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An NMR and Thermodynamic Investigation of the Reaction of Square-Planar Rhodium(I) Compounds with H_2

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Abstract: The reaction of square-planar rhodium(I) complexes of the general formula $(P(4\text{-tolyl})_3)_2RhClB$ with H_2 has been investigated where B is $P(4\text{-tolyl})_3$, pyridine, or tetrahydrothiophene. NMR studies confirm that in all cases the product geometry has the two hydrogens cis to each other and the two phosphines trans to each other. The rate of dissociation of pyridine from the hydride is reported and compared with that of phosphine dissociation. Thermodynamic data for activation of H_2 by the phosphine and tetrahydrothiophene adducts are reported. From this information metal-hydrogen bond strengths can be calculated and the influence of B on this quantity determined.

Activation of molecular hydrogen by metals is an important, fundamental process with relevance to catalytic hydrogenation[1] and storage of H_2 by "dissolution" in metals.[2] It is essential to know metal-hydrogen bond dissociation energies and the influence of the ligands coordinated to a metal on these energies in order to affect desired organometallic chemical reactions; for example, a weak metal-hydrogen bond should facilitate the transformation shown in eq 1. There is a paucity of thermodynamic data relating

$$L + H\text{-}M(CO)_n \rightarrow (HCO)ML(CO)_{n-1} \qquad (1)$$

to the simple fundamental steps involved in organometallic reactions and catalytic processes. We report here the first determination of the effect of ligand variation on the solution enthalpies for the conversion of H_2 to a rhodium hydride. The influence of ligand variation on the metal-hydrogen bond strength can be calculated from the measured data.

The chemical system selected is an extension of earlier work[3,4] in which the acids $[(CO)_2RhCl]_2$ and $[(COD)RhCl]_2$ (COD = cyclooctadiene) were incorporated into the *E* and *C* equation.[5]

$$-\Delta H = E_AE_B + C_AC_B \qquad (2)$$

The first step in the present study involves the characterization of $[(P(4\text{-tolyl})_3)_2RhCl]_2$ as an acid. Determination of the enthalpy of cleaving the dimer and the enthalpy of coordinating the donor, B,

$$[(P(4\text{-tolyl})_3)_2RhCl]_2 + 2B \rightarrow (P(4\text{-tolyl})_3)_2RhCl\cdot B \qquad (3)$$

is the first step to understanding the influence of donor strength on the activation of H_2. Determination of the enthalpies for these processes is followed by a determination of the enthalpy for reaction 4.

$$(P(4\text{-tolyl})_3)_2RhCl\cdot B + H_2 \rightarrow (P(4\text{-tolyl})_3)_2Rh(H)_2Cl\cdot B \qquad (4)$$

Results and Discussion

Acidity of $[(P(4\text{-tolyl})_3)_2RhCl]_2$. The reaction of $[(P(4\text{-tolyl})_3)_2RhCl]_2$ with donors (B) occurs as shown in eq 3.

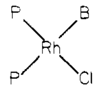
The resulting square-planar adduct could exist as either a cis or trans product, and an interpretation of the thermodynamic data requires comparison of similar geometries. NMR spectroscopy provides conclusive results regarding the solution geometries.

Table I. $\{H^1\}^{31}P$ NMR Chemical Shifts and Coupling Constants for Rhodium(I) and Rhodium(III) Complexes

^{31}P NMR compd	δ multiplet descrptn[a,c]	J(Rh-P), Hz	J(P-P), Hz	J(P-H), Hz
$RhCl(P(4\text{-tolyl})_3)_3$	−46.2 dt	189	38	
	−30.2 dd	143		
$RhCl(P(4\text{-tolyl})_3)_2Py$	−52.0 dd	198	47.3	
	−46.1 dd	167		
$RhCl(P(4\text{-tolyl})_3)_2THTP$	−38.4 dd	116		
	−35.5 dd	116		
$RhCl(P(4\text{-tolyl})_3)_2MeIm$	−53.0			
	−47.8			
$H_2RhCl(P(4\text{-tolyl})_3)_3$	−40.3 dd	114	18	
	−20.7 dt	90		
$H_2RhCl(P(4\text{-tolyl})_3)_2Py$	−41.1 d	118		
	−41.0[b] dt	118[b]		14.4[b]
$H_2RhCl(P(4\text{-tolyl})_3)_2\text{-}THTP$	−36.9 d	117		
$H_2RhCl(P(4\text{-tolyl})_3)_2\text{-}MeIm$	−43.9 d	119		

[a] Chemical shifts in ppm from external 85% H_3PO_4; all values taken at 28 °C. [b] Second set of values, for uncoupled conditions. [c] d refers to a doublet, dd doublet of doublets, dt doublet of triplets.

^{31}P NMR. The ^{31}P NMR spectrum of the square-planar complex $RhCl(P(4\text{-tolyl}_3)_3$ has been reported earlier,[7,8] and our chemical shifts of the doublet of triplets and the doublet of doublets are in agreement with the literature. The ^{31}P spectra of the pyridine (py), tetrahydrothiophene (THTP), and *N*-methylimidazole (MeIm) base adducts (Table I) support the structure shown for I, where the phosphines are cis to each other. The py adduct spectrum (Figure 1) consists of an eight-line pattern (a doublet of doublets). Each inequivalent phosphorus is split by



I

P = P(*p*-tolyl)$_3$; B = py, THTP, MeIm

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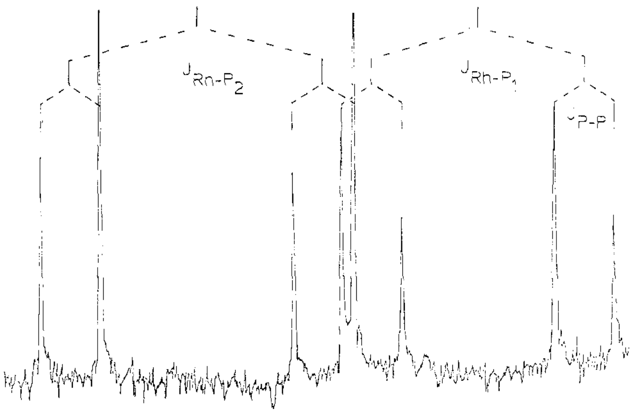

Figure 1. ^{31}P NMR spectrum of RhCl(P(4-tolyl)$_3$)$_2$py.

Table II. Thermodynamic Results for the Interaction of [RhCl(P(4-tolyl)$_3$)$_2$]$_2$ with Various Bases at 24 ± 2 °C

base	ΔH^a	K	E_B	$C_B{}^e$	C/E
P(4-tolyl)$_3$	-4.7 ± 0.3^d	large^b			
pyridine	-4.9 ± 0.2	large^b	1.17	6.40	5.49
THTP	-1.9 ± 0.2	$(1.0 \pm 0.4) \times 10^{2\,c}$	0.34	7.90	23.18
N-methylimidazole	-6.6 ± 0.2	$(2.4 \pm 2.0) \times 10^{4\,c}$	0.9	8.9	9.5

^{a} Units of kcal/mol of monomer formed. ^{b} K_{eq} is unknown but assumed to be very large for the purpose of calculating ΔH_{av}. ^{c} Computer fitted values assuming stoichiometry for $A_2 + 2B = 2AB$. ^{d} Reported errors are standard deviations. ^{e} E and C values obtained from ref 5.

^{103}Rh (J_{Rh-P} = 198, 167 Hz) and a neighboring ^{31}P (J_{P-P} = 47.3 Hz).

The THTP adduct gives a spectrum with smaller coupling constants. Phosphorus–phosphorus coupling is barely observable. In view of the similarity of this adduct's NMR pattern with that for the pyridine adduct, the structures are believed to be the same. On the basis of the observation of equal intensity peaks for the nonequivalent phosphorus ligands, a cis arrangement is assigned to the *N*-methylimidazole adduct.

Thermodynamic Analysis. The thermodynamic data for the reaction described by eq 3 are listed in Table II along with the E_B and C_B values that characterize the donor strength of the bases employed. All reactions were carried out in benzene, and the previously reported[9,10] 0.9 kcal mol^{-1} correction for the benzene–pyridine interaction was made to the data for this system. The uncertainties in the calculated values can be attributed to the extreme O_2 sensitivity of the dimer and of the base adducts formed.

Attempts were made to measure thermodynamic data for eq 3 for a number of oxygen donors (i.e., dimethyl sulfoxide, 4-picoline *N*-oxide, and $(CH_3)_3PO$). The absence of heats of reaction or significant spectroscopic changes indicated that the dimer was not being cleaved by these donors.

The enthalpies for eq 3 should conform to eq 5 for a system

$$-\Delta H + W = E_A E_B + C_A C_B \qquad (5)$$

dominated by σ bonding.[11] The quantity W is the enthalpy needed to cleave the dimer, and E_A and C_A characterize the acidity of the resulting three-coordinate rhodium(I) complex "Rh(P(4-tolyl)$_3$)$_2$Cl", suggested[12] as an intermediate in the catalytic hydrogenation of olefins. By use of the heats in Table II along with reported E_B and C_B values for the bases, simultaneous equations resulted that were solved for W ($=0.5\Delta H$ dissociation of the dimer), E_A, and C_A values for "Rh(P(4-tolyl)$_3$)$_2$Cl". These values are listed in Table III along with the results of the previously studied [Rh(CO)$_2$Cl]$_2$ and [Rh(COD)Cl]$_2$ dimer systems. With only three simultaneous equations (enthalpies for the py, THTP, and MeIm adducts) to solve for three unknowns, these parameters must be considered preliminary. We do note that the C_A/E_A ratio of 0.201 follows the earlier pattern that ligand substitution has changed the acidity of the metal center but not this ratio. Due to the limited number of bases that could be investigated, the assumption was made that the C_A/E_A ratio of the phosphine complex should be much closer to the ratio found for both the CO and COD complexes. Assuming that this ratio should be 0.240, E_A, C_A, and W were determined from the three enthalpies of adduct formation. The results are reported in the last line of Table III. These new values for E_A, C_A, and W fit the measured heats of adduct formation with Rh(P(4-tolyl)$_3$)$_2$Cl within 0.20–0.30 kcal/mol, which is comparable to the estimated precision of these measurements. Thus the actual values of the parameters for this acid most probably are bracketed by those reported in Table III. It is noteworthy that the metal center in Rh(P(4-tolyl)$_3$)$_2$Cl is a stronger acid center than that in (COD)RhCl. This result would suggest metal back-donation in the phosphine complex since the phosphine is a much better σ donor than cyclooctadiene.

Table III. Comparison of the E, C, and W Parameters Determined for the Interaction of Rhodium(I) Chloride Dimers with Various Bases in Benzene

acid	W^a	C_A	E_A	C_A/E_A
[Rh(CO)$_2$Cl]$_2{}^c$	11.3 (1.1)^e	2.02 (0.1)	8.72 (0.8)	0.232
[Rh(COD)Cl]$_2{}^d$	6.3 (0.5)	1.25 (0.04)	4.93 (0.25)	0.254
[Rh(P(4-tolyl)$_2$Cl]$_2$	9.2	1.16	5.77	0.201
	9.84^b	1.29^b	5.41^b	0.240^b

^{a} In units of kcal/mol of adduct formed. ^{b} E_A and C_A estimates determined by fixing $C_A/E_A = 0.240$. ^{c} Reference 3. ^{d} Reference 4. ^{e} Numbers in parentheses represent standard deviations.

If the C_A/E_A ratios of the acids in Table II are the same, it is then possible to apply a single-term version of the E and C equation[10] to these rhodium(I) systems. A one-parameter model requires that a plot of the enthalpies of adduct formation with one acid in the correlation vs. the enthalpies of adduct formation of another acid for the same series of bases be linear with a zero intercept. Since pyridine, MeIm, and THTP heats are known for all three of the rhodium(I) acids, straight lines resulting from the plots of ΔH_{corr} vs. ΔH_{corr} ($\Delta H_{corr} = -\Delta H + W$) for various combinations of the three acids serve as a check for the assumption of a constant C_A/E_A ratio. A good fit of the experimetal data was obtained for such plots. Linear regression analyses for $\Delta H_{corr}(Rh_2(CO)_4Cl_2)$ vs. $\Delta H_{corr}(Rh_2(P(4\text{-tolyl})_3)_4Cl_2)$ and $\Delta H_{corr}(Rh_2(COD)_2Cl_2)$ vs. $\Delta H_{corr}(Rh_2(P(4\text{-tolyl})_3)_4Cl_2)$ indicate slopes of 1.66 ± 0.01 and 0.95 ± 0.03, respectively, with intercepts of 0.70 and 0.25, respectively. The slope of a given line should equal the ratio of the E_A values of the two acids plotted. The predicted slopes are 1.61 and 0.91, respectively.

Reactions of Rh(P(4-tolyl)$_3$)$_2$Cl·B with H$_2$. The square-planar complexes described in the previous section all react with H_2 to form dihydrides as shown in eq 4. In order to understand the influence of donor strength on the position of this equilibrium, it is first necessary to establish the structure of the various dihydrides.

^{31}P NMR. The dihydride complexes of the form Rh(P(4-tolyl)$_3$)$_2$BCl(H)$_2$ were investigated by ^{31}P NMR spectroscopy. In all cases agitation of the appropriate Rh(I) complex under 1 atm of H_2 in the sample tube was sufficient to produce the Rh(III) dihydride complex, although in some cases the spectrum showed the presence of some unreacted Rh(I) complex. The resulting spectra indicates two equivalent phosphorus ligands (Table I). The proton-decoupled spectrum of the pyridine dihydride adduct is shown in Figure 2. This spectrum is assigned to two equivalent phosphorus nuclei split by ^{103}Rh (J_{Rh-P} = 118 Hz). The value of 118 Hz is close to other reported Rh^{III}–P coupling constants.[5] In the absence of proton decoupling at 27 °C, each peak consists

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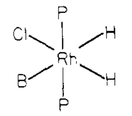
of an unsymmetrical triplet with J_{P-H} of about 14 Hz (Figure 2a). This splitting is assigned to the phosphorus nuclei coupling to inequivalent protons. Further proof for this assignment is presented in the section on the ^{1}H NMR spectra of these complexes.

Variable-temperature studies were performed on these dihydrides to test for any ligand exchange processes that might be occurring. Unlike the $Rh(P(C_6H_5)_3)_3)ClH_2$[8] system reported earlier, the $Rh(P(4\text{-tolyl})_3)_2BCl(H)_2$ systems (B = py, THTP, MeIm) do not show significant changes except for slight shifting of the doublet positions. These results indicate that no dynamic process involving phosphorus exchange occurs on the NMR time scale.

^{1}H NMR. Proton NMR studies were carried out from −50 to +77 °C in hopes of further ascertaining the structure of the dihydrides and possibly obtaining kinetic data on the rate of any ligand dissociation that may be taking place. Recall that this is an integral step for catalytic hydrogenation of olefins since it provides an open coordination site on the metal where the olefin can bind.

Spectral data can be found in Table IV. Hydride resonances for all but the THTP adduct were observed. Such a large excess of THTP was used to split the dimer that the free THTP resonances may have masked the hydride resonances. The equilibrium constant for H_2 addition, measured in the H_2 uptake studies, is also smaller for the THTP adduct than that for the other base adducts.

Spectra for the hydride complexes of the base adducts (py, $P(4\text{-tolyl})_3$, MeIm) at low temperatures show two broad hydride resonances. This supports evidence obtained by ^{31}P NMR spectroscopy that these complexes contain not only trans phosphines but nonequivalent cis hydrides. The proposed structure for these dihydride complexes is II. This structure resembles that proposed for $RhCl(P(C_6H_5)_3)_3(H)_2$.[8] B and the other P ligands were $P(C_6H_5)_3$.



II

B = py, THTP, MeIm; P = P(p-tolyl)$_3$

Each hydride resonance is a broad multiplet of peaks, which represents simultaneous coupling to ^{103}Rh and cis phosphorous nuclei. Because of the differences in the ligands trans to the hydrogens, these multiplets are not mirror images. By use of the fact that the upfield hydride resonance occurs in about the same chemical shift region while the downfield one varies considerably with the base, it appears that the upfield one is due to the hydride trans to the chlorine.

An interesting feature of the pyridine system is the temperature dependence of the spectra, Figure 3. As the temperature increases the hydride resonances approach each other and eventually collapse into a 1:3:3:1 quartet (apparent coupling constant of 18 Hz). The appearance of a quartet might be expected if a kinetic process averages the hydride resonances, and the Rh–H and the two P–H coupling constants are nearly identical. Coupling of the phosphines to the hydrides, observed in both the ^{31}P NMR and ^{1}H NMR spectra, indicates that neither the hydrides nor the phosphines dissociate rapidly from the coordination sphere of the rhodium. With the available data (Table IV) it is possible to make a fairly good calculation of the lifetime of the hydride resonances at 27 °C. A comparison of the calculated and experimental spectra appears in Figure 4. The peak separation in the absence of exchange has been estimated to be 105 Hz while the natural line width is relatively broad due to the unresolved H–H, P–H, and Rh–H couplings. At 27 °C the chemical shift difference between the two resonances is large compared to the coupling constants, allowing a simple AB exchange matrix to adequately simulate the spectrum. The calculated average lifetime of the hydride resonance, τ ($=\tau_{A/2} = \tau_{B/2}$) is estimated to be 0.040 s. By analogy with the $Rh(P(C_6H_5)_3)_3Cl(H)_2$ system,[8] where the phosphine trans to a hydride is known to exchange with free phosphine in solution, we assumed that in the $Rh(P(4\text{-tolyl})_3)_2pyCl(H)_2$ system the pyridine is occupying the trans position and is exchanging with free pyridine in bulk solution. A 3-fold increase in free pyridine produced no changes in the appearance of the hydride spectrum at 27 °C, implying a first-order dissociative mechanism. If the intermediate in the reaction is a trigonal-bipyramid "$Rh(P(4\text{-tolyl})_3Cl(H)_2$" species, the pyridine can attack a position trans to either hydride, which would average the hydride resonances and could collapse the spectrum as observed. The first-order rate constant based on the computer fit of the spectrum is ~50 s^{-1}. The rate constant for exchange of $P(C_6H_5)_3$ from the similar intermediate is 1000 s^{-1} at 25 °C. The smaller rate constant

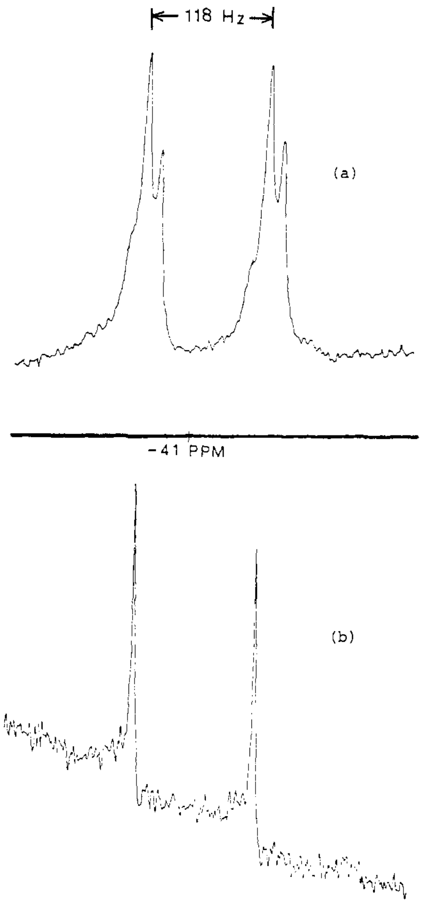


Figure 2. ^{31}P NMR spectra for $(H)_2RhCl(P(4\text{-tolyl})_3)_2py$: (a) proton coupled, (b) proton decoupled.

Table IV. Variable-Temperature ^{1}H NMR Chemical Shift Data for Rhodium(III) Dihydrides

T, °C	δ_1[a]	δ_2[a]	$\Delta\nu_{220}$[b]
	$Rh(P(4\text{-tolyl})_3)_3Cl(H)_2$		
+46			
+28	too broad	−16.9	
0	−9.0	−16.8	1716
−25	−8.9	−16.7	1716
	$Rh(P(4\text{-tolyl})_3)_2(py)Cl(H)_2$		
77		−16.82	0
27	−16.51	−16.86	87
0	−16.30	−16.88	127
−25	−16.15	−16.84	151
−47	−15.99	−16.84	187
	$Rh(P(4\text{-tolyl})_3)_2(MeIm)Cl(H)_2$		
27	−16.40	−17.93	336
−49	−15.79	−17.70	420

[a] Chemical shift in ppm relative to Me_4Si. [b] Frequency shift in Hz between the hydride resonances.

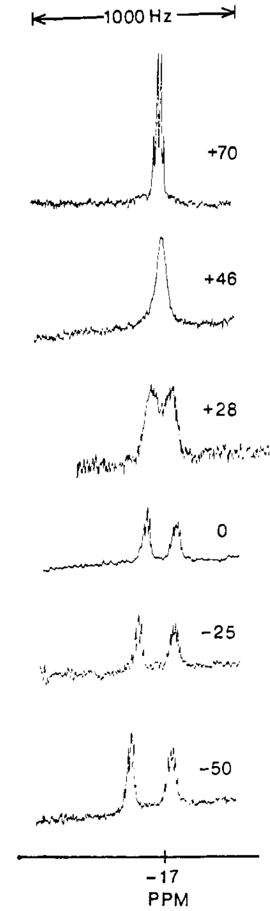


Figure 3. Temperature-dependent 220-MHz ^1H NMR for $RhCl(P(p\text{-}tolyl)_3)_2py(H)_2$, relative to Me_4Si.

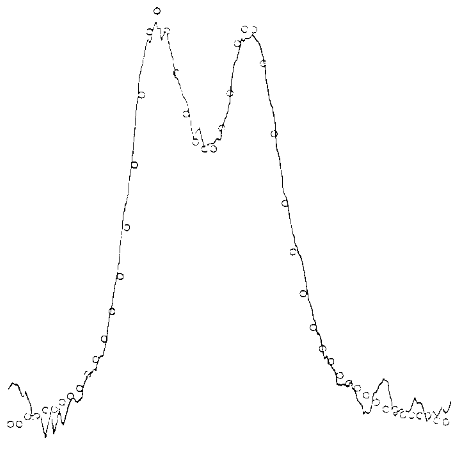


Figure 4. 220-MHz spectrum of $RhCl(P(4\text{-}tolyl)_3)_2(H)_2$ at 27 °C showing experimental (–) and calculated (O) values based on an exchange reaction that assumes first-order dissociation of pyridine.

observed for the exchange of pyridine is consistent with the observed inhibition of the catalytic reaction for the hydrogenation of olefins by pyridine.[12]

Table V. Comparison of Infrared Frequencies for Varous Rhodium Hydrides

compd	$\bar{\nu}_H$, cm^{-1}	ref
$Rh(P(4\text{-}tolyl)_3)_2LCl(H)_2$		
L = $P(4\text{-}tolyl)_3$	2034[a]	this work
	2040	8
L = $P(phenyl)_3$	2078	12
L = pyridine	2065[a]	this work
	2052	12
$HRh(PPh_3)_4$	2147, 2152	13, 14
$HRh(PMePh_2)_4$	2005	15, 16
$H_2Rh(PEtPh_2)_3Cl$	2115	17
$H_2Rh(AsPPh_3)_3$	2030, 2051	18

[a] Very broad bands with unresolved shoulders at high frequency.

Table VI. Thermodynamic Data for the Reaction

$$RhClB(P(4\text{-}tolyl)_3)_2 + H_2 \overset{K}{\rightleftharpoons} RhClB(P(4\text{-}tolyl)_3)_2H_2$$

B	*T*, °C	K^a
$P(4\text{-}tolyl)_3$	9.0	113.7
	30.1	29.9
	35.0	24.4
	44.0	12.2
	53.8	7.27
	$\Delta H^b = 11.0 \pm 0.5^c$ kcal/mol	
THTP	10.0	77.4
	15.0	47.6
	20.6	33.9
	30.0	21.5
	40.0	13.2
	50.0	5.91
	$\Delta H^b = 11.6 \pm 1.0^c$ kcal/mol	

[a] Best fit *K*. [b] Determined by van't Hoff analysis, based on generating an equilibrium constant for each absorbance change after the best $(\epsilon_0 - \epsilon)$ was determined and held constant. [c] 90% confidence interval.

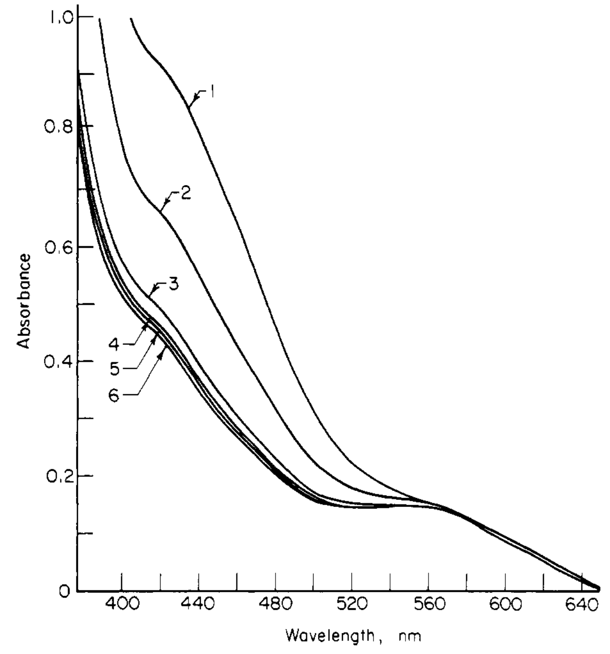


Figure 5. UV spectrum of a toluene solution of 2.98×10^{-3} M $[RhCl(P(4\text{-}tolyl)_3)_2]_2$ and 5.79×10^{-2} M THTP at 10.0 °C in equilibrium with various pressures of H_2: 1, $P_H = 0.00$ atm; 2, $P_H = 0.015$ atm; 3, $P_H = 0.102$ atm; 4, $P_{H_2} = 0.217$ atm; 5, $P_{H_2} = 0.371$ atm; 6, $P_{H_2} = 0.967$ atm).

Infrared Spectra. The Rh(I) and analogous Rh(III) complexes show nearly identical infrared spectra except for a new broad resonance that appears near 2040 cm^{-1} in the Rh(III) dihydride complexes. This is assigned to metal hydride stretching. Other reported Rh(III) hydride complexes have absorption bands in this region. The values of these hydride stretching frequencies in various compounds are listed in Table V. The broad nature of this band makes the numerical assignment of the frequency somewhat uncertain and has led to some uncertainties in previously

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reported values.[12] Although these results support the conclusion that a hydride is in fact the product of the H_2 addition reaction, there is no correlation of these values with base strength (vide infra).

Thermodynamic Analysis of the Oxidative Addition of H_2. The changes that occur in the electronic spectrum of $(P(4\text{-tolyl})_3)_2RhClB$ upon addition of H_2 are illustrated in Figure 5 for the THTP adduct. These changes and their temperature dependence provide a basis for determination of ΔG and ΔS for eq 4. We report, in Table VI, the results for the bases $P(4\text{-tolyl})_3$ and THTP ($C/E = 23.18$) undergoing the reaction in eq 4. Attempts to study the base adducts with pyridine ($C/E = 9.5$) produced inconsistent results due to possible side reactions involving excess base in solution or the extreme O_2 sensitivity of this system. We were able to establish that the equilibrium constant for base binding was at least an order of magnitude greater for this system than for the case where B = $P(4\text{-tolyl})_3$. This larger K also makes an accurate determination of the equilibrium constant more difficult.

The two systems that could be investigated fortunately provided a substantial variation in the strength of binding to the rhodium(I) center (Table II). The equilibrium constant for eq 4 parallels the basicity of these ligands toward rhodium. However, the enthalpy for eq 4 is remarkably independent of the donor strength of THTP or $P(4\text{-tolyl})_3$.

The enthalpy for eq 4 can be combined with the heat of dissociation of H_2 to produce an average metal–hydrogen bond dissociation energy:

$$RhClB(P(4\text{-tolyl})_3)_2(H)_2 \rightarrow RhClB(P(4\text{-tolyl})_3)_2 + H_2$$

$$H_2 \rightarrow 2H\cdot\ (104.2\ \text{kcal mol}^{-1})$$

$$RhClB(P(4\text{-tolyl})_3)_2(H)_2 \rightarrow RhClB(P(4\text{-tolyl})_3)_2 + 2H\cdot$$

These values are of particular importance insofar as a review on thermochemical studies of organometallic compounds states "there is almost no reliable information about the strength of metal–hydrogen bonds in organometallic compounds".[19] Values of 57.6 kcal mol^{-1} and 57.9 kcal mol^{-1} result for the $P(4\text{-tolyl})_3$ and THTP adducts of $RhClB(P(4\text{-tolyl})_3)_2(H)_2$, respectively. At 90% confidence, the minimum value for the THTP adduct would be 57.4 kcal mol^{-1}. Thus the average metal–hydrogen bond energy is found to be very insensitive to differences in the two ligands studied.

The metal–hydrogen bond energy can be compared to others reported in the literature. In a study[20,21] of the influence of ligand variation in the system $Ir(CO)XL_2$ (where L is a series of phosphines and X is Cl^-, Br^-, and I^-), enthalpies of hydrogenation of 2.7–18.1 kcal mol^{-1} were measured corresponding to average metal–hydrogen bond energy variations of 53–61 kcal mol^{-1}. The gas-phase neutral Co–H bond dissociation energy, determined by ion beam techniques,[22] is reported as 39 ± 6 kcal mol^{-1}.

Experimental Section

Reagents. Benzene and toluene used for calorimetric and spectrophotometric studies, respectively, were refluxed overnight and distilled from CaH_2 at atmospheric pressure under N_2. Pyridine was first dried over Linde 4A Molecular Sieves and distilled over CaH_2 at atmospheric pressure. The middle fraction was taken (boiling range 112.0–112.5 °C). Tetrahydrothiophene (THTP) was fractionally distilled over CaH_2 at atmospheric pressure. *N*-Methylimidazole was fractionally distilled over CaH_2 at 10-mmHg pressure and the middle fraction was taken. Tri-4-tolylphosphine was recrystallized from absolute ethanol and vacuum-dried. Deuterated solvents were obtained from Stahler Isotope Chemicals and from Merck, Sharpe, and Dohme. All solvents and liquid bases were degassed through three freeze–pump–thaw cycles and stored in an inert atmosphere box prior to use. Hydrogen and nitrogen gas used for thermodynamic studies were obtained from Linde (Union Carbide) and were of ultrahigh purity (<2 ppm O_2).

Synthesis. $[Rh(P(4\text{-tolyl})_3)_2Cl]_2$ was prepared by a previously reported procedure.[6,8] Anal. Calcd for $C_{84}H_{84}Cl_2P_4Rh_2$: C, 67.5; H, 5.7; Cl, 4.8. Found: C, 67.3; H, 5.7; Cl, 5.0.

Physical Measurements. Calorimetric studies involving $[Rh(P(4\text{-tolyl})_3)_2Cl]_2$ were performed under N_2 by using the syringe technique previously described.[23] in a cell designed to exclude atmospheric O_2 and water. The cell was assembled and filled under a purified N_2 atmosphere and was not flushed with N_2 during the measurements as the dimer in solution is extremely sensitive even to the small quantity of O_2 contained in tank nitrogen. Solutions were magnetically stirred. Measurements were performed under ambient conditions in unthermostated cells at 24 ± 2 °C. Thermal contact between the solution and the base to be injected was established by immersing the capillary tip of the syringe containing the base directly into the solution. The enthalpy of reaction, ΔH, was calculated by using either a computer program written for equilibria of the type $A_2 + 2B \rightleftharpoons 2AB$, previously described,[3] or by assuming an infinite equilibrium constant and calculating the heat per mole of limiting reagent. All measured heats were corrected for the heat of dilution, ΔH_{dil}, of the base solution into the pure solvent. All enthalpies are reported in terms of the number of moles of product formed, which is equivalent to the heat per mole of base injected. Calorimetric data for reaction 3 is contained in Table M-1 of the supplementary material.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Spectra of benzene solutions were obtained in matched 0.2-mm cells. Spectra of the dihydride complexes were obtained by exposing solutions of the rhodium complex to 1 atm of H_2 prior to loading the IR cell. These solutions were observed to be stable for long periods without applying a continuous H_2 pressure as long as the cells were tightly sealed with Teflon stoppers. Manipulation of the solutions during loading was accomplished by using syringe techniques, and the cells were flushed with a slight excess of the hydride solutions so that the solution remaining in the cell was not exposed to atmospheric O_2.

Phosphorus-31 spectra were obtained on a Varian XL-100 FT spectrometer at 40.5 MHz with an ambient probe temperature of 40 °C. Variable-temperature proton NMR spectra were obtained on a Varian HR-220 FT spectrometer at 220 MHz. Line shape calculations were performed with a density matrix computer program that has been described in detail elsewhere.[25] The subroutine for a simple AB spin system was used to calculate the rate of pyridine exchange in the complex $(P(4\text{-tolyl})_3)_2RhClpy(H)_2$. Calculations were performed on an IBM 360 computer.

Thermodynamic studies involving the reaction of $RhCl(P(4\text{-tolyl})_3)_2B$ and H_2 were accomplished with a specially designed hydrogen flow system. In this system a premixed H_2/N_2 gas mixture was bubbled through a 0.1-cm UV–vis cell containing a solution of $RhCl(P(4\text{-tolyl})_3)_2B$. The cell was positioned in the source beam of a Cary 14 UV–vis spectrometer containing a thermostated cell holder. Hydrogen and nitrogen gas were first passed through O_2 traps purchased from L.C. Company, Inc. (remove O_2 to <0.1 ppm). The gasses then entered a Matheson Model 7352 rotameter fitted with no. 610 tubes, allowing accurate determination of the desired $N_2{:}H_2$ ratio. The mixed gas was then bubbled through a toluene bubbler containing a small amount of the rhodium dimer. This saturated the gas with toluene, and the dimer acted as a final O_2 trap. The gas was then slowly bubbled through the UV–vis cell containing the monomeric rhodium base adduct. Gas exiting the cell passed through a mineral oil bubbler to maintain a constant system pressure. A monometer present in the system was used to accurately determine the internal pressure. Solutions of the monomeric base adducts were generated by adding enough base to a rhodium dimer solution to cleave more than 95% of the dimer. Absorbance changes in the visible range (350–650 nm) were recorded for each hydrogen partial pressure.

Equilibrium constants were determined by a previously described method[24] in which the best K^{-1} and $(\epsilon_0 - \epsilon)$ were simultaneously determined. By use of the best fit $(\epsilon_0 - \epsilon)$ for each temperature as a constant, equilibrium constants were generated for each absorbance change. These K's were then used in a van't Hoff analysis to determine 90% confidence intervals for ΔH. In determination of 90% confidence intervals for ΔH, a degree of freedom was subtracted for each temperature used to account for holding the best fit $(\epsilon_0 - \epsilon)$ constant. Thermodynamic data for reaction 4 are contained in Table M-2 of the supplementary material.

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Registry No. RhCl(P(4-tolyl)$_3$)$_3$, 24554-70-9; RhCl(P(4-tolyl)$_3$)$_2$Py, 83984-11-6; RhCl(P(4-tolyl)$_3$)$_2$THTP, 83999-92-2; RhCl(P(4-tolyl)$_3$)$_2$MeIm, 83984-12-7; H$_2$RhCl(P(4-tolyl)$_3$)$_3$, 84025-97-8; H$_2$RhCl(P(4-tolyl)$_3$)$_2$Py, 83984-13-8; H$_2$RhCl(P(4-tolyl)$_3$)$_2$THTP, 83984-14-9; H$_2$RhCl(P(4-tolyl)$_3$)$_2$MeIm, 83984-15-0; [RhCl(P(4-tolyl)$_3$)$_2$]$_2$, 53127-35-8.

Supplementary Material Available: Listing of calorimetric data for reaction 3 and thermodynamic data for reaction 4 (5 pages). Ordering information is given on any current masthead page.

Pyridoxamine and 2-Oxalopropionic Acid in Aqueous Systems: Conditional Imine Formation Constants and Rate Constants of Vitamin B$_6$ Catalyzed Decarboxylation

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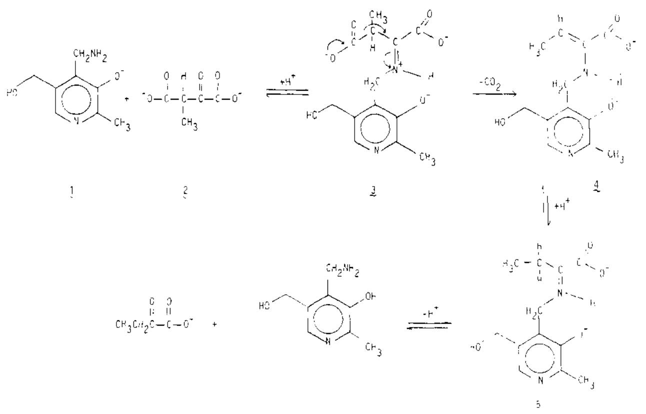
Abstract: The conditional Schiff base formation constants (K_c) of pyridoxamine (PM) and 2-oxalopropionic acid (OPA) were determined spectrophotometrically in basic aqueous solutions. These equilibrium constants exhibit pH dependence with maximum ketimine formation occurring near pH 9.0 ($K_c = 9.6$). The kinetics of the vitamin B$_6$ catalyzed decarboxylation of OPA have been studied spectrophotometrically, and the observed rate constant of decarboxylation (k_{obsd}) exhibited pH dependence with the maximum occurring at approximately the pH corresponding to maximum ketimine formation ($k_{obsd} = 15.6 \times 10^{-4}$ s^{-1} at 1.01×10^{-4} M OPA and 1.00×10^{-5} M PM). Microscopic rate constants (k_{SB}) for the decarboxylation of the Schiff base species present in solution also showed pH dependence with the greatest catalytic activity at pH 7.0 ($k_{SB} = 38.4$ s^{-1}) and the least at pH 12.47 ($k_{SB} = 0.2$ s^{-1}). The relative magnitudes of the k_{SB}'s determined are discussed in terms of the various protonated forms of the OPA:PM ketimine, and the corresponding pK_a's have been estimated from the rate constant-pH profiles.

The kinetic and equilibrium studies of the 2-oxalopropionic acid:pyridoxamine system presented here are part of the series of comprehensive investigations on the decarboxylation of 2-oxalopropionic acid (OPA) to α-ketobutyric acid (AKBA) conducted in this laboratory. Previous kinetic work involved the proton-, aluminum(III)-, copper(II)-, and zinc(II)-catalyzed decarboxylation[1-3] of OPA, and a related study of proton association and metal ion stability constants for each species formed in solution has been reported.[4] Such investigations have been and continue to be of interest because of the importance of β-carboxy-α-ketocarboxylic acids in metabolic reactions in biological systems. Additional investigations reported to date have involved the spontaneous,[5-12] metal ion catalyzed,[8-21] and enzymatic[22] decarboxylation reactions along with the corresponding enolization,[23-25] dehydration,[23,25] and hydration[25] reactions. Additional substrates which have been employed in these studies are oxaloacetic acid (OAA), dimethyloxaloacetic acid (DMOAA), and fluorooxaloacetic acid, which undergo decarboxylation to form pyruvic, α-ketoisovaleric, and fluoropyruvic acids, respectively.

The extensive studies conducted on these substrates provided a nearly complete understanding of the spontaneous and metal ion catalyzed decarboxylation of β-carboxy-α-ketocarboxylic acids. Such knowledge was and still is considered a prerequisite to the interpretation of the vitamin B$_6$ catalyzed systems which in turn are important for comparison with the corresponding enzyme-catalyzed biological processes. Schiff bases of OAA and its analogues with pyridoxamine are probable intermediates for the decarboxylation of the corresponding aminodicarboxylic acids such as L-aspartic acid and may be formed by transamination of the latter.

Scheme I



The decarboxylation of 2-oxalopropionic acid in the presence of pyridoxamine (PM)[26] has been previously reported, but this study was limited to product analysis and the specification of the reaction conditions employed. In that same investigation, Sakkab

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