An Acid–Base Model for Mixed Metal Dimer Formation: Enthalpies of Dimer Cleavage and Adduct Formation of 1,5-Cyclooctadiene–Rhodium(I) Chloride Dimer[1a,b]

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Abstract: Solvation-minimized enthalpies and equilibrium constants have been obtained calorimetrically for the reaction $[RhCl(COD)]_2 + 2B \rightarrow 2[Rh(Cl)(COD)(B)]$, where COD = 1,5-cyclooctadiene. This reaction has been studied with B = pyridine, tetrahydrothiophene, piperidine, 1-methylimidazole, 4-picoline, dimethylthioformamide, morpholine, 1-azabicyclo[2.2.2]octane, dimethylacetamide, 7-oxabicyclo[2.2.1]heptane, triethylamine, hexamethylphosphoramide, acetonitrile, dimethyl sulfoxide, triethyl phosphate, tetrahydrofuran, and pyridine *N*-oxide. From enthalpies measured in benzene, we are able to determine the constant contribution to the enthalpy of the reactions from breaking the rhodium–chloride bridge bonds. We make a comparison of our "solvation-minimized" data with data obtained for the same system in more polar, acidic, solvents. The cyclooctadiene–rhodium chloride dimer, along with the recently investigated bis(carbonyl)rhodium chloride dimer constitutes the first time that second row transition metal Lewis acids have been examined in the context of the *E* and *C* correlation. A comparison of the behavior of these rhodium acids with each other as well as with other known acids is enlightening in view of the notions about bonding in low-valent, heavy metal complexes that have emerged from synthetic studies. A general guideline is offered for the design and synthesis of unsymmetrical bimetallic systems, e.g., $CODRh(Cl)_2Rh(CO)_2$.

Introduction

Because of their significance to the area of homogeneous catalysis,[2-8] the organometallic complexes of the group 8 metals having a d^8 configuration have been extensively studied. Olefin coordination complexes of rhodium(I) have been employed in synthetic,[9-13] spectral,[14-17] kinetic,[18-20] and catalytic[21] studies. It is widely accepted that in many of the catalytic processes involving these materials, coordination of the substrate to the metal is an essential step. In spite of this, there is little quantitative information on the strength of interaction of these heavy-metal complexes with various kinds of Lewis bases.

One of the first reported[11] series of rhodium adducts involved bis(cycloocta-1,5-diene)-μ,μ'-dichloro-dirhodium(I), $[RhCl(COD)]_2$, shown by x-ray analysis to be a halide-bridged dimer with the rhodium atoms in a square-planar configuration. This dimer reacts with amines to form adducts of general formula, [(COD)Rh(Cl)(amine)]. The dimer and its adducts are only slightly soluble in the weakly interacting solvents, cyclohexane and carbon tetrachloride, which one prefers to use to obtain coordinate bond energies. These species are soluble in benzene, but the resulting data might include enthalpic contributions from solvation. This would prevent us from obtaining information about the actual acid–base strength of interaction and the nature of the acceptor properties of the metal center. However, previous work from this laboratory shows that if an acid is held constant and the base varied in the solvent benzene, the enthalpy measured for several bases differs from that in weakly interacting solvents by a constant amount, depending on the acid employed.[22,23] This enables a direct comparison to be made between different bases interacting with this acid. Furthermore, we have reported a procedure which enables us to determine the magnitude of any constant contribution to the enthalpies of a series of adducts.[24] Thus, obtaining the constant contribution (due to solvation energies and cleavage of the chloro-bridged dimer) enables us to determine the "solvent-minimized" enthalpy expected for the monomer RhCl(COD) reacting with bases (i.e., an enthalpy approaching the gas-phase value).

This solvation-minimized enthalpy of adduct formation with various Lewis bases can be used to test our double-scale enthalpy equation,[25]

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

where the subscripts A and B denote acid and base, respectively, while *E* and *C* are two empirically derived parameters assigned to each. A comprehensive listing of these parameters has been reported and the quantitative aspects of Lewis acid–base interactions recently reviewed.[26,27] Before the investigation of the Lewis acidity of rhodium(I) dimeric systems, only two transition metal ion complexes had been incorporated into the *E* and *C* correlation—bis(hexafluoroacetylacetonato)copper(II)[28] and methylcobaloxime[29]—both having metal centers from the first row. It is of interest to test the limitations and scope of our *E* and *C* model by investigating systems quite different from those used in the parameterization. The base parameters were largely derived from enthalpies of formation on systems where the acid–base interaction involved relatively simple σ-bond formation (i.e., hydrogen bonding and charge transfer adducts). The bonding to transition metal acids is much more complex, and there is more likelihood for the *E* and *C* equation to fail. Such failures have the potential of providing new insights about intermolecular interactions. At the very least, the study of transition metal ion and organometallic systems extends these thermodynamic measurements into an area where little quantitative, meaningful data exist, and much speculation about bond strengths is offered.

Experimental Section

Materials. $[RhCl(COD)]_2$ and $[RhCl(CO)_2]_2$ were prepared by previously reported procedures.[10,11,30] Anal. Calcd for $[C_8H_{12}RhCl]_2$: C, 38.97; H, 4.92; Rh, 41.74; Cl, 14.38; mol wt, 493. Found: C, 39.09; H, 4.85; Rh, 41.67; Cl, 14.50; mol wt (in benzene), 490. Calcd for $[C_2O_2RhCl]_2$: C, 12.36; Cl, 18.24. Found: C, 12.69; Cl, 18.40.

Tetrahydrothiophene (THTP) was dried over CaH_2 for 24 h and fractionally distilled from fresh CaH_2 at atmospheric pressure. Tetrahydro-1,4-oxazine (morpholine) and triethyl phosphate (TEP) were fractionally distilled at reduced pressure from BaO. *N,N*-Dimethylthioformamide (DMTF) was fractionally distilled under reduced pressure at least twice and stored in a desiccator over calcium sulfate in the absence of light. In all distillations, only the middle fraction was collected. Reilly Tar and Chemical Corp. pyridine *N*-oxide was sublimed at 110 °C at ~0.5 mm. All other reagents were obtained and purified as previously described.[24,28-33]

Solutions were prepared in a nitrogen-filled glove bag using thoroughly dried glassware. The calorimeter cells were dried and flushed with nitrogen prior to use.

Apparatus and Procedure. The description of the modified calorimeter and the experimental procedure have been previously re-

Table I. Thermodynamic Results for the Interaction of $[RhCl(COD)]_2$ with Various Bases at 24 ± 1 °C: a Comparison of Corrected Measured Enthalpies vs. E and C^a Calculated Enthalpies

Base	E_B	C_B	K^b	$-\Delta H_{meas}{}^{c,j}$	$-\Delta H_{cor}{}^{d,j}$	$-\Delta H_{calcd}{}^{e,j}$
Pyridine	1.17	6.40	1.1×10^3	6.6 ± 0.05	13.8^f	13.8
Pyridine (triethyl phosphate)	1.17	6.40	4.1×10^3	7.1 ± 0.03	13.2	13.
4-Picoline	1.26	6.47^g	4.7×10^3	7.2 ± 0.1	14.5^f	14.3
4-Picoline (tetrahydrofuran)	1.26	6.47	8.7×10^2	7.7	13.8	14.3
Tetrahydrothiophene	0.341	7.90	2.4×10^1	5.3 ± 0.02	11.5	11.6
1-Methylimidazole	0.934	8.96	Very large	9.7 ± 0.2	16.0	15.8
Piperidine	1.01	9.29	2.8×10^5	10.1 ± 0.06	16.4	16.6
Dimethyl sulfoxide	1.34	2.85	7.6×10^1	3.8 ± 0.14	10.1	10.2
Quinuclidine[h]	0.704	13.2	1.8×10^1	7.0 ± 0.02	13.3	20.0
Dimethylthioformamide	i	i	1.0×10^6	8.9 ± 0.2		
Morpholine	i	i	7.2×10^3	9.8 ± 0.1		

[a] E and C numbers taken from ref 27. The solvent employed in these studies is benzene unless otherwise indicated in parentheses in the base column. [b] In units of l./mol for the reaction $A_2 + 2B \rightarrow 2AB$. [c] Actual measured enthalpies uncorrected for the enthalpy of dimerization and solvent interactions, i.e., enthalpies for the reaction $[RhCl(COD)]_2 + 2B \rightarrow 2RhCl(COD)\cdot B$. [d] Enthalpies corrected for one-half the endothermic enthalpy of dimerization and for any acid interaction with benzene solvent (together, a constant correction of 6.27 kcal/mol). $-\Delta H_{calcd} = -\Delta H_{meas} + W$. [e] Enthalpies calculated using eq 1 and $E_A = 4.93$, $C_A = 1.25$ for RhCl(COD). As in past work in which there is a constant contribution to the measured $-\Delta H$, we report E_A and C_A parameters for predicting enthalpies devoid of this constant contribution. [f] Also corrected for 1.0 kcal/mol specific interaction of pyridine (or 4-picoline) with benzene. [g] Recently refined parameters $E_B = 1.26 \pm 0.03$ and $C_B = 6.47 \pm 0.1$. (Calculated using enthalpies of adduct formation with iodine, *p*-fluorophenol, phenol, *m*-trifluoromethylphenol, Rh(COD)Cl, and $Rh(CO)_2Cl$ of $-\Delta H$ = 7.8, 8.3, 8.3, 9.1, 14.3, and 23.9 kcal/mol, respectively.) [h] This base was not included in the determination of E_A and C_A for RhCl(COD). In this case, the large discrepancy between the experimental and calculated enthalpies suggests the existence of steric hindrance to adduct formation. [i] Reliable E_B and C_B parameters have not yet been determined for this base. [j] In enthalpy units of kcal/mol of adduct formed.

ported.[29,34] The computer program for simultaneous determination of enthalpies and equilibrium constants has also been described.[29] In all instances, the reliability of the calculated quantities was checked by graphing K^{-1} vs. ΔH to demonstrate that the data points gave rise to lines with appreciably different slopes.

Characterization of Compounds. The monomeric Rh(COD)Cl·pip and Rh(COD)Cl·py adducts were isolated as solid, stable yellow compounds by stripping the solvent from the solution following calorimetry experiments. The piperidine adduct behaved in accord with literature[11] reports of decomposition at 150–170 °C. Anal. Calcd for Rh(COD)Cl pip, $C_{13}H_{23}NClRh$: C, 47.07; H, 6.99; N, 4.22; Cl, 10.69; mol wt, 332. Found: C, 47.01; H, 6.76; N, 4.06; Cl, 10.73; mol wt in (benzene), 355. The monomeric adducts as well as the $[RhCl(COD)]_2$ dimer were characterized by ^1H NMR, ^{13}C NMR, and ir spectra. The ^1H NMR spectra were recorded in $CDCl_3$ solutions at ambient temperature on a Jeolco C-6OH spectrometer using tetramethylsilane as the internal reference. The ^{13}C Fourier transform NMR spectra were measured in C_6D_6 solution at 25.1 MHz with a Varian XL-100 spectrometer. An internal ^2H lock signal was used for field stabilization. Tetramethylsilane was used as the internal ^{13}C standard. Infrared spectra recorded as Nujol mulls and the $CHCl_3$ solution on a Perkin-Elmer Model 457 grating infrared spectrophotometer or a Beckmann IR-12 instrument were found to agree with the literature.[35] Attempts at isolating analogous pure solid, monomeric adducts for THTP and quinuclidine from the calorimetric solutions were not successful.

Results

The concentrations, volumes, and heat evolved for the reaction of $[RhCl(COD)]_2 + 2B \rightarrow 2[Rh(Cl)(COD)(B)]$ in benzene are available in the microfilm edition. The experimentally measured enthalpy H' reported is the total heat evolved, corrected for the heat of solution of the added pure base solution in benzene at the corresponding concentration. Thermodynamic data for the interaction of $[RhCl(COD)]_2$ with various bases in benzene solvent are reported in Table I. The E and C values of bases used in this study are also listed in this table along with the enthalpies calculated from the E and C equation. As in past work, we have reported E and C values which predict enthalpies which are devoid of any constant enthalpy contributions. Thus, the E and C calculated enthalpies should be compared to measured values of the enthalpy which have been corrected for one-half the enthalpy of dimerization and any constant enthalpy contributions from solvent interactions, i.e., $-\Delta H_{cor}$. The uncorrected measured enthalpy, in units of kilocalories/mole of adduct formed, is reported in Table I as $-\Delta H_{meas}$.

Table II contains bases which showed little or no measurable interaction with $[RhCl(COD)]_2$ by our calorimetric procedure. These included several oxygen donors and two nitrogen donors—the weak donor, acetonitrile, and the bulky donor, triethylamine. Attempts were also made to obtain desired enthalpic data via displacement reactions in an oxygen donor as solvent, B′,

$$(COD)Rh\cdot Cl\cdot B' + C_5H_5N \rightarrow (COD)Rh\cdot Cl\cdot C_5H_5N + B' \quad (2)$$

using the strong donors pyridine or 4-picoline to displace coordinated solvent. Low-dielectric constant, oxygen-donor solvents (specifically, B′ = tetrahydrofuran, triethyl phosphate, and 7-oxabicyclo[2.2.1]heptane) were selected, since nonspecific solvation contributions to the measured enthalpic data were expected to be low. A rough value for the enthalpy of adduct formation of (COD)RhCl·B can be obtained using displacement reaction experiments, only if the dimer is completely cleaved by the solvent (or its extent of cleavage known). Molecular weight determinations showed that the dimer remains almost completely intact in tetrahydrofuran as well as bridged ether, indicating very low equilibrium constants for cleavage of the dimer by these oxygen donors to form 1:1 adducts.

Discussion

***E* and *C* Parameters for 1,5-Cyclooctadiene–Rhodium(I) Chloride Monomer.** Since $[RhCl(COD)]_2$ exists as a dimer in solution, the calorimetrically measured enthalpies of interaction of $[RhCl(COD)]_2$ with various bases must be corrected for the enthalpy of dimerization in order to cast these enthalpies into a form amenable to the E and C equation. In other words, instead of the usual simple adduct formation reaction $A + B \rightarrow AB$ employed in the E and C approach, the enthalpy measured with the dimer corresponds to

$$A_2 + 2B \rightarrow 2AB \quad (3)$$

Table II. Lewis Bases Which Showed Little or No Measurable Interaction in Benzene at 24 ± 1 °C via the Calorimetric Procedure for the Reaction $[RhCl(COD)]_2 + 2B \rightarrow 2RhCl(COD){\cdot}B$

Base	E_B	C_B[a]	$-\Delta H_{calcd}$[b,d]	Predicted $-\Delta H$ $(A_2 + 2B)$[c,d]
N,N-Dimethylacetamide	1.32	2.58	9.5	3.4
7-Oxabicyclo[2.2.1]-heptane	0.887	4.11	9.5	3.6
Pyridine N-oxide	1.34	4.52	12.0	5.9
Triethyl phosphate	1.36	1.81	8.8	2.6
Tetrahydrofuran	0.978	4.27	10.0	3.9
Hexamethylphosphoramide	1.52	3.55	11.7	5.6
Triethylamine	0.991	11.09	18.5	12.4
Acetonitrile	0.886	1.34	5.9	

[a] E and C numbers taken from ref 27. [b] Enthalpies calculated using eq 1 and $E_A = 4.93$ and $C_A = 1.25$ for RhCl(COD). The precision expected in these enthalpies is ±0.2 kcal/mol. [c] These are the values for the enthalpies that we expect to measure experimentally. They are obtained from $(-\Delta H_{calcd} - W)$, where W includes one-half of the endothermic enthalpy of dimerization. [d] In enthalpy units of kcal/mol of adduct formed for the reaction described in the title.

The enthalpy for eq 3 is related to the enthalpy of simple adduct formation as follows:

$$\begin{tikzcd} A_2 \arrow[d, "-\Delta H_{dimer}"'] & + & 2B \arrow[d] \arrow[r, "\Delta H_{meas}"] & 2AB \\ 2A & + & 2B \arrow[r, dash, "2\Delta H_{association}"'] & {} \arrow[u] \end{tikzcd}$$

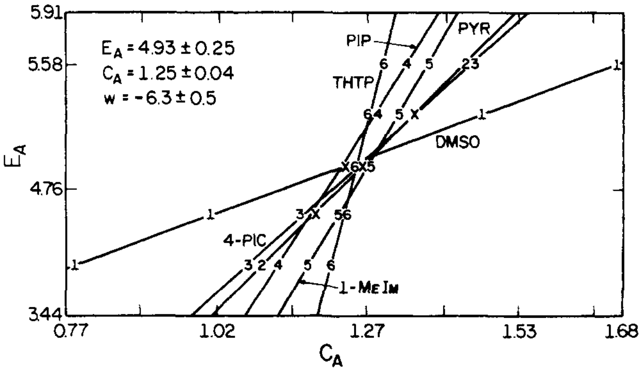
Thus, one needs to account for the constant contribution to the measured enthalpy from the heat it takes to break a mole of the dimer and divide the resulting enthalpy by two in order to obtain data consistent with other 1:1 adducts studied in E and C work. Our computer program solves the $A_2 + 2B \rightleftarrows 2AB$ equilibrium and yields a net enthalpy for the reaction in terms of kilocalories/mole of adduct formed. This value has an unresolved contribution from one-half the heat of dimerization of A_2 included in it.

A recently reported procedure[24] enables one to factor out such a constant contribution from data on a series of adducts in which it is present. One solves a series of equations of the form

$$-\Delta H_{meas} + W = E_A E_B + C_A C_B \qquad (4)$$

for the best set of acid (or base) parameters and the constant enthalpy contribution W. A series of different bases (i.e., different C_B/E_B ratios) should be used. For this particular case, W is the constant contribution to the enthalpy from both one-half the enthalpy of dissociation of $[RhCl(COD)]_2$ plus that from solvation.

Using the data in Table I in the column $-\Delta H_{meas}$, we obtain values of $E_A = 4.93$, $C_A = 1.25$, and $W = 6.3$ kcal/mol (calculated per mole of monomer) with marginal standard deviations of 0.25, 0.04, and 0.5, respectively. The quality of the fit can be graphically displayed by holding W constant at 6.3 kcal/mol as shown in Figure 1. The slopes of the various lines for the six bases employed are significantly different, since bases were used which afforded a wide range of C_B/E_B ratios (varying from 2.1 to 23.2). Thus, reasonable confidence may be placed in the E_A and C_A parameters determined for this acid. It should be emphasized that the standard deviation of 0.5 in W does not introduce this error into our ability to predict the enthalpy of reaction corresponding to eq 3 when a W of 6.3 kcal/mol is employed along with the corresponding E_A and C_A parameters.



Plot of E_A vs. C_A Rh(COD)Cl

Figure 1.

Table III. A Comparison of Thermodynamic Results for the Interaction of Rhodium(I) Chloride Dimers with Various Lewis Bases in Benzene at 24 ± 1 °C: $[L_2RhX]_2 + 2B \rightarrow 2L_2{\cdot}Rh{\cdot}X{\cdot}B$

	$[Rh(COD)Cl]_2$		$[Rh(CO)_2Cl]_2$[d]	
B	$-\Delta H_{meas}$[a,b]	$-\Delta H_{calcd} - W$[a,c]	$-\Delta H_{meas}$[a,b]	$-\Delta H_{calcd} - W$[a,c]
Pyridine	7.6 ± 0.05[e]	7.5	12.6 ± 0.2[e]	11.8
4-Picoline	8.2 ± 0.1[e]	8.3	12.6 ± 0.3[e]	13.0
Tetrahydrothiophene	5.3 ± 0.02	5.3	7.6 ± 0.3	7.6
1-Methylimidazole	9.7 ± 0.2	9.6	15.3 ± 0.1	14.9
Piperidine	10.1 ± 0.06	10.3	15.7 ± 0.6	16.3
Me_2SO	3.8 ± 0.14	3.9		
DMA			5.3 ± 0.07	5.4

Acid	E_A	C_A	C_A/E_A	W[a]
Rh(COD)Cl	4.93 ± 0.25	1.25 ± 0.04	0.25	−6.3 ± 0.5
$Rh(CO)_2Cl$[d]	8.72 ± 0.8	2.02 ± 0.1	0.23	−11.3 ± 1.1

[a] In units of kcal/mol of adduct formed. [b] Actual measured enthalpies. [c] Enthalpies calculated from $-\Delta H_{meas} = E_A E_B + C_A C_B - W$ [d] Taken from ref 37. [e] Corrected for 1.0 kcal/mol specific interaction of pyridine with benzene.

It is of interest to compare our results for the interaction of the 1,5-cyclooctadiene–rhodium(I) chloride dimer toward various Lewis bases with analogous results obtained for the bis(carbonyl)rhodium(I) chloride dimer.[36,37] In replacing the diolefin of $[Rh(COD)Cl]_2$ with the poorer donor carbonyl ligands, one obtains a much better Lewis acid in $[Rh(CO)_2Cl]_2$. The decreased enthalpies of adduct formation for the former as seen in Table III is reflected in the magnitudes of both the E_A and C_A parameters. The values of 8.72 and 2.02 for E_A and C_A, respectively, of the bis(carbonyl) complex are decreased to 4.93 and 1.25 in the COD complex. Thus, although the E_A and C_A parameters for $[Rh(CO)_2Cl]_2$ are almost twice those obtained for $[Rh(COD)Cl]_2$, the C_A/E_A ratios for these two rhodium(I) acids are quite similar. It is significant to note that in qualitative terms, the very pronounced change in substituent in these two compounds has had little effect on the relative importance of covalent and electrostatic donor preference.

The results we have obtained are consistent with the idea of increased σ donation and decreased π acceptance by olefins compared to carbonyl ligands. Recent self-consistent-field $\chi\alpha$-scattered wave calculations on the electronic structure of

Table IV. Comparison of C_AC_B/E_AE_B Ratios for 1,5-Cyclooctadiene Rhodium(I) Chloride with Other Acids Using the Reference Base Pyridine[a]

Acid	C_A	E_A	C_A/E_A	C_B/E_B	C_AC_B/E_AE_B
I_2	1.00	1.00	1.0	5.5	5.5
Cu(hfac)$_2$	1.32	3.46	0.38	5.5	2.1
$B(CH_3)_3$	1.70	6.14	0.28	5.5	1.5
Rh(COD)Cl	1.25	4.93	0.25	5.5	1.4
Rh(CO)$_2$Cl	2.02	8.72	0.23	5.5	1.3
Methylcobaloxime	1.53	9.14	0.17	5.5	0.92
Phenol	0.44	4.33	0.10	5.5	0.56
$CHCl_3$	0.16	3.02	0.05	5.5	0.29

[a] The E and C numbers for these acids and the reference base, pyridine, are taken from ref 27.

Table V. Data Plotted in Figure 2

Base	P_B[a]	[Rh(COD)Cl]$_2$ $-\Delta H_{COD}$[c,d]	[Rh(CO)$_2$Cl]$_2$ $-\Delta H_{CO}$[c,d]
DMA	1.97		16.6
DMSO	2.05	10.1	
THTP	2.32	11.6	18.9
pyr	2.77	13.9[g]	23.9[g]
4-pic	2.96	14.5[g]	23.9[g]
1-MeIm	3.17	16.0	26.6
pip	3.33	16.4	27.0
Cl_{COD}	1.26[b]	6.3[e]	
Cl_{CO}	1.31[b]		11.3[f]

Plot	Theor Slope	Slope found[i,j]	Intercept found[i,j]
$-\Delta H_{CO}$ vs. $-\Delta H_{COD}$	1.77[h] ± 0.23	1.67 ± 0.30	−0.15 ± 4.1
$-\Delta H_{COD}$ vs. P_B	4.93[k] ± 0.25	4.97 ± 0.35	−0.11 ± 0.97
$-\Delta H_{CO}$ vs. P_B	8.72[k] ± 0.75	8.0 ± 1.1	0.70 ± 3.1

[a] Calculated from eq 7, $P_B = E_B + (C_A/E_A)C_B$. [b] Obtained by extrapolation from the graph in Figure 2 for W_{COD}, W_{CO}. [c] Actual measured enthalpies in benzene corrected for the constant contribution W. [d] In units of kcal/mol of adduct formed. [e] $-W_{COD}$, the enthalpy required to break a Rh(COD)–Cl bond. [f] $-W_{CO}$, the enthalpy required to break a Rh(CO)$_2$–Cl bond. [g] Corrected for 1.0 kcal/mol specific interaction of pyridine (or 4-picoline) with benzene. [h] Theoretical slope = E_{CO}/E_{COD}. [i] Obtained from a least-squares fit of the data. Theory predicts a zero intercept. [j] 90% confidence interval. [k] Theoretical slope = E_A.

Zeise's anion[38] show that the σ-bonding component is far more important than π backbonding in the total bonding description of ethylene to Pt. The bond formed between the metal and olefin ligand is accompanied by a weakening of the bond to the chlorine in the position trans to the olefin. This is manifested in the smaller enthalpy required to cleave the rhodium–chlorine bridge bond in the COD dimer compared to the bis(carbonyl) dimer. The decreased Lewis acidity of the COD dimer reflected quantitatively in the E_A and C_A parameters for these two Rh(I) centers is also in complete accord with a decreased σ donation and/or increased π acceptance in carbonyl ligands compared with olefins.

Comparison of the behavior of this transition metal acid with other known acids is enlightening in view of ideas about bonding in low valent, heavy metal complexes. If the C parameters relate to covalent bonding and the E parameters to electrostatic bonding, then the relative covalent character of acid–base adducts might be compared by comparing their C_AC_B/E_AE_B ratios.[25,26] As shown in Table IV, Rh(COD)Cl lies between the two transition metal acids, Cu(hfac)$_2$[28] (C = 1.40 and E = 3.39) and methylcobaloxime[29] (C = 1.53 and E = 9.14) in terms of its C/E ratio. The C_A/E_A ratio is such that one observes with the acid an enthalpic preference for sulfur donors over oxygen donors. The large C/E ratio for Cu(hfac)$_2$ is surprising when compared to the rhodium acids. However, this relatively large ratio is seen upon inspection to be due to an unusually small E_A value for this copper system when compared, for example, to methyl cobaloxime or even $CHCl_3$. This can be attributed to repulsion from flanking atom electron density in the copper adducts reducing the importance of the electrostatic contribution.[39]

It is conceivable that the Rh(COD)Cl fragment might present certain steric requirements to an incoming ligand, The calculated enthalpy of 20.0 kcal/mol for formation of the Rh(COD)-Cl-quinuclidine adduct compared to the corrected measured value of 13.3 kcal/mol supports the existence of steric hindrance to adduct formation. Indeed, molecular models of this rhodium dimer show possible steric interactions with quinuclidine which are absent with pyridine. Steric hindrance and/or low equilibrium constants might also account for why we were unable to measure "expected" enthalpies predicted from our E and C equation for triethylamine, hexamethylphosphoramide, and pyridine N-oxide with [Rh(COD)Cl]$_2$. With the exception of acetonitrile, the remaining bases that showed negligible heats of interaction with [Rh(COD)Cl]$_2$ in Table II are all oxygen donors. Even if steric effects are absent in each of these latter cases, it would still be extremely difficult to measure an enthalpy as small as that predicted by the E and C equation with our present calorimetric technique (especially if the equilibrium constant is also low), since the enthalpy measured is the net enthalpy of adduct formation and the heat required to break the dimer (~12.6 kcal/mol as estimated from W). To check on the validity of using the E_B and C_B parameters for dimethyl sulfoxide (Me_2SO) as an oxygen donor, infrared spectral data for Me_2SO in benzene solution with varying concentrations of [Rh(CO)Cl]$_2$ added were examined. Coordination through the sulfur in Me_2SO would have been indicated by an observed increase in the S=O stretching frequency compared to that of free Me_2SO, which absorbs ~1050 cm^{-1}.[40-42] However, the infrared spectra gave no indication of the sulfur-bonded adduct within the range of concentrations employed in the calorimetric experiment.

A One-Parameter Treatment. It is possible to gain some insight into the formation of mixed dimer species such as $Rh_2Cl_2(COD)(CO)_2$ from the present data. There is considerable interest in the design and preparation of novel mixed cluster systems for use as potential catalysts; but, as yet, few generalizations exist to guide one in their preparation. With these considerations in mind, it is of interest to determine the enthalpies of formation of mixed dimers. One can show that when the C_A/E_A ratios of a series of acids are similar, the E and C equation can be converted from the double-scale enthalpy relation shown in eq 1 to a single-scale enthalpy relation.[26] A one-parameter model requires that a plot of the enthalpies of adduct formation of one acid vs. the enthalpies of adduct formation of another acid for the same series of bases be linear with a zero intercept.[26,43,44] We obtain a good fit of our experimental data to the one-parameter model for such a plot as indicated in Table V.

The one-parameter linear correlation for these acids with similar C_A/E_A ratios can be readily derived from the E and C equation by rearranging eq 1 to give

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

or

$$-\Delta H = E_AP_B \qquad (6)$$

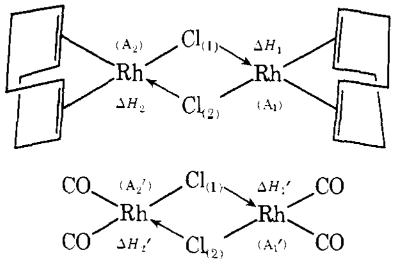
where

$$P_B = E_B + (C_A/E_A)C_B \qquad (7)$$

Equation 6 is a linear relationship with a zero intercept and a slope equal to E_A for the particular acid. Figure 2 is a plot of the enthalpies of adduct formation for each rhodium dimer vs. the base parameter, P_B, calculated from eq 7, for a given Lewis base. All the experimentally measured enthalpies employed in eq 6 are corrected for the constant contribution W, i.e., those in Table I under the heading $-\Delta H_{\text{cor}}$. Again, as shown in Table V, good agreement within experimental error is obtained between the theoretical and experimental slopes and intercepts. (The graph as shown in Figure 2 does not extend to the origin.) If for some reason, a given base (or acid) can only be studied with one of a series of acids (or bases) with a similar C/E ratio, a one-parameter equation is of value in predicting enthalpies of reaction toward the other acids of this type. In the next section we shall show how this approach can be effectively utilized to aid in predicting bridge cleavage energies.

Bridge Cleavage Energies. The values of W obtained above in benzene are clearly dominated by the bridge cleavage energies. It has been shown[45,46] that in benzene one obtains similar enthalpies to those obtained in CCl_4 or hexane when one corrects for the specific acid-base interactions. Since this dimer remains intact in benzene, any specific acid-base interactions would occur at the two vacant coordination sites of each rhodium center in the square-planar dimer. These positions are still vacant in the adduct. The only way coordination of solvent could contribute to the observed enthalpy is to have a pronounced difference between the enthalpy of coordination of the solvent in the dimer and the adduct. Since the enthalpy of this interaction, if it exists, is expected to be small, the difference would be even smaller. This argument receives support by virtue of the fact that the enthalpies of adduct formation measured in the nonpolar, basic solvents, triethyl phosphate and tetrahydrofuran, are very similar to those measured in benzene (see Table I). If the strength of basic solvent coordination to the free acid (giving rise to either a five- or six-coordinate species in solution) varied greatly from that expected for the adduct, the difference in the enthalpy measured in tetrahydrofuran and benzene or in triethyl phosphate and benzene would have been appreciable instead of the 0.5 kcal/mol actually found. The actual differences are those expected for a very weak interaction of this sort or for slight differences in the nonspecific solvation of adduct and acid which might exist in these slightly more polar solvents. Thus, we can safely conclude that W from the benzene solvent data is comprised predominantly of the energy to cleave the dimer.

Since we know the enthalpy for the Rh(L)-chloride bridge cleavage, W_{COD} and W_{CO}, we can extrapolate from the plot in Figure 2 to obtain estimates of P_B for Cl_{COD} and Cl_{CO}, i.e., for the donor chlorides on the COD and bis(CO) complexes. These P_B's represent an average basicity for the two steps in which the chlorides form the two acid-base bonds in each dimer as shown below. We can think of dimerization as a two-step process where ΔH_1 and ΔH_2 represent the enthalpies of forming the two consecutive acid-base bridge bonds for the COD dimer and $\Delta H_1'$ and $\Delta H_2'$ for the bis(carbonyl) dimer. The enthalpy of dissociation, W, is an average of cleaving both bonds in the dimer.



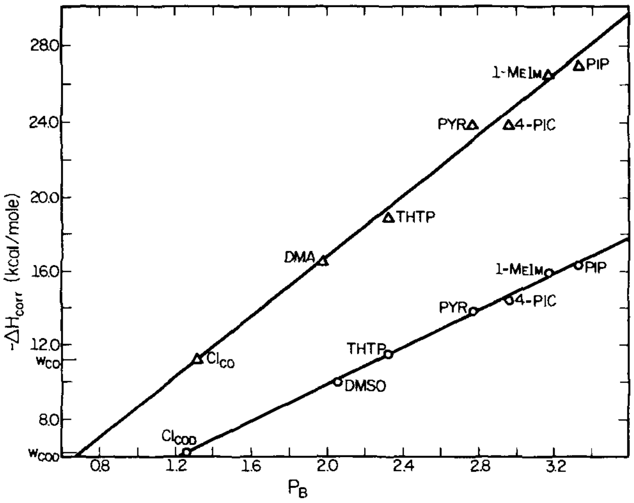


Figure 2. Plot of corrected enthalpies of adduct formation for $[Rh(L)Cl]_2$ with various Lewis bases in benzene vs. a base parameter P_B. Symbols used: ○, L is COD; △, L is $(CO)_2$.

In employing this approach, we are, in effect, assuming that, after the first bridge forms, any minor increase in the acidity of the rhodium site A_2 can be accommodated by using an average value for the E_A and C_A parameters. To a good approximation, we can write $E_{A_1} \approx E_{A_2} = E_A$ and $C_{A_1} \approx C_{A_2} = C_A$. Then

$$\Delta H_1 = E_A E_{Cl_{(2)}} + C_A C_{Cl_{(2)}} \qquad (8)$$

$$\Delta H_2 = E_A E_{Cl_{(1)}} + C_A C_{Cl_{(1)}} \qquad (9)$$

The following relationship can then be derived:

$$^1/_2(\Delta H_1 + \Delta H_2) = E_A E_{Cl} + C_A C_{Cl} \qquad (10)$$

where

$$E_{Cl} = {}^1/_2(E_{Cl_{(2)}} + E_{Cl_{(1)}}) \qquad (11)$$

and

$$C_{Cl} = {}^1/_2(C_{Cl_{(2)}} + C_{Cl_{(1)}}) \qquad (12)$$

Thus, the average enthalpy of the two-step bridge cleavage can be predicte by using an average E_B and C_B number for the coordinated chloride of each complex.

We next consider the prediction of the average bridge dissociation energy using eq 6. Using COD and CO subscripts to label the acid centers and unprimed and primed P_B values to label the basic chlorides on the COD and bis(carbonyl) complexes, respectively, we write

$$-W_{\text{COD}} = E_{\text{COD}} P_{Cl} \qquad (13)$$

$$-W_{\text{CO}} = E_{\text{CO}} P_{Cl}' \qquad (14)$$

Here W is written as an exothermic process, i.e., formation of the bridge bond. Since we note that the ratio of $W_{\text{CO}}/W_{\text{COD}}$ is 1.79 and the ratio of $E_{\text{CO}}/E_{\text{COD}}$ is 1.77, the ratio of P_{Cl}'/P_{Cl} must be close to one or $P_{Cl}' = P_{Cl}$.

Using Figure 2, the average bridge dissociation enthalpy can be used to predict P_B values of 1.26 and 1.31 for the basic chlorides of the monomeric "(COD)RhCl" and "$(CO)_2$RhCl" species, respectively. This does indeed lead us to the interesting observation that there is essentially no difference in the basicity of the coordinated chloride acting as a Lewis base in forming the bridge bond in the CO and COD dimers. Thus, the difference between the heats of dimerization for the CO and COD dimer (22.6 and 12.6 kcal/mol, respectively) is due solely to

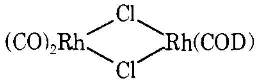
Table VI. Thermodynamic Results for the Reaction $[Rh(COD)Cl]_2 + 2B \rightarrow 2[Rh(COD)(Cl)(B)]$ in Acidic Solvents at 24 ± 1 °C

Base	Solvent	$-\Delta H_{meas}$[a]	Base correction[b]	$-\Delta H_{net}$[a,c]	$\Delta H_{solvn\text{-}min}$[d]	Δ[e]
Me_2SO	Chloroform[f]	2.0 ± 0.1	4.5	12.8	10.1	2.7
THTP	Chloroform[f]	7.9 ± 0.1	2.3	16.4	11.5	4.9
Piperidine	Chloroform[f]	9.2 ± 0.2	4.5	20.0	16.4	3.6
Quinuclidene	Chloroform[f]	3.0 ± 0.3	4.2	13.5	13.3	0.2
Pyridine	Dichloromethane[g]	9.6 ± 0.6	2.0	17.9	13.8	4.0

[a] In units of kcal/mol of adduct formed. [b] Enthalpy correction for the specific interaction of the base with the acidic solvent calculated from eq 1 using $E_A = 3.02$, $C_A = 0.16$ for $CHCl_3$ and $E' = 1.66$, $C' = 0.01$ for CH_2Cl_2. [c] Enthalpies corrected for one-half the enthalpy of dimerization ($W = 6.3$ kcal/mol) and any specific interactions between the base and the hydrogen-bonding solvent. [d] "Solvation-minimized" enthalpies measured in benzene and corrected for $W = 6.3$ kcal/mol. [e] Deviation between $-\Delta H_{net}$ and $-\Delta H_{solvn\text{-}min}$. [f] Chloroform data from R. A. Kabler, unpublished results. [g] Taken from ref 50.

the difference in acidity of the two rhodium centers in $Rh(CO)_2Cl$ and $Rh(COD)Cl$.

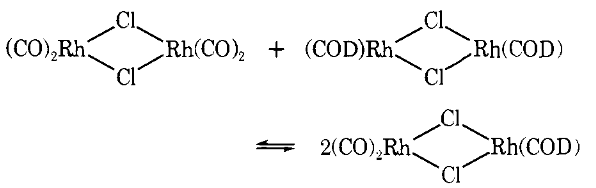
We are now in a position to predict the enthalpy of formation of the mixed dimer



It will be given by

$$-\Delta H_{mixed} = E_{CO}P_{Cl} + E_{COD}P_{Cl}' \qquad (15)$$

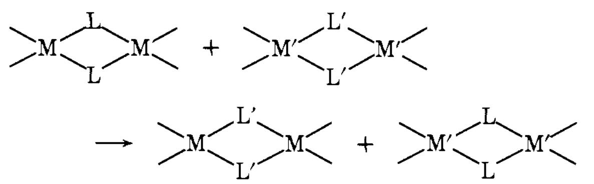
which is the average of that for formation of the two symmetrical dimers or on the order of ~17.6 kcal/mol. Since the net enthalpy for the reaction



(16)

is the sum of the enthalpies for dissociating the two symmetrical dimers and the enthalpy for forming the unsymmetrical bridged molecule from the monomeric fragments, a net enthalpy of about zero is predicted. The position of the above equilibrium will be determined by entropic considerations. A purely statistical analysis would lead to an equilibrium constant of four.

Thus, in general, for any case where the C/E ratios for the two metal centers is similar and the P_B value of the bridging ligands comparable, there will be no net enthalpic driving force for forming the mixed dimer regardless of the acid strength of the two metal centers or the relative values of C_B and E_B which lead to the same P_B. In order to maximize the enthalpic driving force for forming any mixed dimer system, it is necessary to increase the P_B parameter of the bridging atom(s) on the less acidic center and decrease the P_B parameter of the bridging ligand on the more acidic center. This change would allow the strong acid center to take advantage of the more basic bridging group, leading to a larger enthalpy for converting the symmetrical dimers into the mixed ones. Of course, pushed to an extreme, such properties of the acid and bridging centers might simply lead to an exchange of the bridging groups, i.e.,



(17)

This general guideline for the design and synthesis of mixed dimers can be readily seen from the form of eq 13–15 because the enthalpy for forming the mixed dimer is $-\Delta H_{mixed} + [W_{COD} + W_{CO}]$. Once again, the obvious value of quantitative assessments of acid and base parameters for various systems is apparent.

Solvation Contributions in Hydrogen Bonding Solvents. In order to obtain meaningful thermodynamic data concerning the bond strength of Lewis bases coordinating to the rhodium center, it is necessary that there be minimal contributions to the measured enthalpies from solvation energies. Attempts to measure some enthalpies of adduct formation in the weakly interacting solvents[22,47] CCl_4 and C_6H_{12} failed due to the insolubility of the adducts in these nonpolar solvents. In the previous section, arguments were presented to support the supposition that the enthalpies measured in benzene for this system are relatively free of solvation contributions. It is of interest to compare our "solvation-minimized" benzene data with studies of $[Rh(COD)Cl]_2$ in acidic solvents such as methylene chloride and chloroform. A previous study[48] on solvation contributions to enthalpies measured in methylene chloride cautions against the use of acidic solvents for the study of $Rh_2L_2Cl_2$ dimeric acids. Specific hydrogen-bonding interactions between solvents such as CH_2Cl_2 and $CHCl_3$ and the basic chlorine atoms of the rhodium adducts $Rh(COD)Cl{\cdot}B$ are expected to be different from comparable interactions in the case of the dimer. In Table VI, we see a comparison of enthalpies measured in acidic solvents with the solvation-minimized enthalpies used to determine the E_A and C_A parameters for our rhodium Lewis acid center. The $-\Delta H_{net}$ enthalpies reported have been corrected for the specific hydrogen-bonding interaction of the base with the solvent. This does not correct for all of the terms in a solvation enthalpy cycle; but if there are no specific interactions of the acid or adduct with the solvent, this correction is expected to produce a solvation-minimized enthalpy. The fact that it does not is seen by looking at the difference, the last column in Table VI. After the correction is made for the specific interaction of the free base with chloroform, all of these corrected enthalpies are more exothermic than the corresponding values in benzene solvent. This difference indicates greater solvation of the adduct than of the reactants. We attribute this to a more ionic metal–chlorine bond, which results in a more basic chlorine atom. Hydrogen bonding of chloroform to a chloride ion which is coordinated to a transition metal ion has been noted in previous work.[49] A hydrogen-bonding interaction of chloroform with the chloride of the square planar adduct would account for the excess solvation energy found in this solvent.

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Supplementary Material Available: a listing of calorimetric data (5 pages). Ordering information is given on any current masthead page.

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The Structure of a Monomeric Oxygen Carrying Cobalt Complex: Dioxygen-*N,N′*-(1,1,2,2-tetramethyl)ethylenebis(3-*tert*-butylsalicylideniminato)(1-benzylimidazole)cobalt(II)

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Abstract: The synthesis and structural characterization of a new oxygen-carrying cobalt complex, *N,N′*-{1,1,2,2-tetramethyl}ethylenebis(3-*tert*-butylsalicylideniminato)cobalt(II), abbreviated Co(t-Bsalten), and its monomeric σ-bonded dioxygen complex with 1-benzylimidazole as the axial base, Co(t-Bsalten)(bzImid)(O_2) are reported. The M–O_2 structural parameters for Co(t-Bsalten)(bzImid)(O_2) have been determined to a greater precision than previously attained. Co(t-Bsalten) crystallizes in the monoclinic space group $P2_1/c$ with a = 12.728 (1) Å, b = 10.642 (2) Å, c = 19.643 (3) Å, β = 95.22 (2)°, and Z = 4. Anisotropic least-squares refinement gave R = 0.085 for 4349 independent diffractometry data. Data were collected at both room temperature and −152 °C for Co(t-Bsalten)(bzImid)(O_2). It crystallizes as an acetone solvate in the monoclinic space group $P2_1/c$ with a = 11.918 (1) Å, b = 21.331 (5) Å, c = 17.267 (2) Å, β = 108.89 (1)°, and Z = 4 at room temperature and a = 11.933 (4) Å, b = 21.238 (11) Å, c = 17.004 (2) Å, and β = 109.86 (3)° at −152 °C. Anisotropic least-squares refinement R = 0.062 for 1395 independent diffractometry data with $I > 3\sigma(I)$ and R = 0.077 for 1437 reflections with $I > 3\sigma(I)$ at room temperature and −152 °C, respectively. Co(t-Bsalten) is a planar molecule. The cobalt atom in Co(t-Bsalten)(bzImid)(O_2) is octahedrally coordinated with a Co–N(bzImid) distance of 1,974 (8) Å and a Co–O_2 distance of 1.873 (7) Å. The O–O bond length is 1.273 (10) Å and the Co–O–O bond angle is 117.5 (6)°. The x-ray results for Co(t-Bsalten)(bzImid)(O_2) are consistent with a superoxide ion, O_2^-, bonded to Co(III).

In 1938, Tsumaki[2a] described the preparation of *N,N′*-ethylenebis(salicylideniminato)cobalt(II), Co(salen), a compound which reversibly absorbed molecular oxygen from the atmosphere. This compound and many others closely related to it were studied extensively by Calvin and his collaborators in 1944–1945.[2b] Calvin determined that Co(salen) absorbed one molecule of oxygen per two cobalt atoms. No single-crystal x-ray work was undertaken by Calvin's group.

In subsequent years x-ray structural determinations have been carried out on a number of compounds which bind oxygen with a 2:1 metal-to-oxygen ratio. Only recently have 1:1 complexes with various metals been characterized by single-crystal x-ray crystallography. Some of these have heavy-metal centers which bind oxygen symmetrically by a π-bond. Such a π-bonded structure has been proposed by Griffith[3] as the mode of O_2 binding in oxyhemoglobin and oxymyoglobin. The