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.[8−10] We have been interested in clarifying the exact partitioning of the steric and electronic ligand energetic contributions present in tertiary phosphine-based systems by means of solution calorimetry.[11−14] We have achieved this in

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part for the classical $[RhCl(CO)_2]_2$ complex, eq 5.[13] The

$$[RhCl(CO)_2]_2 + 4ER_3 \rightarrow 2RhCl(CO)(ER_3)_2 + 2CO \quad (5)$$

ER_3 = phosphine, phosphite, arsine

$[RhCl(CO)_2]_2$ complex can be easily converted to Rh(acac)$(CO)_2$ (**1**), eq 6.[15] In the present paper, our

$$[RhCl(CO)_2]_2 + 2acacH \rightarrow 2Rh(acac)(CO)_2 + 2HCl \quad (6)$$

solution calorimetric work is extended to the related organorhodium−phosphine system Rh(acac)(CO)(PR_3) (acac = acetylacetonate; PR_3 = tertiary phosphine).

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 of 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, 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 the literature values. This calorimeter has been previously described,[20] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

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

^{1}H 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 and ^{1}H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under the experimental calorimetric conditions.

Solution Calorimetry. Calorimetric Measurement of Reaction between Rh(acac)$(CO)_2$ (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(acac)$(CO)_2$ was accurately weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of P$(NC_4H_4)_3$ (0.113 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(acac)(CO)[P$(NC_4H_4]_3$ was found to be quantitative under these reaction conditions. Control reactions with Hg and no phosphine showed no reaction. The enthalpy of reaction, 4.3 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations. The final enthalpy value listed in Table 1 (−3.6 ± 0.1 kcal/mol) represents the enthalpy of ligand substitution with all species in solution. This methodology represents a typical procedure involving all organorhodium reactions investigated in the present study.

Enthalpy of Solution of Rh(acac)$(CO)_2$ (1). In order to consider all species in solution, the enthalpy of solution of **1** had to be directly measured. This was performed by using a

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

$$Rh(CO)_2(acac)_{(soln)} + PR_3(soln) \xrightarrow[30\ °C]{CH_2Cl_2} Rh(CO)(acac)(PR_3)_{(soln)} + CO$$

L	complex	ν_{CO} (cm^{-1})	$-\Delta H_{(rxn)}$[a]
PPh_2(*o*-Tol)	Rh(CO)(acac)[PPh_2(*o*-Tol)]	1976	2.4(0.2)
P(*p*-$CF_3C_6H_5$)$_3$	Rh(CO)(acac)[P(*p*-$CF_3C_6H_5$)$_3$]	1986	3.2(0.1)
P(*p*-ClC_6H_5)$_3$	Rh(CO)(acac)[P(*p*-ClC_6H_5)$_3$]	1982	3.2(0.3)
P(*p*-FC_6H_5)$_3$	Rh(CO)(acac)[P(*p*-FC_6H_5)$_3$]	1980	3.5(0.1)
P(C_4H_4N)$_3$	Rh(CO)(acac)[P(NC_4H_4)$_3$]	2012	3.6(0.1)
P(C_4H_4N)$_2$(C_6H_5)	Rh(CO)(acac)[P(NC_4H_4)$_2$(C_6H_5)]	2003	3.8(0.3)
P(*m*-CH_3OPh)$_3$	Rh(CO)(acac)[P(*m*-CH_3OPh)$_3$]	1978	4.0(0.2)
P(C_4H_4N)(C_6H_5)$_2$	Rh(CO)(acac)[P(NC_4H_4)(C_6H_5)$_2$]	1990	4.1(0.3)
P(OPh)$_3$	Rh(CO)(acac)[P(OPh)$_3$]	2008	4.2(0.3)
PPh_2(*p*-Tol)	Rh(CO)(acac)[PPh_2(*p*-Tol)]	1977	4.2(0.1)
P(*m*-Tol)$_3$	Rh(CO)(acac)[P(*m*-Tol)$_3$]	1976	4.2(0.3)
P(*p*-$CH_3C_6H_5$)$_3$	Rh(CO)(acac)[P(*p*-$CH_3C_6H_5$)$_3$]	1974	4.7(0.1)
PPh_3	Rh(CO)(acac)[PPh_3]	1978	4.8(0.3)
P(*p*-$CH_3OC_6H_5$)$_3$	Rh(CO)(acac)[P(*p*-$CH_3OC_6H_5$)$_3$]	1973	6.2(0.2)
PCy_3	Rh(CO)(acac)[PCy_3]	1959	9.6(0.1)
PPh_2Me	Rh(CO)(acac)[PPh_2Me]	1974	10.8(0.2)
P^iPr_3	Rh(CO)(acac)[P^iPr_3]	1960	11.2(0.1)
$PPhMe_2$	Rh(CO)(acac)[$PPhMe_2$]	1970	14.2(0.1)

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

similar procedure as the one described above, with the exception that no ligand was added to the reaction cell. The enthalpy of solution, 7.9 ± 0.1 kcal/mol, represents the average of five individual determinations.

Synthesis. The compound Rh(acac)(CO)$_2$ (**1**) was synthesized according to literature procedures.[21] Other organorhodium complexes, Rh(acac)(CO)[P(*p*-ClC_6H_5)$_3$], Rh(acac)(CO)-[P(*p*-$CH_3C_6H_5$)$_3$], Rh(acac)(CO)[P(OPh)$_3$], Rh(acac)(CO)(PPh_3), Rh(acac)(CO)([P(*p*-$CH_3OC_6H_5$)$_3$], Rh(acac)(CO)(PPh_2Me), and Rh(acac)(CO)(PCy_3) have been previously reported.[22,23] In all other cases, an analogous synthetic procedure was used leading to the isolation of following organorhodium complexes.

Rh(acac)(CO)(P(NC_4H_4)$_3$). In the glovebox, 100 mg (0.39 mmol) of Rh(CO)$_2$(acac) and 20 mL of CH_2Cl_2 were charged into a 50 mL flask. To this solution, 88.8 mg (0.39 mmol) of P(NC_4H_4)$_3$ was added. The reaction mixture was stirred for 20 min, during which time liberation of carbon monoxide was observed. The solution was filtered and evacuated to dryness. The resulting red-brown product was washed with hexane and dried thoroughly in vacuum. Yield: 155 mg (86%). ^{1}H NMR (CD_2Cl_2, δ, mult) 1.86 (s, 3H $-CH_3$), 2.12 (s, 3H $-CH_3$), 5.60 (s, 1H, $-$CH), 6.38 (s, 6H, pyrrole), 6.96 (s, 6H, pyrrole). IR (ν_{CO}, CH_2Cl_2): 2012 cm^{-1}. Anal. Calcd for $C_{18}H_{19}O_3N_3PRh$: C, 47.06; H, 4.17; N, 9.15. Found: C, 47.00; H, 3.88; N, 8.93.

Rh(acac)(CO)(P(NC_4H_4)$_2$Ph). Yield: 155 mg (85%). ^{1}H NMR (CD_2Cl_2, δ, mult): 1.75 (s, 3H, $-CH_3$; 2.10 (s, 3H, $-CH_3$; 5.55 (s, 1H, $-$CH), 6.37 (s, 4H, pyrrole) 7.12 (s, 4H pyrrole), 7.14−7.55 (m, 5H $-$Ph). IR (ν_{CO}, CH_2Cl_2): 2002 cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_3N_2PRh$; C, 51.06; H, 4.29; N, 5.96. Found: C, 50.88; H, 4.29; N, 5.48.

Rh(acac)(CO)(P(NC_4H_4)Ph$_2$). Yield: 150 mg (80%). ^{1}H NMR (CD_2Cl_2, δ, mult): 1.68 (s, 3H, $-CH_3$), 2.09 (s, 3H, $-CH_3$) 5.50 (s, 1H, $-$CH), 6.35 (s, 2H, pyrrole) 7.15 (s, 2H pyrrole), 7.43−7.51 (m, 10H $-$Ph). IR (ν_{CO}, CH_2Cl_2): 1990 cm^{-1}. Anal. Calcd for $C_{22}H_{21}O_3NPRh$: C, 54.88; H, 4.40; N, 2.91. Found: C, 54.55; H, 4.04; N, 2.73.

Rh(acac)(CO)(P(*p*-CF_3Ph)$_3$). Yield: 227 mg (85%). ^{1}H NMR ($CDCl_3$, δ, mult): 1.61 (s, 3H, $-CH_3$), 2.13 (s, 3H, $-CH_3$), 5.49 (s, 1H, $-$CH), 7.69−7.82 (m, 12H $-$Ph). IR (ν_{CO}, CH_2Cl_2): 1987 cm^{-1}. Anal. Calcd for $C_{27}H_{19}O_3F_9PRh$: C, 46.55; H, 2.75. Found: C, 45.95; H, 2.49.

Rh(acac)(CO)(P(*p*-FPh)$_3$). Yield: 169 mg (80%). ^{1}H NMR ($CDCl_3$, δ, mult): 1.62 (s, 3H, $-CH_3$), 2.08 (s, 3H, $-CH_3$), 5.44 (s, 1H, $-$CH), 7.06−7.64, (m, 12H $-$Ph). IR (ν_{CO}, CH_2Cl_2): 1981 cm^{-1}. Anal. Calcd for $C_{24}H_{19}O_3F_3PRh$: C, 52.75; H, 3.51. Found: C, 52.34; H, 3.38.

Rh(acac)(CO)(PPh_2Me). Yield: 110 mg (77%). ^{1}H NMR ($CDCl_3$, δ, mult): 1.76 (s, 3H, $-CH_3$), 1.80 (s, 3H, $-CH_3$), 1.86 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$), 4.45 (s, 1H, $-$CH), 7.40−7.82, (m, 5H $-$Ph). ^{31}P NMR (THF-d_8, δ, J_{P-H}) : 21.9 (d, 167. IR (ν_{CO}, CH_2Cl_2): 1971 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_3PRh$: C, 45.67; H, 4.93. Found: C, 45.57; H, 4.87.

Rh(acac)(CO)(PPh_2(*o*-Tol)). Yield: 158 mg (86%). ^{1}H NMR ($CDCl_3$, δ, mult): 1.61 (s, 3H, $-CH_3$) 2.07 (s, 3H, $-CH_3$) 5.47 (s, 1H, $-$CH) 2.46 (s, 3H, $-CH_3$), 6.85−7.80, (m, 10H, $-$Ph). IR (ν_{CO}, CH_2Cl_2): 1976 cm^{-1}. Anal. Calcd for $C_{25}H_{24}O_3PRh$: C, 59.30; H, 4.78. Found: C, 59.14; H, 4.49.

Rh(acac)(CO)(PPh_2(*p*-Tol)). Yield: 179 mg (86%). ^{1}H NMR (CD_2Cl_2, δ, mult): 1.63 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$), 5.45 (s, 1H, $-$CH), 2.38 (s, 3H, $-$CH), 2.38, s, 3H, $-CH_3$), 7.21−7.66, (m, 10H, $-$Ph). IR (ν_{CO}, CH_2Cl_2): 1977 cm^{-1}. Anal. Calcd for $C_{25}H_{24}O_3PRh$: C, 59.30; H, 4.78. Found: C, 58.84; H, 4.69.

Rh(acac)(CO)(P(*m*-Tol)$_3$). Yield: 185 mg (86%). ^{1}H NMR (CD_2Cl_2, δ, mult): 1.65 (s, 3H, $-CH_3$), 2.07 (s, 3H, $-CH_3$), 5.46 (s, 1H, $-$CH), 2.34 (s, 3H, $-CH_3$), 7.27−7.56 (m, 12H, $-$Ph). IR (ν_{CO}, CH_2Cl_2): 1976 cm^{-1}. Anal. Calcd for $C_{27}H_{28}O_3PRh$: C, 60.68; H, 5.28. Found: C,60.60; H, 5.28.

Rh(acac)(CO)(P(*m*−CH_3OPh)$_3$). Yield: 155 mg (86%). ^{1}H NMR (CD_2Cl_2, δ, mult): 1.65 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$), 5.46 (s, 1H, $-$CH, 3.73 (s, 3H, $-OCH_3$), 6.96−7.32 (m, 12H, $-$Ph). IR (ν_{CO}, CH_2Cl_2): 1978 cm^{-1}. Anal. Calcd for $C_{27}H_{28}O_6PRh$: C, 55.68; H, 4.85. Found: C, 55.67; H, 4.80.

Rh(acac)(CO)(P^{i}Pr$_3$). Yield: 130 mg (86%). ^{1}H NMR (CD_2Cl_2, δ, mult): 1.85 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 5.46 (s, 1H, $-$CH), 1.31 (s, 6H, $-CH_3$), 2.37 (s, 1H, $-$CH). IR (ν_{CO}, CH_2Cl_2): 1961 cm^{-1}. Anal. Calcd for $C_{15}H_{28}O_3PRh$: C, 46.16; H, 7.23. Found: C, 46.62; H, 7.02.

Results and Discussion

The use of Rh(acac)(CO)$_2$(**1**) as a versatile synthetic precursor and precatalyst for hydroformylation has been reported.[3] Direct entry into the thermochemistry of Rh(acac)(CO)(PR$_3$) complexes is made possible by the rapid and quantitative reaction of **1** with stoichiometric amounts of phosphine and phosphite ligands, eq 7.[3] This

$$Rh(acac)(CO)_2 + PR_3 \rightarrow Rh(acac)(CO)(PR_3) + CO \quad (7)$$

PR_3 = phosphine and phosphite

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 the phosphine ligands with their respective enthalpies of reaction, in solution, is presented in Table 1.

The donor properties of tertiary phosphine ligands can be modulated by varying the electronic and steric parameters.[4] This is usually achieved by variation of the substituents bound to the phosphorus atom. The binding affinities of specific phosphine ligands are

(21) Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156−3160

(22) (a) Trzeciak, A. M.; Ziolkowski. *J. Organomet. Chem* **1992**, *429*, 239−244 (for P(OPh)$_3$, PPh_3, P(*p*-$MePh)_3$, and PPh_2Me complexes). (b) Basson, S. S.; Leipoldt, J. G.; Roodt, A.; Venter, J. A.; Van der walt, T. J. *Inorg. Chim. Acta* **1986**, *119*, 35−38. (for P(*p*-$ClPh)_3$ and P(*p*-MeOPh)$_3$ complexes). (c) Freeman, M. A.; Young, D. A. *Inorg. Chem.* **1986**, *25*, 1556−1560 (for PCy_3 complex).

(23) (a) In the course of the redaction of this manuscript, a report of Rh(acac)(CO) (P(NC_4H_4)$_x$Ph$_{3-x}$ (x = 1−3) complexes appeared.[23b] The synthetic methodology is slightly different, and the spectroscopy was reported in different solvents. We, therefore, report our analytical data here. (b) Trzeciak, A. M.; Glowiak, T.; Grzybek, R.; Ziolkowski, J. J. *J. Chem. Soc., Dalton Trans.* **1997**, 1831−1837.

commonly explained in terms of stereoelectronic effects, yet these two factors are not easily separated. We have been involved in determining the exact partitioning/relative importance of such effects in a number of organometallic systems. In the present system, single variable correlations between the steric or electronic parameters and the enthalpies of reaction does not lead to linear fits. Correlation coefficients (R) of 0.11 and 0.56 are obtained for the steric and electronic vs enthalpy data relationships, respectively. A common approach in physical inorganic/organometallic chemistry is to examine such effects while maintaining one of the two parameters constant. The most common approach makes use of a series of isosteric phosphines.[24] This can be achieved by investigating the effects of specific substitution at the para position of the aryl grouping bound to the phosphorus center. We have recently reported on the thermochemical effects of such variations in ruthenium,[11i] iron,[12c] and rhodium[13a] systems (eqs 8−10).

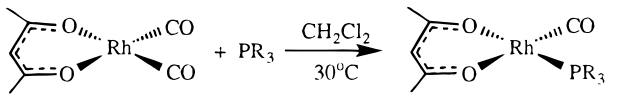
$$CpRu(COD)Cl_{(soln)} + 2\,PR_{3(soln)} \xrightarrow[30^oC]{THF} CpRu(PR_3)_2Cl_{(soln)} + COD_{(soln)} \quad (8)$$

$$(BDA)Fe(CO)_{3(soln)} + 2\,PR_{3(soln)} \xrightarrow[50^oC]{THF} OC-Fe(PR_3)_2(CO)_{(soln)} + BDA_{(soln)} \quad (9)$$

$$[RhCl(CO)_2]_2 + 4\,PR_3 \xrightarrow[30^oC]{CH_2Cl_2} 2\,R_3P(OC)Rh(Cl)PR_3 + 2\,CO \quad (10)$$

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

The overall importance of the electronic effects will be dictated by the final structural arrangements of the ligands around the metal center. In the ruthenium case mentioned above, a cis arrangement of the ligands leads to the observation of the overwhelming importance of steric effects. The final geometry is pseudo-octahedral, and the importance of the steric effects is compounded by the crowding present in having six occupied coordination sites around the Ru center. In the iron case, the final geometry involves a trigonal bipyramidal arrangement of the ligands, where the two phosphine ligands occupy mutually trans (trigonal bipyramidal apical) positions. This leads to a relief of the steric crowding around the metal center and electronic effects are observed to dictate the magnitude of the measured reaction enthalpies. The rhodium system presented in eq 10 follows a similar trend since the two incoming phosphines adopt a mutually trans orientation in the final square planar complex. On the basis of these simple geometric and structural arguments, the ligand displacement reaction enthalpy data for the present Rh(acac)(CO)(PR_3) system might be expected to be influenced primarily by electronic effects, eq 11. In order to



(11)

(24) A specific example for the two ruthenium systems can be found in ref 11i. Other examples can be found in refs 1 and 4a.

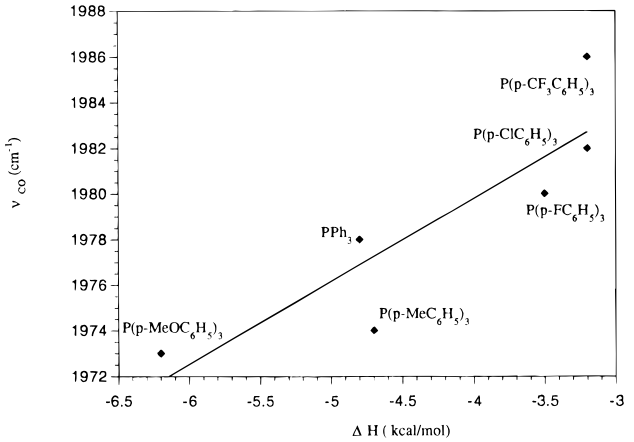


Figure 1. Carbonyl stretching frequency (cm^{-1}) vs enthalpies of reaction (kcal/mol) for the P(p-$XC_6H_4)_3$ series in the Rh(acac)(CO)(PR_3) system. Slope = 3.6; R = 0.88.

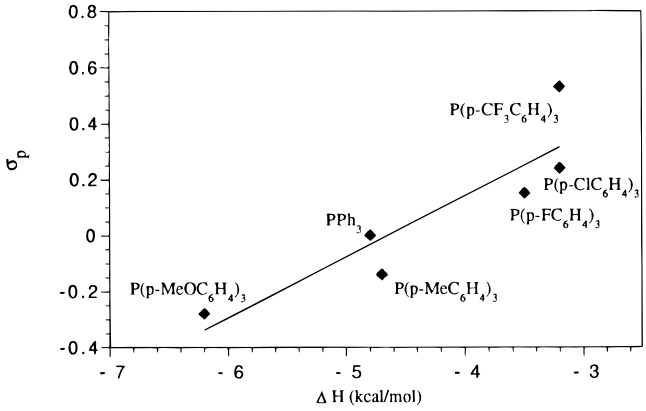


Figure 2. Hammett σ_p parameter vs enthalpies of reaction (kcal/mol) for the P(p-$XC_6H_4)_3$ series in the Rh(acac)(CO)-(PR_3) system. Slope = 0.22; R = 0.90.

verify this hypothesis, two series of phosphine ligands possessing isosteric properties were examined.

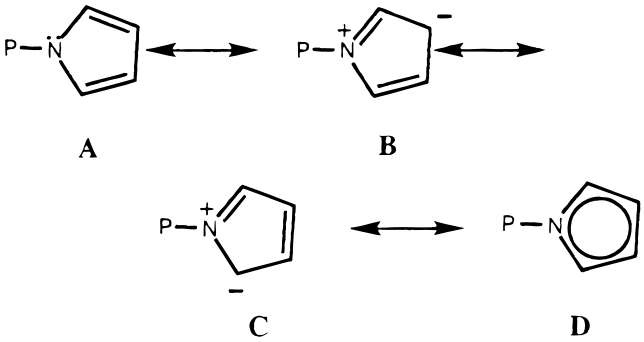
P(p-$XC_6H_4)_3$ Series (X = H, Cl, F, Me, MeO, CF_3). Within this series, the Tolman cone angle[4a] (steric parameter) is kept constant at 145°. The electron-donating property of the phosphine is modulated by substituents at the aryl para position. A single-component relationship can be established between the enthalpy data and the carbonyl stretching frequency, Figure 1. This last parameter reflects the amount of electron density donated by the incoming phosphine ligand which is then back-donated from the Rh metal center into the CO π^* orbital. This relationship clearly shows a proportional dependence of the enthalpy data on the electronic parameter. Another way to quantify the donicity of the phosphine is to examine the electronic contribution attributed to the phenyl para substituent. Therefore, a Hammett-type relationship[25] (Figure 2) can be constructed which shows similar effects as the electronic relationship shown in Figure 1.

Both relationships are linear but span only a narrow range of enthalpy values and therefore, cannot unambiguously reflect a predominant electronic effect in the present system.

The $P(C_6H_5)_{3-x}(NC_4H_4)_x$ Series (x = 1−3). Moloy and Petersen have reported on the synthesis and

(25) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1992; pp 278−286.

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°.[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*-pyrrolylphosphines 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*-pyrrolylphosphines 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, eq 12. The pyrrolyl moiety, known for its π

$$[RhCl(CO)_2]_2 + 4PR_3 \rightarrow 2RhCl(CO)(PR_3)_2 + 2CO \quad (12)$$

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

involvement, should also greatly affect the binding ability of the phosphine in the present system. Ziolkowski and co-workers have recently reported on the reactivity of **1** with these pyrrolyl-substituted phosphine ligands, eq 13.[23a] They have commented on the π

$$Rh(acac)(CO)_2 + PR_3 \rightarrow Rh(acac)(CO)(PR_3) + CO \quad (13)$$

$$PR_3 = P(NC_4H_4)_3;\ P(NC_4H_4)_2Ph;\ P(NC_4H_4)Ph_2$$

involvement of these phosphines in this rhodium system as monitored by infrared spectroscopy. The thermochemical information quantitatively supports this poorer donor trend on increasing the number of pyrrolyl substituents on phosphorus. Furthermore, a correlation between the enthalpy of reaction and the carbonyl stretching frequency of the product affords a linear relationship with a good fit (Figure 3).

The extent of π involvement in the bonding present in this system is surely diminished due to the competing influence of CO as an ancillary ligand. If both ligands compete for back-donation from the metal, CO will surely exert a more important effect. This extent of π involvement in bonding has recently been illustrated in another rhodium system and will be reported shortly.[26] The overall effect of this series of pyrrolyl-substituted phosphine ligands, in the present system, is principally guided by its poor σ-donating capabilities. It is for this reason that although they possess similar cone angles as the para-substituted triphenylphosphine, they should be considered a different class of ligands in the present system.

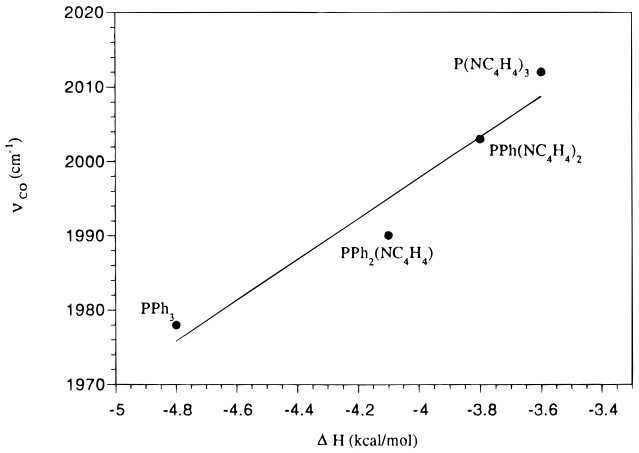


Figure 3. Carbonyl stretching frequency (cm^{-1}) vs enthalpies of reaction (kcal/mol) for the $P(C_6H_5)_{3-x}(NC_4H_4)_x$ ($x = 0-3$) series in the Rh(acac)(CO)(PR_3) system. Slope = 27.5; $R = 0.97$.

Other General Trends. The phosphine electronic parameter appears to have a small contribution compared to previously examined systems. No single factor dictates the magnitude of the enthalpy of reaction across the present series of phosphine ligands. Phosphine steric factors do play a role since the sterically very demanding pair of phosphine ligands PCy_3 ($\theta = 170°$) and P^iPr_3 ($\theta = 160°$) display enthalpy values opposite to the relative order of donation (i.e., the P^iPr_3 ligand binds more strongly, although it is known to be a poorer donor than PCy_3). Sterics have to be at the origin of this difference. Another subseries of interest are the PPh_xMe_{3-x} ligands. Here, a general increase in the enthalpy of reaction is measured with the increase in phosphine basicity associated with a larger degree of Me substituents. This enthalpy increase is somewhat linear going from $PPh_3 < PPh_2Me < PPhMe_2$.[27] A word of caution in drawing any further conclusions from the experimental enthalpies of reaction measured in this study: 14 phosphine ligands display an enthalpy of reaction spanning some 4 kcal/mol. Small steric factors, however subtle, may in fact contribute to the enthalpy of reaction and significantly affect the relative stability of the organorhodium complexes discussed in view of this small range of enthalpies of reaction.[28]

(26) Huang, J.; Haar, C. M.; Marshall, W. J.; Moloy, K. G.; Nolan, S. P. Submitted for publication.

(27) Attempts were made to investigate the enthalpy of reaction of the PMe_3 and PEt_3 ligands with **1** in stoichiometric amounts. The results proved to be 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.

(28) A QALE analysis[10] performed by one of the reviewers suggests that within the series of phosphine ligands investigated the percent contribution to the enthalpy of reaction is as follows: 21% electronic, 47% steric, and 32% from an aryl effect. We thank the reviewer for this contribution.

Conclusion

The labile nature of the first Rh−CO bond in Rh(acac)$(CO)_2$ (**1**) was used to gain access into the thermochemistry of ligand substitution of tertiary phosphine ligands. The enthalpy trend can be explained in terms of both steric and electronic contributions to the enthalpy of reaction, phosphine sterics playing a more important role than electronics. Quantitative relationships are established between the phosphine electronic parameters and measured enthalpies of reaction within two subsets of phosphine ligands, and both display a good correlation to this single electronic parameter. Yet, the enthalpy values cover only a short range. The overall factors dictating the magnitude of the reaction enthalpies are a combination of steric and electronic effects. Further thermochemical investigations focusing on related systems are presently underway.

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