first order with respect to both of the reagents. The values of the rate constant from six different curves were 9.5, 9.3, 8.4, 10.2, 9.1, and 6.8 l. $mol^{-1}$ $s^{-1}$ or 8.6 ± 0.6. The standard deviation of the calculated and observed temperatures was 0.0005 for the six curves with some trending observed in two cases. One can place a limit on the rates of reactions 1 and 2 of not less than 80 l. $mol^{-1}$ $s^{-1}$ since these reactions are complete in the time of mixing.

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# Thermodynamic and Spectroscopic Studies of the Reaction of Lewis Bases with Di-$\mu$-chloro-tetracarbonyldirhodium(I)

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**Abstract:** A detailed calorimetric and spectroscopic study of the acid–base chemistry of $[(CO)_2RhCl]_2$ in poorly solvating media is presented. Enthalpies of adduct formation with ten bases are reported which vary considerably in their basic properties; e.g., nitrogen, sulfur, and oxygen donors are reported. The data can be correlated with the *E* and *C* model thus extending this treatment for the first time to low-valent, second-row transition metal systems. An enthalpy of 22.6 kcal $mol^{-1}$ of dimer is required to cleave the chloro bridges. The procedure for factoring this bridge cleavage enthalpy out of the measured enthalpy data is described. We are now in a position to predict enthalpies of adduct formation with all of the bases in the *E* and *C* correlation and can understand why many substances do not effect bridge cleavage. The structures of the complexes in solution are deduced from infrared and $^{13}C$ NMR studies.

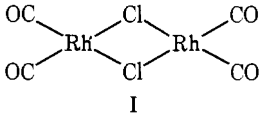
Recent work from this laboratory[3] has concerned itself with the study of quantitative aspects of Lewis acid–base interactions. The relationship first proposed by Drago and Wayland in 1965[4,5] (eq 1)

$$-\Delta H = E_A E_B + C_A C_B \tag{1}$$

has been tested on numerous systems, but, to date, only two transition metal complexes have been included in the correlation, namely, bis(hexafluoroacetylacetonato)copper(II)[6] and methylatobis(dimethylglyoximato)cobalt(III).[7] We thought it would be enlightening to attempt an extension of the correlation to other transition-metal-containing Lewis acids, particularly to one containing a low-valent second-row transition metal. The acid–base interaction in metal systems is potentially more complex than in the simple systems studied previously[3] because a $\pi$ back-bonding contribution to the stability of the M–L bond may exist.

Metal complexes of this type are interesting because of their importance in a number of catalytic reactions. For example, the well-known hydrogenation catalyst $[(C_6H_5)_3P]_3RhCl$[8] can be considered as the $(C_6H_5)_3P$ adduct of $\{[(C_6H_5)_3P]_2RhCl\}_2$. Recently, Tolman et al.[9] have investigated the system RhCl-triarylphosphine-$H_2$-olefin. Kinetic data indicated that the species $RhP_2Cl$ was an important intermediate in the reaction with $H_2$. In many catalytic processes, coordinatively unsaturated intermediates of this type are very important. A characteristic reaction of this type of compound is the addition of a ligand to the open coordination position. The energetics and kinetics of this type of reaction are usually difficult to study. By determining the bridge cleavage enthalpy of the chloro-bridged dimer, we can derive thermodynamic data for interaction of the species $Rh(CO)_2Cl$ with a series of bases.

The complex di-$\mu$-chloro-tetracarbonyldirhodium(I) (I) is



I

known to undergo reactions of various types with Lewis bases, depending on the experimental conditions used and the specific base involved.[10-18] The work in this area is too extensive to be dealt with here in detail, but certain results are worthy of mention.

The most common reaction which has been observed is shown in eq 2.

$$\text{I} + 2\text{L} = \underset{\text{II}}{2\text{Rh(CO)}_2\text{LCl}} \qquad (2)$$

This has been found with a large number of ligands containing halide, oxygen, and nitrogen donor atoms.[10-14] For ligands containing heavier group 5 or 6 donor atoms, reaction 2 describes the initial reaction with limited amount of ligand, but other reactions (3, 4 (with $n$ = 2 or 3), 5, and 6) are reported depending on conditions.[15-17]

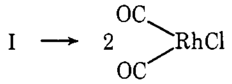
$$\text{I} + 2\text{L} = [\text{L(CO)RhCl}]_2 + 2\text{CO} \qquad (3)$$

$$\text{I} + 6\text{L} = 2\text{Rh(CO)ClL}_n + 2\text{CO} \qquad (4)$$

$$\text{I} + 6\text{L} = 2\text{RhClL}_3 + 4\text{CO} \qquad (5)$$

$$\text{I} + 8\text{L} = 2[\text{RhL}_4]\text{Cl} + 4\text{CO} \qquad (6)$$

In this investigation, we have concerned ourselves mostly with reactions of type (2), about which we have gathered calorimetric and spectroscopic data. These data are sufficient to characterize the chemical and stereochemical course of the reaction and have allowed us to calculate $E_A$ and $C_A$ parameters for the acid "Rh(CO)$_2$Cl". Our data have also allowed us to calculate the enthalpy of dissociation of [Rh(CO)$_2$Cl]$_2$, i.e., the enthalpy of reaction 7.



$$\text{I} \longrightarrow 2\,(\text{OC})_2\text{RhCl} \qquad (7)$$

## Experimental Section

Elemental analyses and molecular weights were done by the Microanalytical Laboratory of the University of Illinois. *N,N*-Dimethylacetamide (DMA) gave a molecular weight of 120 (monomer = 87) in benzene at 0.06 F, and is thus not aggregated to the extent it is in saturated hydrocarbons.[19]

**Instrumentation.** Infrared spectra of solids were run as Nujol mulls on a Perkin-Elmer 457 spectrometer from 250 to 4000 cm$^{-1}$ and on a Beckman IR-7 from 1800 to 2200 cm$^{-1}$. Solution spectra in this latter region were also run on the IR-7. Frequencies on the 457 are believed accurate to $\pm 3$ cm$^{-1}$; on the IR-7, to $\pm 1$ cm$^{-1}$.

ESR spectra were run on a Varian E-9 X-band spectrometer operating at a frequency of 9.103102 GHz.

$^{13}$C NMR spectra were obtained in CDCl$_3$ or in 2:1 mixtures of natural abundance and fully deuterated acetone, benzene, or toluene, using a Varian Associates XL-100 FT spectrometer operating at 25.16 MHz with internal deuterium lock. The solutions were prepared and run under N$_2$. The spectra were run immediately after preparation, or the solutions were frozen until spectra could be run. Usually, within the time of a run, extensive decomposition of the sample was indicated by darkening of the solution and formation of a dark precipitate. The $^{13}$C chemical shifts were measured relative to the internal solvent resonances and are reported in parts per million downfield from internal Me$_4$Si using the following conversions.[20]

$$\delta_{\text{Me}_4\text{Si}} = \delta_{(\text{CH}_3)_2\text{CO}} - 30.43 \text{ ppm}$$

$$\delta_{\text{Me}_4\text{Si}} = \delta_{\text{C}_6\text{H}_6} - 128.57 \text{ ppm}$$

$$\delta_{\text{Me}_4\text{Si}} = \delta_{\text{CDCl}_3} - 76.98 \text{ ppm}$$

$$\delta_{\text{Me}_4\text{Si}} = \delta_{(\text{C}_6\text{H}_5\text{CH}_3)} - 21.23 \text{ ppm}$$

**Materials.** For synthetic purposes, all materials were of reagent or better grade. For the thermodynamic measurements, the following purification methods were used.

**Solvents.** MCB Spectrograde benzene was refluxed over P$_4$O$_{10}$ 1 h, then fractionally distilled at atmospheric pressure onto Linde 4A molecular sieves. It was then purged with dry N$_2$ for at least 2 h before use. Reagent grade ethyl acetate and dioxane were both stored over calcium hydride overnight, refluxed over the calcium hydride for 1 h, then distilled, purged, and stored as above.

**Bases.** Pyridine (py),[21] tetrahydrothiophene (THTP),[22] *N,N*-dimethylacetamide (DMA),[21] 1-methylimidazole (MeIM),[23] pyridine *N*-oxide (pyO),[24] and 1-phospha-2,6,7-trioxa-4-ethylbicyclo[2.2.2]octane (caged phosphite)[7] were obtained commercially and purified as previously described. Piperidine (pip) and 4-methylpyridine (4-pic) were stored overnight over BaO, refluxed over fresh BaO for 1 h, then fractionally distilled and purged as above. Cyclohexene was washed four times with dilute aqueous FeSO$_4$, then with distilled water, and placed over P$_4$O$_{10}$ overnight. It was then distilled from fresh P$_4$O$_{10}$, and purged as above. 2,2,6,6-Tetramethylpiperidine-*N*-oxyl (TMPNO) was prepared by the literature method.[25] Triphenylphosphine was recrystallized twice from absolute ethanol, then dried under vacuum over P$_4$O$_{10}$. 3,5-Dichloropyridine (Cl$_2$py) was recrystallized twice from hexane and dried under vacuum over Drierite. *N,N*-Dimethylthioformamide (DMTF) was prepared by refluxing 100 g (1.37 mol) of *N,N*-dimethylformamide with 122 g (0.275 mol) of P$_4$S$_{10}$ in 250 ml of xylene for 4 h. The yellow solution was decanted from the dark brown tarry residue, the solvent was mostly removed on a Rotovap at reduced pressure, and the concentrated solution vacuum distilled twice through a 1 × 20 cm Vigreaux column. The first fraction contains residual solvent, and the second, the desired product, bp 102–103°. Anal. Calcd for C$_3$H$_7$NS: C, 40.42; H, 7.91; S, 35.96. Found: C, 40.41; H, 7.92; S, 35.38.

**Metal Complexes.** Di-$\mu$-chloro-tetracarbonyldirhodium(I) was prepared by the literature method.[26]

**Preparation of Rh(CO)$_2$ClL Compounds. L = py, 4-Picoline.** Both of these complexes have been previously reported.[10,11] The complex with py is orange (mp 66°, lit.[10] 68°), and that with 4-pic is bright red (mp 104°).

**L = MeIm.** A 0.094-g (0.24 mmol) portion of I was dissolved in 6 ml of 1:2 (v:v) benzene:hexane. MeIm, 0.039 ml (0.041 g, 0.51 mmol), in 3 ml of benzene was added dropwise with stirring. The resulting solution was placed in a freezer for 1 h, and the resulting crystals were filtered off, yielding 0.062 g (49%) of a golden-yellow solid which turns blue upon grinding, mp 92–93°.

**L = pyO.** A 0.098-g (0.25 mmol) portion of I was dissolved in 5 ml of warm hexane. To this was added 0.048 g (0.61 mmol) of pyO in 1.5 ml of benzene, yielding an immediate orange precipitate which was filtered after standing in a freezer for 1 h, and recrystallized from benzene–hexane. Yield = 0.132 g (90%). Anal. Calcd for C$_7$H$_5$NO$_3$ClRh: C, 29.04; H, 1.74; Cl, 12.25; Rh, 35.55. Found: C, 29.19; H, 1.62; Cl, 12.20; Rh, 33.29. Mp 115.5–116.5°.

**L = Cl$_2$py.** A 0.096-g (0.246 mmol) portion of I was dissolved in 3 ml of warm hexane. To this was added 0.0735 g (0.50 mmol) of Cl$_2$py in 2 ml of hexane. A deep red precipitate formed immediately. The mixture was placed in a freezer for 30 min, then filtered. Yield = 0.14 g (83%).

Similar reactions were performed with Et$_3$N, quin, THTP, DMA, pip, and hexamethylphosphoramide. In all cases, a reaction took place (as evidenced by a color change and the formation of a precipitate or oil), but the products proved to be too difficult to isolate in pure form. A similar reaction with TMPNO gave back only starting material.

**Calorimetry.** The calorimetric experiments involving Rh$_2$(CO)$_4$Cl$_2$ were generally performed under N$_2$, using the syringe method previously described[7] in a cell designed to exclude atmospheric O$_2$ and water.[27] The initial measurements were performed with no special precautions of this type and, in a number of cases, a precipitate appeared on passing the stoichiometric point in the calorimetric run. This did not occur when the reactions were performed under N$_2$.

However, with this cell, a small variable contribution to the observed heat $H'$ arises from the fact that the syringe and solution are not in contact, and thermal equilibrium is not as well established as in our other work. This leads to some larger reported inaccuracies in the reported $\Delta H$ values. Whenever possible, a $\Delta H_{\text{dil}}$ value obtained in the same experiment has been used to correct the observed heats.

In most cases, assumption of an infinite equilibrium constant was justified by the data. In these cases, $\Delta H$ was calculated by dividing the heat evolved (corrected for the heat of solution or dilution) by the number of moles of base injected (i.e., the number of moles of adduct formed). In cases where this assumption was not justified, a computer program was used to calculate the values of the equilibrium constant and the enthalpy of reaction. This program uses the same basic approach[22,28,29] to solution of the relevant equations as previous ones for the situation involving a reaction of the general form

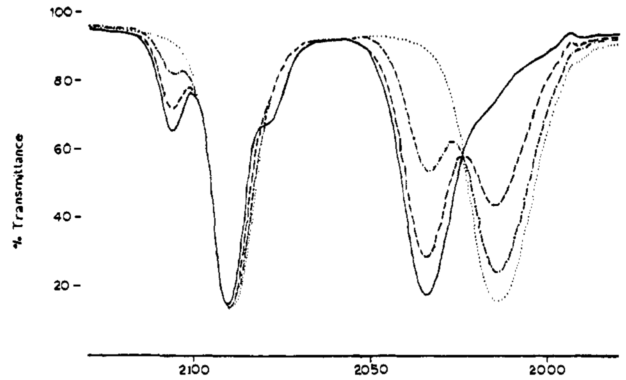


**Figure 1.** Infrared spectra of $Rh_2(CO)_4Cl_2$ plus varying amounts of pyridine in $CHCl_3$. Concentration of $Rh_2(CO)_4Cl_2$ is $3.24 \times 10^{-3}$ in all cases. Symbols used: — = no added pyridine, - - - = [py] = $2.20 \times 10^{-3}$ M, -·-·- = [py] = $4.40 \times 10^{-3}$ M, ····· = [py] = $6.60 \times 10^{-3}$ M.

$$A + B \rightleftarrows AB \qquad (8)$$

but differs in the fact that the equations relating to the equilibrium in operation here (eq 9)

$$A_2 + 2B \rightleftarrows 2AB \qquad (9)$$

are cubic, rather than quadratic, and are not as easily solved by a formula. The approach taken was an iterative, approximative one, in which the root of the relevant equation is found by systematically reducing the size of the interval in which it can mathematically be located, until the length of the interval represents a relative error of less than one part in $10^8$.

## Results

**(1) Infrared Spectra.** Table I of the microfilm edition presents the observed infrared frequencies in the range 1700-2200 $cm^{-1}$ for compounds involved in this study, along with some literature data for comparison. (See the paragraph at the end of this paper regarding supplementary material.) Spectra in $C_6H_6$, EtOAc, or dioxane were taken on solutions after calorimetry runs. These contained approximately 10% excess base in all cases except for the donors DMA, TMPNO, and bridged ether, which had a greater excess, and $(C_6H_5)_3P$ and quinuclidine, which had less than the stoichiometric amount of base. The cell path length was 0.5 mm, and the concentration of all solutions was approximately $3 \times 10^{-3}$ M.

The spectral changes upon addition of base to $Rh_2(CO)_4Cl_2$ are illustrated in Figure 1. $Rh_2(CO)_4Cl_2$ in $CHCl_3$ shows three major peaks at 2035, 2091, and 2106 $cm^{-1}$. At a py:Rh ratio of 1, the peaks at 2035 and 2106 $cm^{-1}$ have completely disappeared. Appearance of isosbestic points at 2024, 2060, and 2095 $cm^{-1}$ indicate the presence of only two spectroscopically independent species in equilibrium. Spectra with other bases or in other solvents show similar behavior.

The observation of two almost equally intense bands in the $\nu_{CO}$ region of the infrared spectra confirms the cis geometry of $Rh(CO)_2ClL$ in all cases. This is in accord with the x-ray crystallographic results on $Rh(CO)_2Cl(Cy_3PO)$[12] and $Rh(CO)_2Cl(TPDA)$[13] (TPDA = 3,5,7-triphenyl-4*H*-1,2-diazepine). A compound with the trans geometry would also have two infrared active carbonyl bands, but the "symmetric" stretch would be expected to have a greatly reduced intensity relative to the "asymmetric" stretch. Observation of more than two peaks in the mull spectra of the solids is probably due to solid-state lattice effects.

The spectrum of I in basic solvents such as EtOAc, dioxane, or $CH_3CN$ is similar to that of adducts of the form $Rh(CO)_2ClL$—two equally intense peaks separated by approximately 75 $cm^{-1}$. The shift from the free dimer indicates that the dimer has been converted to a solvent adduct, $Rh(CO)_2Cl(solvent)$. The fact that the dimer is broken in $CH_3CN$ indicates that the reported[30] $^{13}C$ NMR spectrum of I in $CH_3CN$ is actually a spectrum of $Rh(CO)_2Cl(CH_3CN)$, with the two possible CO environments averaged due to solvent exchange (vide infra).

In contrast, the infrared spectrum of I in cyclohexene indicates that most (at least 70%) of the rhodium remains in the dimeric form (peaks at 2104, 2088, 2075, 2032, 2012 $cm^{-1}$), with a much smaller amount as $Rh(CO)_2Cl(cyclohexene)$ (peaks at 2075, 2024 $cm^{-1}$). The equilibrium constant for the interaction of I with cyclohexene is thus apparently quite small. Crude $E'$ and $C'$ numbers[31] for cyclohexene[32] predict that the $\Delta H$ for this interaction would be small, well under 5 kcal/mol. Since this is less than the enthalpy required to break the bridge in $Rh_2(CO)_4Cl_2$ (vide infra), it is not surprising that this equilibrium constant is so small, and that so little bridge-breaking occurs, even with the 300-fold excess of cyclohexene. Tolman et al.[9] found that cyclohexene also has little or no tendency to cleave the bridge in $[P_2RhCl]_2$ (P = $(C_6H_5)_3P$ or $(p\text{-}CH_3C_6H_4)_3P$). The exo double bond in $\alpha,\alpha$-diphenylfulvene appears to be a stronger base than cyclohexene since it breaks the bridge in $Rh_2(CO)_4Cl_2$.[18]

**(2) ESR Spectra.** An ESR spectrum of a solution 0.0419 M in $Rh_2(CO)_4Cl_2$ and $4 \times 10^{-4}$ M in TMPNO was run in hexane at room temperature. A three-line spectrum with $a_N$ = 15.5 G, $g$ = 2.004 was obtained. There was no observable broadening or splitting which could be attributed to $^{103}Rh$ ($I = \frac{1}{2}$, 100% abundant). TMPNO itself has $a_N$ = 15.21 G in cyclohexane; the $a_N$ values increase to 16-17 G upon complexation with hydrogen-bonding acids.[33] The $a_N$ value observed here indicates a very small interaction with $Rh_2(CO)_4Cl_2$ under these conditions, in complete accord with the synthetic, infrared, and calorimetric results with this base.

**(3) $^{13}C$ NMR Spectra.** At the outset of this work, the $^{13}C$ NMR spectra of I or its adducts $Rh(CO)_2ClL$ had not been reported, except for a mention of the $^{13}C$-$^{103}Rh$ coupling constant in I.[34] Since that time, a brief report has appeared. We wish here to report some observations on the $^{13}C$ NMR spectra of some compounds from this study.

With a natural abundance $^{13}C$ sample of I, no resonances in the region 170-250 ppm downfield of $Me_4Si$ (the normal range for $^{13}CO$ shifts in metal carbonyls[30,35]) were located. A sample of I was enriched to approximately 30% $^{13}CO$ by bubbling labeled CO (90.5 atm % $^{13}CO$, Merck, Sharp and Dohme, Canada Limited) through a $CH_2Cl_2$ solution of natural abundance I for 5 h. The spectrum of this enriched sample (approximately 0.08 M in benzene or $CDCl_3$) showed a doublet centered at 177.3 ($C_6H_6$) or 177.6 ($CDCl_3$) ppm downfield of $Me_4Si$, with $J_{^{13}C-^{103}Rh}$ = 76.6 ($C_6H_6$) or 77.7 ($CDCl_3$) Hz. The spectrum is in very good agreement with that of Todd et al.,[30] but the coupling constant is in disagreement with the earlier report of 69.9 Hz.[34]

The spectrum of a 0.05 M benzene solution of $Rh(CO)_2Cl(pip)$ (prepared in situ from the enriched I) shows a broad peak at 238.6 ppm, the breadth indicating that some exchange process is occurring in solution. A similarly prepared benzene solution of $Rh(CO)_2Cl(py)$ showed a sharp doublet at room temperature, centered at 183.1 ppm (with $J_{C-Rh}$ = 69.9 Hz). The retention of Rh-C coupling indicates that the exchange process with L = py is almost certainly

$$Rh(CO)_2ClL + L^* = Rh(CO)_2ClL^* + L$$

rather than a process involving CO exchange. In the case of the piperidine complex, the room temperature exchange rate is apparently slower than for the pyridine complex, and the spectrum is intermediate between fast and slow exchange. A spectrum of $Rh(CO)_2Cl(py)$ in toluene at −60° showed a fairly sharp doublet of doublets in the metal carbonyl region,

**Table III.** Calorimetric Results for the Reactions $Rh_2(CO)_4Cl_2 + 2L = 2Rh(CO)_2ClL$

| L | $C_B$[a] | $E_B$[a] | $-\Delta H_{obsd}$[b,c] | $-\Delta H_{calcd}$[d] | $K_{eq}$[c,e] |
|---|---|---|---|---|---|
| Pyridine | 6.40 | 1.16 | 12.5 ± 0.2 | 11.8 | Large |
| 4-Picoline | 6.47[f] | 1.26[f] | 12.5 ± 0.3 | 13.9 | Large |
| 1-Methylimidazole | 8.96 | 0.937 | 15.3 ± 0.1 | 14.9 | Large |
| Piperidine | 9.32 | 1.01 | 15.7 ± 0.6 | 16.3 | Large |
| *N,N*-Dimethylacetamide | 2.58 | 1.32 | 5.3 ± 0.1 | 5.4 | 53.8 ± 3.8 |
| Tetrahydrothiophene | 7.90 | 0.341 | 7.6 ± 0.3 | 7.6 | Large |
| Ethyl acetate | 1.74 | 0.975 | 0.3[g] | 0.7 | —[h] |
| 3,5-Dichloropyridine | — | — | 7.7 ± 0.3 | | $>10^{14}$ |
| Pyridine *N*-oxide | 4.52 | 1.34 | 6.5 ± 0.1 | | $(7.9 \pm 2.5) \times 10^5$ |
| *N,N*-Dimethylthioformamide | — | — | 12.0 ± 0.1 | | Large |
| Dioxane | 2.38 | 1.09 | ~0.5[i] | | —[h] |

[a] From ref 3, except as noted. [b] Kilocalories per mole of adduct. [c] Errors are one standard deviation. [d] Calculated from $-\Delta H + W = E_AE_B + C_AC_B$, with $E_A = 8.72$, $C_A = 2.02$, and $W = +11.3$ kcal mol$^{-1}$ of monomer. [e] Units of liter per mole. "Large" indicates that computer program was not used (see text). [f] M. P. Li and R. S. Drago, submitted. [g] Calculated from $-\Delta H_{obsd}$ with pyridine and 4-picoline in benzene (see above) and in EtOAc (−12.03 ± 0.25 and −12.40 ± 0.24 kcal/mol, respectively). [h] See text. [i] Calculated from $-\Delta H_{obsd}$ with 4-picoline in benzene (see above) and in dioxane (−12.02 ± 0.22 kcal/mol).

one doublet centered at 181.3 ppm and one centered at 185.6 ppm, with $J_{C-Rh} = 73$ and 67 Hz, respectively. The difference in chemical shifts of 4.3 ppm is due to the nonequivalent CO groups in the adduct. Assignment of signals to specific CO groups is not possible at present.

**(4) Reaction of $Rh_2(CO)_4Cl_2$ with Phosphites.** Reaction of $Rh_2(CO)_4Cl_2$ with $(CH_3O)_3P$ has been reported[16] to give $\{Rh(CO)Cl[(CH_3O)_3P]\}_2$, as indicated in reaction 3. Reaction of I with limited amounts of phosphines (i.e., less than 1 mol of phosphine/mole of Rh) gave compounds of the type $Rh(CO)_2ClL$ initially, and the dimeric compounds $[L(CO)RhCl]_2$, III (arising from loss of CO), precipitate slowly on standing. This solid did not form during the time and conditions of a calorimetric run.[15] Too few experimental details of the reaction with L = phosphite were given[16] to determine if this sequence of reactions also operates in that case. Investigations in this laboratory[36] indicate that reaction of I with $(CH_3O)_3P$ in benzene results in successive displacement of the carbonyls. Since the dimeric product (resulting from a reaction other than the one which we wish to study) appears immediately, calorimetric data for the adduct formation reaction (2) cannot be obtained with phosphite donors.

**(5) Calorimetry.** The calorimetric data for the reactions of I with various bases are found in Table II in the microfilm edition. Given there are the moles of base injected and heat evolved in calorimetric runs involving pyridine, 4-picoline, MeIm, THTP, piperidine, DMTF, pyO, $Cl_2py$, DMA, and $(C_6M_5)_3P$ in benzene, as well as reactions of pyridine and 4-picoline in other solvents. The values obtained for $\Delta H$ and $K_{eq}$ are presented in Table III. The enthalpy values reported there for pyridine and 4-picoline have been corrected for 0.9 kcal/mol for their interaction with benzene.[37] The known $E_B$ and $C_B$ numbers[3] for the bases are also reported in Table III. The enthalpies of reaction of I with the bases EtOAc and dioxane were obtained via displacement reactions in a manner analogous to the methylcobaloxime-THF enthalpy reported previously.[7] For this reason, $K_{eq}$ cannot be determined. Complications from solvation effects and incomplete cleavage of the dimer in this solvent lead to only approximate enthalpies.

Attempts were made to obtain calorimetric data on systems involving quinuclidene, bridged ether, and TMPNO as donors, but the results could not be used due to complications arising from either formation of a precipitate (quinuclidene) or low equilibrium constant (TMPNO, bridged ether).

Since none of the adducts of the form $Rh(CO)_2ClL$ possesses sufficient solubility in $CCl_4$ or alkanes, a less ideal solvent, benzene, had to be used. In the absence of specific interactions, benzene is not expected to give rise to large solvation energies. It has been shown[38] to obey the ESP solvent correction procedures[39] for several different acids. If any specific interaction were to exist between benzene and the metal complexes involved, it is expected that it would be of very comparable magnitude in the reactant I and product II.

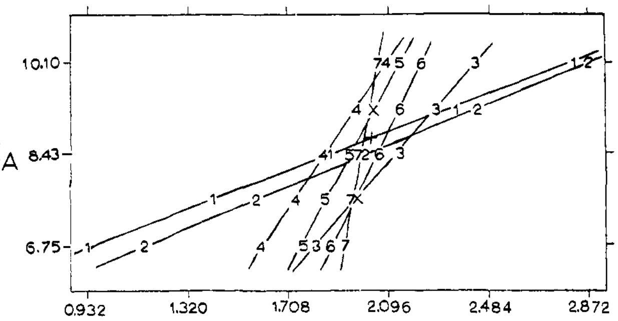


Figure 2. $E_A$ vs. $C_A$ plot for $Rh(CO)_2Cl$ with $W = +11.3$ kcal/mol (eq 1). Symbols used: 1 = EtOAc, 2 = DMA, 3 = pyridine, 4 = 4-picoline, 5 = piperidine, 6 = MeIm, and 7 = THTP.

In the absence of specific interactions, the only factors contributing to the observed enthalpies are the enthalpy of adduct formation, $\Delta H_{AB}$, and the enthalpy of dissociation of the dimer, $\Delta H_{diss}$. These are related by eq 10.

$$-\Delta H_{AB} = -\Delta H_{obsd} + \frac{1}{2}\Delta H_{diss} \qquad (10)$$

In a case such as this, where a constant contribution ($\Delta H_{diss}$ is independent of the base) to the observed enthalpies is present, the procedure of Guidry and Drago[21] can be used to solve the "extended" *E* and *C* equation (eq 11).

$$-\Delta H_{obsd} + W = E_AE_B + C_AC_B \qquad (11)$$

The *E* and *C* parameters have their original significance, and, in this case, *W* is the constant contribution, i.e., $\frac{1}{2}\Delta H_{diss}$. Using the data from Table II for EtOAc, DMA, THTP, pyridine, 4-picoline, piperidine, and MeIm, values of $E_A = 8.72$, $C_A = 2.02$, and $W = +11.3$ kcal/mol were obtained, with marginal standard deviations of 0.8, 0.08, and 1.1, respectively. A plot of the simultaneous equations which were solved to produce this *E* and *C* fit is shown in Figure 2. The wide range of *C*/*E* ratios (i.e., wide range of slopes) for the bases employed is apparent from this figure. The deviation of 1.1 in the value of $-\frac{1}{2}\Delta H_{diss}$ will not affect the internal consistency of the predictions of the enthalpies for base-$Rh(CO)_2Cl$ interactions with the *E* and *C* equation, or the $\Delta H_{obsd}$ values obtained by adding $W$ to $\Delta H_{AB}$. However, this constant source of uncertainty must be taken into account when the $E$ and $C$ values for the acidity of "$Rh(CO)_2Cl$" are compared with other acids. For such purposes, we can employ a constant value (i.e., one without uncertainty) of +11.3 kcal/mol for $\frac{1}{2}\Delta H_{diss}$, and arrive at errors of 0.32 and 0.05 in $E_A$ and $C_A$, respectively.

Dioxane and pyO are difficult to purify: dioxane because of its ready formation of peroxides, and pyO because of its very hygroscopic nature. Data on these systems were omitted from the $E_A$, $C_A$, $W$ fits. Particularly, in the case of dioxane, when a substance is used as a solvent, a small concentration (relative to concentration of solvent molecules) of impurity can still be of comparable magnitude to the concentrations of acid and base employed. In the case of pyO, steric interactions may also be of some consequence in the enthalpy. The bases $Cl_2py$, DMTF, and $(C_6H_5)_3P$ cannot be included in the $E$ and $C$ fit, since $E_B$ and $C_B$ parameters are not presently available for these compounds. $(C_6H_5)_3P$ would probably not fit well even if valid $E_B$ and $C_B$ numbers were available (vide infra).

The $C_A/E_A$ ratio of 0.23 found for $Rh(CO)_2Cl$ is relatively large when compared with that of most other acids for which $E_A$ and $C_A$ numbers are known. It is much larger than typical hydrogen-bonding acids ($C_A/E_A \sim 0.10$), and about equal to that of $B(CH_3)_3$ ($C_A/E_A = 0.28$). Qualitatively, this indicates a large relative importance of covalency in the bonding, as expected for a low-valent metal complex with ligands such as CO. Also interesting are the magnitudes of $E_A$ and $C_A$. They are both larger than for most of the acids in the correlation at present. Since $Rh_2(CO)_4Cl_2$ is easily purified and handled, it is a valuable reference acid for $E$ and $C$ work with donors which are not $\pi$-acceptors. Were it not for the endothermic contribution of $\frac{1}{2}\Delta H_{diss}$, the experimental heats of interaction would be quite large.

The value of $\Delta H_{diss}$ = 22.5 kcal mol$^{-1}$ of dimer is of quite reasonable magnitude. It compares with the value of 23.8 kcal/mol for the chloro-bridged species $Fe_2Cl_6$.[40] Some data on other halide-bridged dimeric metal complexes have recently been published.[41]

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**Supplementary Material Available:** Calorimetric and infrared data (Tables I and II) (10 pages). Ordering information is given on any current masthead page.

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