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Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Metal Synergism in the Coordination Chemistry of a Metal–Metal Bonded System: $Rh_2(C_3H_7COO)_4$

RUSSELL S. DRAGO,* JOHN R. LONG, and RICHARD COSMANO

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An earlier study on the thermodynamic and electrochemical properties of Rh_2But_4 (But = butyrato) led to the conclusion that π back-bonding in d^{14} metal dimer systems is responsible for some unusual cluster chemistry. In an attempt to more fully understand the influence that substitution on one metal center in a cluster has on a second metal center, further studies on Rh_2But_4 have been carried out. This problem could not be investigated in the solvent benzene, because coordination of this solvent occurred. To gain further support for benzene coordination and to investigate the influence of $\Delta H_{1:1}$ on $\Delta H_{2:1}$, we carried out analogous studies in CH_2Cl_2. In contrast to the results in benzene, $\Delta H_{2:1}$ is not as negative as $\Delta H_{1:1}$ for all adduct formation reactions measured in CH_2Cl_2. Evidence that π-back-bonding stabilization is important in adducts of the dimer is supported by the data in CH_2Cl_2. A mathematical model has been developed that can be used to set an upper limit of π stabilization in the 2:1 adduct for those bases which undergo a π-back-bonding interaction with Rh_2But_4. This permits an unprecedented comparison of the extent of π-back-bond stabilization upon coordination of sequential competitive π-acceptor ligands. A novel application of isosbestic points is presented that improves the determination of the four values for K_1, K_2, ϵ_1, and ϵ_2.

Introduction

In an earlier study,[1] thermodynamic and electrochemical studies of the base adducts of tetrakis(μ-butyrato)-dirhodium(II) (Rh_2But_4) were reported. This work indicated that dimeric metal–metal bonded systems with a d^{14} electronic configuration were very effective at metal to ligand π back-bonding. The electronic configurations of the adducts were described in terms of electron-pair donation from the filled π^* orbital of Rh_2But_4. The electronic structure of this acid, shown in Figure 1, was deduced from earlier EPR studies[2] of a free-radical base and is in agreement with the results of a subsequent SCF–Xα molecular orbital calculation.[3] Enhanced π-back-bonding capability was attributed to the radical extension of the filled π^* orbital that arose from the metal–metal interaction. This constitutes one of the few demonstrated mechanisms whereby metal–metal synergism in a metal cluster leads to reactivity in a cluster, which differs from that of a single-metal complex.

The thermodynamic data for coordination of the first base to the dimer was compared to that for coordination of the second base to the other site. Although the equilibrium constant was considerably lower for the coordination of the second base than for coordination of the first, the enthalpy of adduct formation of each of the two steps was nearly identical in several instances. It was proposed that the solvent benzene coordinated to the free acid and reaction of the acid with added bases, B, involved a displacement reaction (eq 1). Variation

$$Rh_2But_4(C_6H_6)_2 + B \rightleftarrows Rh_2But_4C_6H_6B \rightleftarrows Rh_2But_4B + C_6H_6 \quad (1)$$

in the position of these equilibria made a comparison of the data for forming a one-to-one and a two-to-one base adduct impossible. In order to gain further information concerning the inductive transfer of the influence of base coordination in a metal–metal system, to verify coordination by benzene, and to gain further support for, as well as quantitative estimates of, the π-back-bonding stabilization, we reinvestigated the thermodynamics of adduct formation in CH_2Cl_2 as solvent. It has been shown[4] that CH_2Cl_2 is a weakly hydrogen-bonding solvent, but a procedure has been reported that enables one to correct thermodynamic data obtained in this solvent for this effect.

Experimental Section

A. Synthesis and Purification. Metal Complexes. Rhodium acetate[5] was prepared by literature methods. Conversion to the butyrate was effected by an exchange reaction with butyric acid in which rhodium acetate (0.5 g) was refluxed in a solution of butyric acid (14 mL) and butyric anhydride (1 M) at approximately 100 °C ($P \simeq 150$ mmHg) for 3 h, while under nitrogen. After all but 5 mL of the solvent was distilled off, the remaining material was cooled at −20 °C overnight, followed by filtering and rinsing with cold pentane. The solid product was extracted with hot benzene and filtered, and the filtrate was concentrated to 5 mL. Green rhodium(II) butyrate crystallized out of the cooled solution. The product was filtered, rinsed with cold pentane, and then dried in vacuo for several hours at 100 °C over NaOH. The yield was 0.6 g.

Anal. Calcd for $Rh_2C_{16}H_{28}O_8$: C, 34.68; H, 5.09. Found: C, 34.74; H, 4.99.

Due to limited solubility in benzene ($<10^{-3}$ M), a molecular weight determination in this solvent was carried out in a supersaturated solution: found 563.

A solution (1 mL) of 0.0160 g (2.89×10^{-5} mol) of rhodium butyrate and pyridine (5.78×10^{-5} mol) in benzene was also used for a molecular weight determination. A value of 707 was obtained compared to a molecular weight of 712 for the 2:1 adduct.

Bases. The bases used in this study have been employed in earlier work and were purchased from the sources described there and purified as described.[6] All distillations were carried out under nitrogen or argon, and all manipulations were carried out in an inert-atmosphere box or an N_2-filled glovebox.

Solvents. Reagent grade toluene and benzene were dried over Linde 4-Å sieves for at least 24 h.[6c] Methylene chloride[6a] was stirred with sulfuric acid until further discoloration of the acid ceased, washed with aqueous carbonate, washed with water, dried over $CaCl_2$, and then distilled from P_4O_{10} (bp 41 °C) and stored over Linde 4-Å molecular sieves.

B. Calorimetry Data Collection. The calorimeter has been described previously.[6c,7] Recently it has been modified to eliminate the reference cell by the utilization of an electronic base line compensator.[8] A 50-mL, inert-atmosphere calorimetry cell[6c] was used for all measurements.

A "Hamilton Gas Tight" 1-mL syringe, calibrated with a set of 13 plunger-stops,[7] was used for the addition of bases into the calo-

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(1) R. S. Drago, S. P. Tanner, R. Richman, and J. R. Long, *J. Am. Chem. Soc.*, **101**, 2897 (1979).

(2) R. M. Richman, T. C. Kuechler, S. P. Tanner, and R. S. Drago, *J. Am. Chem. Soc.*, **99**, 1055 (1977).

(3) J. G. Norman and H. J. Kolari, *J. Am. Chem. Soc.*, **100**, 791 (1978).

(4) R. S. Drago, J. Nusz, and R. Courtright, *J. Am. Chem. Soc.*, **96**, 2082 (1974).

(5) P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970).

(6) (a) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, 1972; (b) F. L. Slejko and R. S. Drago, *Inorg. Chem.*, **12**, 176 (1973); (c) M. P. Li, R. S. Drago, and A. J. Pribula, *J. Am. Chem. Soc.*, **99**, 6900 (1977); (d) R. Guidry and R. S. Drago, *ibid.*, **95**, 759 (1973); (e) G. Vogel and J. Stahlbush, *Inorg. Chem.*, **16**, 950 (1977).

(7) (a) T. D. Epley and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 5770 (1967); (b) R. S. Drago and T. D. Epley, *ibid.*, **91**, 2883 (1969); (c) R. L. Courtright, R. S. Drago, J. Nusz, and M. Nozari, *Inorg. Chem.*, **12**, 2809 (1973); (d) G. C. Vogel, Ph.D. Thesis, University of Illinois, 1965.

(8) R. Mayer, University of Illinois, private communication.

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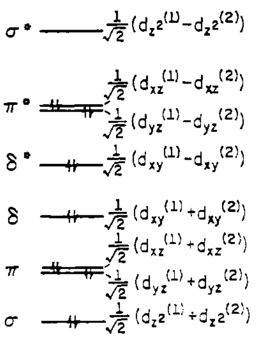

Figure 1. Qualitative MO diagram of rhodium butyrate showing combinations of metal 4d orbitals only. This rhodium(II) dimer, being a d^7–d^7 system, has 14 electrons in the metal–metal molecular orbitals.

rimeter cell. The syringe was calibrated by measuring the amount of deionized water that was displaced through the use of each plunger-stop. Precision of 5 ppt, or better, was obtained for each addition.

Because of the hygroscopic nature of the compounds used, the following precautions were taken: (a) All glassware was predried in vacuo at 70 °C. (b) The compounds were weighed either while inside a dry box or while in a sealed flask. (c) All sample manipulations and the assembling of the calorimeter cell were performed in a nitrogen-filled glovebag; granular P_4O_{10} was used as a desiccant.

Because of the importance of achieving thermal equilibrium, all samples, solutions, solvents, and glassware were stored overnight in the same room.

Analysis of Data

A. Spectroscopy. Qualitative Analysis of Isosbestic Points. For systems involving multiequilibrium processes, the equilibrium constants should be determined independently of the calorimetric experiment since the four parameters K_1, K_2, $\Delta H_{1:1}$, and $\Delta H_{2:1}$ defined below are frequently highly correlated.

equil	equil const	molar enthalpy
$A + B \rightleftarrows AB$	$K_1 = \frac{[AB]}{[A][B]}$	$\Delta H_{1:1}$
$AB + B \rightleftarrows AB_2$	$K_2 = \frac{[AB_2]}{[AB][A]}$	$\Delta H_{2:1}$

An exception to this is the situation in which the first equilibrium constant is very large, $>10^8$; for these systems, approximating K_1 as 10^8, and letting the computer vary K_2 to give the best fit, will give very reasonable estimates of $\Delta H_{1:1}$ and $\Delta H_{2:1}$. If K_1 is not this large, simultaneous analysis of repeated calorimetric runs sometimes gives satisfactory results. The change in the visible spectra of the rhodium dimers, resulting from addition of a Lewis base, is particularly useful for determining the equilibrium constants. As is seen in Figure 2,[1] as the mole ratio of base to rhodium dimer increases, one first observes isosbestic behavior for the free acid A and the 1:1 adduct AB at 616 nm. This is followed by isosbestic behavior for the 1:1 and 2:1 adducts at 547 nm. Equilibrium constants were evaluated from a best fit of the absorbance data at several wavelengths. The number of unknowns can be minimized by selecting the isosbestic wavelengths as two of the wavelengths used in the analysis. At the AB/AB_2 isosbestic point, for example, the extinction coefficient for the 1:1 adduct, ϵ_1, is known and equals the extinction coefficient for the 2:1 adduct, ϵ_2.

It should be noted that special conditions are required for the existence of a first and second isosbestic point as seen in Figure 2. First, the K_1/K_2 ratio must be large. If $K_1 \simeq K_2$ or $K_1 < K_2$, the concentration of AB will not get very large before a significant amount of AB_2 will form. If $K_1 \ll K_2$, an isosbestic point may be seen, but it would correspond to the presence of A and AB_2, since AB_2 would form as soon as any AB is formed. The equilibrium expression would be

$$A + 2B \rightleftarrows AB_2$$

Hence, only for those spectral curves for which [B] is very low will $[AB_2] \approx 0.0$, for this will not yield a well-defined isosbestic point. Second, the difference between the molar absorptivities (e.g., $|\epsilon_0 - \epsilon_1|$) needs to be large at frequencies above and below that of the isosbestic point. This will ensure that the spectral curves that go through the isosbestic point will have greatly varying slopes. Third, the range of base concentrations needs to be chosen properly. A series of relatively low base concentrations is needed to define the first isosbestic point, and a series of relatively high base concentrations is needed to define the second isosbestic point. As mentioned previously, when these three conditions are met, the presence of the isosbestic points will greatly facilitate the analysis of the data.

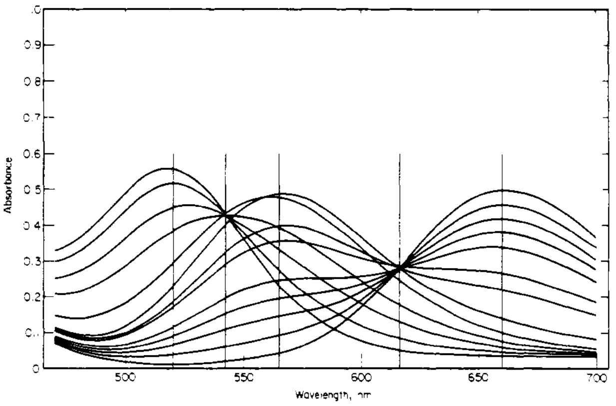

Figure 2. Spectrophotometric titration of rhodium(II) butyrate with pyridine. The vertical lines indicate the wavelengths selected for analysis.

Estimation of Spectral Parameters. The success in finding the correct solution for the data for the best K's and ϵ's depends on the initial guesses of the parameters (i.e., K_1 and K_2 and ϵ_0, ϵ_1, and ϵ_2 for each wavelength). For the alleviation of the paradox of needing to know the values of the parameters before the computer program is executed to calculate the same, a few algorithms for estimating the parameters were developed.

a. K_1. K_1 may be estimated through the use of those spectral curves that go through the first isosbestic point. In this region the concentration of the 2:1 adduct is virtually zero, and data that lie in this region may be analyzed as a simple 1:1 equilibrium system. Values for K_1 and $\Delta\epsilon = \epsilon_0 - \epsilon_1$ will be obtained by this method. Alternatively, a rough estimate of K_1 may be obtained from the slope of a plot of [AB] vs. [A][B] (see the section for estimating ϵ_1). For most systems, however, the concentration of AB will never get very large before appreciable amounts of AB_2 will form; thus, the range of complexation of the acid will be limited and prevent a reasonable estimation of the equilibrium constant by this method.[9]

b. K_2. K_2 cannot be determined by the above method in the region of the second isosbestic point since the base exists in three "forms": free, AB, and AB_2. Knowledge about similar systems may allow one to estimate K_2 once an approximate value for K_1 is known. Otherwise, it is best to hold all other parameters (e.g., K_1, ϵ_0, ϵ_1, ...) constant and let the computer program vary K_2.

c. ϵ_0. The molar absorptivity of the free acid, ϵ_0, may be calculated from the absorption spectra of the free acid.

d. ϵ_1. For most systems, the molar absorptivity of the 1:1 adduct, ϵ_1, is the most difficult parameter to estimate since

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(9) T. Beugelsdijk and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 6466 (1975).

the concentration of the 1:1 adduct is not directly measurable. For those systems, however, that demonstrate isosbestic behavior for the first equilibrium, $A + B \rightleftarrows AB$, $\epsilon_1 = \epsilon_0$, and ϵ_1 is obtained directly from the spectra. Similarly, for those systems that demonstrate isosbestic behavior for the second equilibrium, $AB + B \rightleftarrows AB_2$, $\epsilon_1 = \epsilon_2$, and ϵ_1 is obtained directly from the spectra. For those systems that demonstate both the first and the second isosbestic points, it is possible to estimate ϵ_1 for all nonisosbestic wavelengths. Deviations from the second isosbestic point are indicative of the presence of the free acid. If one works with those spectral curves for which the first isosbestic point is maintained, it is possible to calculate the concentration of the free acid from the magnitude of the deviation from the second isosbestic point. It is then possible to use these values to calculate ϵ_1 for any nonisosbestic wavelength. The derivation of this technique is given below. Although the derivation assumes that a 1-cm path length was employed, the derivation is generalized to allow any path length by dividing all absorbance values by the path length.

For those spectral curves for which the first isosbestic point is maintained

$$\mathrm{Abs}_i = \epsilon_0[\mathrm{A}]_i + \epsilon_1[\mathrm{AB}]$$

and

$$A_\mathrm{T} = [\mathrm{A}]_i + [\mathrm{AB}]_i$$

where Abs_i is the absorbance of the ith spectral curve, A_T is the total (or formal) concentration of the acid, which is assumed to be constant for each ith spectral curve, and $[\mathrm{A}]_i$ and $[\mathrm{AB}]_i$ are the concentrations of the free acid and the 1:1 adduct for the ith spectral curve, respectively. These two equations can be combined to give

$$\begin{aligned}\mathrm{Abs}_i &= \epsilon_0[\mathrm{A}]_i + \epsilon_1(A_\mathrm{T} - [\mathrm{A}]_i)\\ &= [\mathrm{A}]_i[\epsilon_0 - \epsilon_1] + \epsilon_1 A_\mathrm{T}\end{aligned}$$

which upon rearrangement gives

$$[\mathrm{A}]_i = \frac{\mathrm{Abs}_i - \epsilon_1 A_\mathrm{T}}{\epsilon_0 - \epsilon_1}$$

The above holds for any wavelength; however, if the wavelength of the second isosbestic point is chosen, ϵ_1 is known, as are all the other quantities on the right-hand side of the equation. Thus one is now able to calculate the concentration of the free acid for those spectral curves that go through the first isosbestic point.

Now, for any *nonisosbestic* wavelength, yet still for spectral curves for which the first isosbestic point is maintained, we have

$$\mathrm{Abs}_i = \epsilon_0[\mathrm{A}]_i + \epsilon_1[\mathrm{AB}]_i$$

which upon rearrangement gives

$$\epsilon_1 = \frac{\mathrm{Abs}_i - \epsilon_0[\mathrm{A}]_i}{[\mathrm{AB}]_i}$$

Substituting $[\mathrm{AB}]_i = A_\mathrm{T} - [\mathrm{A}]_i$ gives

$$\epsilon_1 = \frac{\mathrm{Abs}_i - \epsilon_0[\mathrm{A}]_i}{A_\mathrm{T} - [\mathrm{A}]_i}$$

Having already calculated the $[\mathrm{A}]_i$ values, this equation allows one to calculate the molar absorptivity of the 1:1 adduct for any nonisosbestic wavelength using spectral curves that go through the first isosbestic point. In practice a fair amount of scatter is obtained, in which case the different estimations of ϵ_1 may be averaged together. The advantage of this method is that it allows one to estimate $[\mathrm{A}]_i$, $[\mathrm{AB}]_i$, and ϵ_1 without any knowledge of K_1 or K_2.

e. ϵ_2. Analogous equations may be derived for the calculation of the molar absorptivity of the 2:1 complex, ϵ_2; however, in practice it is generally sufficient to use the limiting spectra to estimate this quantity.

Spectroscopic K_1K_2 Program. The program that analyzes spectroscopic data for the best fit values of the equilibrium constants and molar absorptivities has been described previously.[10] The program attempts to find the values for the K's and ϵ's that minimize the sum of the squares of the deviations of observed from calculated absorbances:

$$\sum_{j=1}^{M}\sum_{i=1}^{N}(\mathrm{Abs}(\lambda_j)_{i,\mathrm{calcd}} - \mathrm{Abs}(\lambda_j)_{i,\mathrm{obsd}})^2$$

where N is the number of spectral curves, M is the number of wavelengths, $\mathrm{Abs}(\lambda_j)_{i,\mathrm{calcd}}$ is the calculated absorbance for the ith spectral curve at the jth wavelength, and $\mathrm{Abs}(\lambda_j)_{i,\mathrm{obsd}}$ is the analogous observed quantity.

B. Calorimetry. Workup of Raw Data. Due to the errors involved in the measurement of the evolved heat (some random, others not), care must be taken in the analysis of the raw calorimetric data. Two sources of nonrandom errors may arise. The first is a nonlinear change in temperature in response to added heat. This problem is partially alleviated by adjusting the size of each base injection so that each addition results in nearly the same temperature change and by making the magnitude of the calibration heats as close as possible to that of the previous injection. The second is a change in the heat capacity of the solution resulting from the sequential additions of base. This, as well as most random errors, can be handled by performing a linear least-squares fit of the observed calibration heats (in units of cal·cm^{-1}) as a function of added volume.

Calorimetric K_1K_2 Program. A new program was developed to analyze calorimetric data. For given values of K_1 and K_2 the program calculates the best $\Delta H_{1:1}$ and H_T (i.e., $\Delta H_{1:1} + \Delta H_{2:1}$). The equilibrium constants should be measured independently.

When $K_1 > 10^6$, very good estimates of $-\Delta H_{1:1}$ and $-\Delta H_{2:1}$ were obtained without determining the equilibrium constants spectrophotometrically. By assuming a very large value for K_1 (e.g., $\geq 10^7$) and allowing the value of K_2 to be varied by the computer, we determined the values for K_2, $-\Delta H_{1:1}$, and $-\Delta H_{2:1}$ that give the best fit to the calorimetric data. This procedure has been verified by analyzing calorimetric data that had been analyzed with use of spectroscopically determined equilibrium constants; the two sets of H values agreed within 0.2 kcal·mol^{-1}, but the K_2 values determined by calorimetry have large error limits.

***E*, *C*, and *W* Program.** A description of the computer program that is able to solve for two (E and C) or three (E, C, and W) parameters has been reported previously.[6d] Using experimentally determined enthalpies, the program calculates the best fit values of the unknown parameters (E, C, and W) to the equation

$$-\Delta H - W = E_\mathrm{A}E_\mathrm{B} + C_\mathrm{A}C_\mathrm{B} \qquad (2)$$

where W is any constant contribution to the enthalpy, while the E_B and C_B values were obtained from ref 11.

Results and Discussion

Qualitative Features. As mentioned previously, many metal carboxylates are known to form both 1:1 and 2:1 adducts with Lewis bases in the solid state.[12] Good evidence that all three

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[10] T. O. Maier and R. S. Drago, *Inorg. Chem.*, **11**, 1861 (1972); T. Kuechler, Ph.D. Thesis, University of Illinois, 1977.

[11] R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973); *Coord. Chem. Rev.*, **33**, 251 (1980).

[12] (a) Y. Koh and G. Christoph, *Inorg. Chem.*, **17**, 2590 (1978); (b) D. Collins, F. A. Cotton, and C. Murillo, *ibid.*, **15**, 1861 (1976); (c) F. A. Cotton and J. Norman, Jr., *J. Am. Chem. Soc.*, **94**, 5697 (1972).

Table I. Thermodynamic Data for the Formation of 1:1 and 2:1 Base Adducts of Dimeric Rhodium(II) Butyrate in Benzene Solution[a]

base	K_1	K_2	$-\Delta H_{1:1}$, kcal·mol^{-1}	$-\Delta H_{2:1}$, kcal·mol^{-1}
MeCN	1.7 (0.2) × 10^3	27.0 (2)	5.1 (0.2)	8.3 (0.4)
py[b]	1.6 (0.2) × 10^8	2.4 (0.2) × 10^4	11.2 (0.2)	11.2 (0.3)
N-MeIm[c]	~10^9	8 × 10^4	12.4 (0.7)	10.5 (0.5)
pip[c]	~10^9	6 × 10^4	13.2 (0.3)	12.5 (0.4)
THTP	1.7 (0.1) × 10^7	1.9 (0.3) × 10^4	11.0 (0.3)	10.3 (0.4)
caged phosphite	9.1 (0.7) × 10^7	2.6 (0.1) × 10^4	12.9 (0.2)	11.3 (0.2)
4-pic-*N*-O[d]	2.4 (0.3) × 10^5	2.9 (0.3) × 10^2	~7	~8
Me_2SO	1.1 (1) × 10^5	5.5 (0.3) × 10^2	6.6 (0.2)	6.5 (0.4)

[a] All spectroscopic and calorimetric measurements were performed with supersaturated solutions of the free acid; the solutions were not supersaturated with respect to the 1:1 or 2:1 adduct at any time. The influence of errors in K on the ΔH's was checked by varying both K_1 and K_2 by two marginal standard deviations. The larger error obtained, by either this procedure or the calorimetric data fit, is reported as the error limit. Data are from ref 1. [b] A correction of 0.9 kcal·mol^{-1} needs to be applied to each $-\Delta H$ value to correct for the pyridine–benzene interaction that is broken up upon 1:1 and 2:1 adduct formation.[11] [c] ΔH values were calculated from calorimetric data by fixing K_1 at 1 × 10^9 and fitting $\Delta H_{1:1}$, $\Delta H_{2:1}$, and K_2. The ΔH values obtained are not changed within experimental error by variations of the fixed value of K_1 by a factor of 10^2. [d] In earlier experiments a lower value was reported because precautions were not taken to avoid moisture pickup; vide infra. These enthalpies are estimated by using ESP and the CH_2Cl_2 data.

species, free acid, 1:1 adduct, and 2:1 adduct, exist in solution is obtained from spectroscopic studies. A typical spectrum of the rhodium carboxylates and their adducts is shown in Figure 2. At low concentrations of base, an isosbestic point for the free acid and 1:1 adduct is seen. At high concentrations of base the spectral curves no longer go through the first isosbestic point but do go through a new isosbestic point for the 1:1 and 2:1 base adduct. At intermediate concentrations of base, the spectral curves go through neither isosbestic point. This implies that all three species are present: free acid and 1:1 and 2:1 adducts.

From the molecular orbital diagram (Figure 3) it can be seen that the dimer can function as a Lewis acid by accepting electron density from one or two Lewis bases in the antibonding σ^* molecular orbital. This interaction raises the energy of both the σ and σ^* levels, with adduct stability arising largely from the stabilization of the essentially donor lone pair orbitals and is represented in the schematic MO diagram of Figure 3a. Since the lowest energy transition is $\pi^* \rightarrow \sigma^*$, the effect of adduct formation is to blue shift the band associated with this transition to higher energy. Further, if the base is a good π acceptor, the filled π^* orbital of the acid will be lowered as it donates electron density of the π-acceptor orbitals of the base to also shift the $\pi^* \rightarrow \sigma^*$ transition to a higher energy.

Thermodynamic Data. a. Benzene Solutions. The thermodynamic data in benzene solution were reported earlier[1] and are summarized here in Table I for comparison with the results in methylene chloride. There are several interesting aspects to the data in Table I. The equilibrium constants for binding indicate a greatly decreased acceptor capability for coordination of the second base relative to the first. Statistical considerations for noninteracting metal centers would lead to $K_1 = 4K_2$ if the metal centers were uncoupled. The observed ratio of K_1 to K_2 is much greater, as would be expected if the inductive effect of base coordination was effectively transmitted through the metal–metal bond to weaken the Lewis acidity of the second metal center. For most of the bases studied in this solvent, however, the enthalpy for coordinating the second base is about the same as that for coordinating the first. This is surprising in view of the 3 or 4 orders of magnitude decrease in K_2 compared to K_1. Since entropy effects this large could not be anticipated in the acid–base interaction, solvent participation (i.e., benzene coordination to the acid) was proposed.

b. Methylene Chloride Solutions. To verify benzene coordination, the Lewis acid–base properties of rhodium(II) butyrate were investigated in the very poorly basic solvent methylene chloride. This solvent is an acidic solvent and in solution[4] is not expected to function as a donor via a specific interaction with the acid through the axial sites. Another advantage of using methylene chloride is the high solubility of rhodium butyrate in this solvent (>4 × 10^{-3} M), eliminating the need to work in supersaturated solutions, as was the case for the benzene solution work. A tabulation of the raw spectroscopic and the raw calorimetric data for the base binding of rhodium(II) butyrate in methylene chloride is presented in the supplementary material. The thermodynamic parameters that best fit the data are reported in Table II.

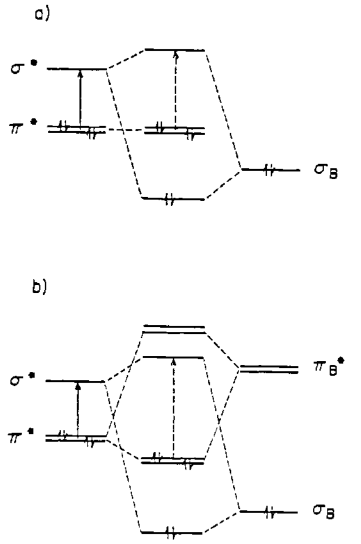

Figure 3. Effect of base coordination on the highest filled and lowest unfilled MO's and the resultant effect on the energy of the optical transition: (a) σ-bonding bases only; (b) σ- and π-bonding bases.

In Table II the equilibrium constants for base binding indicate a greatly decreased acceptor capability for coordination of the second base relative to the first, as was seen for the benzene solution data. However, in CH_2Cl_2 the enthalpies indicate an "inductive" effect, leading to a decreased enthalpy for coordinating the second base compared to the first for all bases studied. Hence, the data obtained from methylene chloride solutions support the earlier proposal of benzene coordination.

Since methylene chloride undergoes a specific hydrogen-bonding interaction with Lewis bases,[4] which is broken up when the base coordinates to the rhodium dimer, a correction needs to be applied to the $-\Delta H_{1:1}$ and $-\Delta H_{2:1}$ values of Table II. As shown in the literature,[4] this correction can be predicted by the E and C equation using $E_A' = 1.66$ and $C_A' = 0.01$ to correct for hydrogen bonding to donors by the solvent methylene chloride. The solvation-corrected enthalpies are presented in Table III. The detailed procedure for making these

Table II. Thermodynamic Data for the Formation of 1:1 and 2:1 Base Adducts of Dimeric Rhodium(II) Butyrate in Methylene Chloride Solution[a]

base	K_1	K_2	$-\Delta H_{1:1}$, kcal·mol^{-1}	$-\Delta H_{2:1}$, kcal·mol^{-1}
MeCN	$1.15\ (0.05) \times 10^3$	$1.1\ (0.1) \times 10$	7.8 (0.6)	6.8 (1.5)
py	$1.115\ (0.001) \times 10^7$	$9.88\ (0.05) \times 10^3$	14.6 (0.2)	8.5 (0.2)
N-MeIm[b]	$\sim 10^8$	2.1×10^3	13.7 (0.4)	9.9 (0.5)
pip[b]	$\sim 10^8$	1.2×10^3	13.2 (0.2)	8.9 (0.2)
4-pic-*N*-O	$8.2\ (0.3) \times 10^4$	$1.89\ (0.045) \times 10^2$	8.6 (0.3)	5.7 (0.5)

[a] These values give the best fit of calculated to observed evolved heat. [b] ΔH values were calculated from calorimetric data by fixing K_1 at 1×10^8 and fitting $\Delta H_{1:1}$, $\Delta H_{2:1}$, and K_2. The ΔH values obtained are not changed within experimental error by variations of the fixed value of K_1 by a factor of 10^2.

Table III. Solvation-Corrected Enthalpies for Dimeric Rhodium(II) Butyrate[a]

base	$-\Delta H_{1:1}$, kcal·mol^{-1}	$-\Delta H$(*E* and *C*)[c]	$-\Delta H_{2:1}$, kcal·mol^{-1}	$-\Delta H_T$, kcal·mol^{-1}	π stabilization, kcal·mol^{-1}	
					1:1 adduct	2:1 adduct
MeCN	9.3	4.6	8.3	17.6	4.7	4.7
py	16.6	12.2	10.5	27.1	4.4	1.4
N-MeIm	15.4	14.9	11.5	26.9		
pip	15.0	15.5	10.7	25.7		
THTP[b]	14.9	11.5	10.3	25.2	3.4	1.2
caged phosphite[b]	16.8	10.2	11.3	28.1	6.6	2.9
4-pic-*N*-O	11.0	11.0	8.0	19.0		
Me_2SO[b]	10.5		6.5	17.0		
C_6H_6		2.2				
CO						
bridged ether		8.3				

[a] Unless indicated otherwise, enthalpy values are those obtained from methylene chloride solutions.[1] [b] $-\Delta H_{1:1}$ was obtained by adding −3.9 kcal·mol^{-1}, for benzene dissociation, to the 1:1 enthalpy measured in benzene; $-\Delta H_{2:1}$ is that obtained from benzene solution. [c] With use of *N*-methylimidazole, piperidine, and 4-picoline *N*-oxide, $E_A = 3.21$ ($\sigma = 0.99$) and $C_A = 1.32$ ($\sigma = 0.14$).

corrections will be discussed in later sections.

The *E* and *C* model can be used to give a qualitative idea about the relative importance of covalent and electrostatic contributions to the σ bond and to predict the magnitude of the σ-bonding interactions of Lewis acid–base adducts. The application of this equation to Rh_2But_4 is complicated by the extensive π^* metal to ligand back-bonding ability of this rhodium dimer. Of the donors studied, we have presented evidence for the existence of π stabilization in the acetonitrile, pyridine, cage phosphite, dimethyl sulfoxide, carbon monoxide, and possibly tetrahydrothiophene adducts.[1] This leaves *N*-methylimidazole, piperidine, and 4-picoline *N*-oxide as σ donors that can be used in an *E* and *C* fit of the solvent-corrected data for the 1:1 adducts. Values of 3.21 and 1.32 for E_A and C_A yield the best fit to the enthalpies of adduct formation of these donors. With only three enthalpies that involve "σ-only" interactions, these values must be regarded as tentative.

"σ-Only" enthalpies, calculated for all of the donors of Table III with use of the *E* and *C* equation, are listed in the column $-\Delta H$(*E* and *C*). The measured $-\Delta H_{1:1}$ values for all donors that were not used to determine E_A and C_A are much larger than the *E* and *C* predicted enthalpy for a σ-type interaction. The extra stabilization has been attributed to a π-back-bonding interaction that includes π stabilization plus synergistic stabilization in the σ bond. Values of 3–7 kcal·mol^{-1} exist in the acetonitrile, pyridine, tetrahydrothiophene, and caged phosphite adducts. Thus the revised *E* and *C* values based on more accurate solvation-minimized data continue to show the extensive π-back-bonding stabilization reported earlier[1] for this system from an analysis of the thermodynamic, spectroscopic, and electrochemical data. Furthermore, for the first time we have an appreciation for the magnitude of the stabilization from this effect.

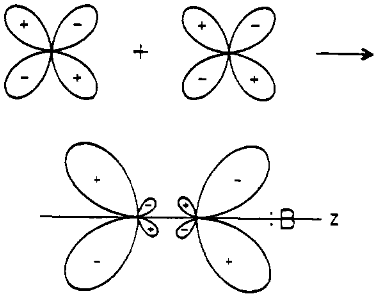

Figure 4. Diagram showing rhodium d_{xz} (or d_{yz}) orbital combination to form the corresponding π^* orbitals, which are capable of undergoing π back-bonding to B.

The polarization of the π^* orbitals in a metal–metal bond, illustrated in Figure 4, is proposed to enhance the π-back-bonding capabilities of metal clusters in which these orbitals are filled. We can view one of the metals as a "ligand" that is very effective in polarizing the filled π^* d orbitals of the other metal. When a ligand with a filled d shell (tin(II), arsenic(III), selenium(II), etc. donors) coordinates to a metal, the metal d orbitals are not polarized as extensively by this type of ligand because the completed d shell is stabilized and the radial extension contracted. Thus, the effect proposed here is expected to be characteristic of a metallic ligand, that is, a cluster compound.

Inductive Transfer to Neighboring Atoms in Metal Clusters. Some differences have been reported regarding the effect of substitution on one metal center on the reactivity at a second center. Cooperativity was proposed[13a] in the substitution reactions of $Ir_4(CO)_{12}$. On the other hand[13b] no such effect was reported for $Co_4(CO)_{12}$. It is important in assessing cooperative effects to distinguish between kinetic and thermodynamic factors. There are a whole host of influences, including synergism, that can contribute to substitutional rate differences. Accordingly, it will be difficult to generalize about cluster effects on reaction rates unless identical reaction mechanisms are compared. The demonstration or lack of synergism in thermodynamic data is much more direct. Data from this study bear on the question of synergism in metal clusters. The essential question is, "What is the influence of coordination of the first base on the acidity of the second metal center?"

For systems such as the metal carboxylates, which form 1:1 and 2:1 adducts, only the free acid can be characterized by the *E* and *C* equation; the 1:1 adduct cannot be characterized due to experimental difficulties. An acid is generally characterized by measuring the enthalpies of adduct formation for that acid and a series of bases and then solving a series of simultaneous equations (of the form of eq 2) for the unknowns, C_A and E_A. For the case in which a 1:1 adduct AB forms a

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(13) (a) K. J. Karel and J. R. Norton, *J. Am. Chem. Soc.*, **96**, 6812 (1974); (b) P. Chini and B. T. Heaton, *Top. Curr. Chem.*, **71**, 1 (1977); (c) D. J. Darensbourg and M. J. Incorvia, *Inorg. Chem.*, **19**, 2585 (1980).

Table IV. "e'" and "c'" Interpretation of the 2:1 Enthalpies of Adduct Formation for Rhodium(II) Butyrate

base	C^2/E^2 [a]	E_{AB} [b]	C_{AB} [b]	$-\Delta H_{2:1}$	$-\Delta H_{2:1}$- (e' and c') [c]
MeCN	2.3	2.18	1.27	8.3	3.6
py	29.9	1.85	1.09	10.5	9.1
N-MeIm	92.0	2.13	0.99	11.5	10.9
pip	84.6	2.04	0.98	10.7	11.2
THTP	533.6	2.81	1.03	10.3	9.1
caged phosphite	136.8	2.57	1.09	11.3	8.4
4-pic-*N*-O	13.5	1.63	1.14	8.0	7.9
C_6H_6	162	3.08	1.28		2.1

[a] E and C numbers were obtained from ref 11. The wide range of C^2/E^2 ratios indicates that the e' and c' values for this acid are well determined. [b] E_{AB} and C_{AB} were estimated by using eq 4 and 5. [c] With use of *N*-methylimidazole, piperidine, and 4-picoline *N*-oxide, $e' = 1.16$ ($\sigma = 0.93$; MSD/CSD = 1.5) and $c' = 0.0364$ ($\sigma = 0.0176$; MSD/CSD = 1.5).

2:1 adduct, the determination of E_{AB} and C_{AB} values would require that the reaction of AB with a series of bases B′ to form ABB′ be studied. In general, a straightforward measurement of the enthalpies of adduct formation between AB and a series of bases B′ is not possible as there would be free A and AB′, ABB′, AB_2, and AB'_2 in the system due to equilibrium considerations. This is unfortunate since a knowledge of the E and C parameters of the 1:1 adduct would provide direct information as to the ways and extents to which coordination at the first metal site influences the Lewis acid–base properties of the second metal site. To obtain this desired information, one can seek a relationship between E_A and E_{AB} and between C_A and C_{AB} and then attempt a fit of the available data to such a model. E_{AB} and C_{AB} represent the E and C parameters for the 1:1 adduct, AB. The validity of the model can be inferred from the quality of the fit of the data to the model.

There are, a priori, two restraints with which a model for estimating C_{AB} and E_{AB} must comply: (1) The model must be symmetrical; that is

$$-H_{T(ABB')} \equiv (E_AE_B + C_AC_B) + (E_{AB}E_{B'} + C_{AB}C_{B'}) \quad (3a)$$

$$= -H_{T(AB'B)} \equiv (E_AE_{B'} + C_AC_{B'}) + (E_{AB'}E_B + C_{AB'}C_B) \quad (3b)$$

where $H_{T(ABB')}$ is the total heat evolved for the stepwise reaction $A + B \rightarrow AB + B' \rightarrow ABB'$. $H_{T(AB'B)}$ is the total heat evolved for the stepwise reaction $A + B' \rightarrow AB' + B \rightarrow AB'B$. In other words, the model must predict the same value for the total heat evolved, H_T, regardless of the order of base binding. (2) The model must be physically reasonable. A model that fits both of these requirements is given by eq 4 and 5.

$$E_{AB} = E_A - e'E_B \quad (4)$$

$$C_{AB} = C_A - c'C_B \quad (5)$$

With this model, the E and C parameters of the 1:1 adduct have been reduced (for positive e' and c') from that of the free acid by an amount that is proportional to the corresponding parameter of the base. This assumption is reasonable in that it treats the inductive effect of the base, which is quantified by the E_B and C_B values, as a first-order perturbation upon the acidity of the acid. A second-order perturbation could include cross terms, for example, E_B's influence upon C_A. The inclusion of these terms, however, is not justifiable at this time. The e' and c' values can be viewed as constants that characterize the ability of the acid to transmit the inductive effects of the base.

By substituting eq 4 and 5 into eq 3a, eq 6 is obtained after

$$-H_{T(ABB')} = -H_{T(AB'B)} = E_A(E_B + E_{B'}) + C_A(C_B + C_{B'}) - e'E_BE_{B'} - c'C_BC_{B'} \quad (6)$$

rearrangement. As can be seen from eq 6, this model does possess the appropriate symmetry. An expression to calculate $\Delta H_{2:1}$ from eq 6 can be derived by combining eq 2 (with $W = 0$) with eq 6, realizing that

$$-H_T = -\Delta H_{1:1} - \Delta H_{2:1} \quad (7)$$

The following expression results after simplification:

$$-\Delta H_{2:1} = -\Delta H_{1:1} - e'E_BE_{B'} - c'C_BC_{B'} \quad (8)$$

that is, for positive e' and c' values, the $\Delta H_{2:1}$ will be less negative than $\Delta H_{1:1}$ (recall $-\Delta H_{1:1}$ is a positive number). When B = B′, the only unknowns for a series of 1:1 and 2:1 enthalpies that involve σ-only interactions are e' and c'.

Of the bases studied, *N*-methylimidazole, piperidine, and 4-picoline *N*-oxide were used to determine the e' and c' values for rhodium(II) butyrate. The results of fitting the calorimetric data to this model are presented in Table IV. The values $e' = 1.16$ and $c' = 0.0364$ for rhodium(II) butyrate yield the best fit to the data. "σ-only" $-\Delta H_{2:1}$ values, calculated for all of the bases with use of eq 2 and the E_{AB} and C_{AB} values predicted by eq 4 and 5, are listed in the column $-\Delta H_{2:1}$(e' and c'); the E_{AB} and C_{AB} values are also presented. In Table IV the predicted "σ-only" enthalpies of rhodium(II) butyrate are within 0.6 kcal·mol^{-1} of the measured enthalpies for *N*-methylimidazole, piperidine, and 4-picoline *N*-oxide. Since the determination of the e' and c' values is influenced not only by the errors present in the $-\Delta H_{1:1}$ values but also by the errors present in the $-\Delta H_{2:1}$ values, this 0.6 kcal·mol^{-1} deviation is not unreasonably large. The measured enthalpies of the other bases, acetonitrile, pyridine, tetrahydrothiophene, and caged phosphite, however, are 1–5 kcal·mol^{-1} larger than the "e'" and "c'" predicted σ-only values.

The excess stabilization in the experimental 2:1 adduct over that expected for a σ-only interaction is attributed to σ stabilization in the 2:1 adduct. Subtracting the calculated and experimental enthalpies for the four π-acceptor ligands (i.e., CH_3CN, C_5H_5N, THTP, and caged phosphite) results in values of 4.7, 1.4, 1.2, and 2.9 kcal·mol^{-1} of stabilization, respectively. These values constitute an upper limit on the π stabilization for they include an enhanced contribution from the σ interaction that resulted from π back-bonding in the 1:1

Table V. Solvent-Corrected Enthalpies (kcal·mol^{-1}) for the Formation of 1:1 and 2:1 Base Adducts of Dimeric Rhodium(II) Butyrate in CH_2Cl_2 [a]

	CH_2Cl_2		benzene		$\Delta\Delta H(CH_2Cl_2) - \Delta\Delta H(C_6H_6)$		
base	$-\Delta H_{1:1}$	$-\Delta H_{2:1}$	$\Delta H_{1:1}$	$\Delta H_{2:1}$	$-\Delta\Delta H_{1:1}$	$-\Delta\Delta H_{2:1}$	$-\Delta\Delta H_T$ [c]
MeCN	9.3	8.3	5.1	8.3	4.2	0	4.2
py [b]	16.6	10.5	12.1	12.1	4.5	−1.6	2.9
N-MeIm	15.4	11.5	12.4	10.5	3.0	1.0	4.0
pip	15.0	10.7	13.2	12.5	1.8	−1.8	0.0
4-pic-*N*-O	11.0	8.0	7.0	8.0	4	0	4

[a] $-\Delta H_{1:1}$ and $-\Delta H_{2:1}$ have been corrected for a methylene chloride–base interaction by using $E_A' = 1.66$ and $C_A' = 0.01$ for methylene chloride.[4] [b] A correction of 0.9 kcal·mol^{-1} has been made to $-\Delta H_{1:1}$ and $-\Delta H_{2:1}$ to correct for a pyridine–benzene interaction.[12] [c] $\Delta\Delta H_T = \Delta\Delta H_{1:1} + \Delta\Delta H_{2:1}$.

adduct. When these values are compared to the values of 4.7, 4.4, 3.4, and 6.6 kcal·mol^{-1} stabilization from π^* back-bonding in the 1:1 adduct (difference in $\Delta H_{1:1}$ and $\Delta H(E$ and $C)$), some interesting conclusions result. The strong σ donor pyridine so extensively weakens the π^* back-bonding in the 2:1 adduct that only 1.4 kcal·mol^{-1} (compared to 4.4) of extra stabilization results. On the other hand, the weak σ donor CH_3CN has π stabilization in the 2:1 adduct that is comparable to the π^* back-bonding stabilization in the 1:1 adduct. The strong σ donor THTP and caged phosphite systems behave similarly to pyridine.

These results suggest that σ-inductive effects provide an efficient mechanism for decreasing π-back-bonding stabilization by weakening the acidity of the metal center and probably lengthening the metal–ligand bond. This would indicate that effective metal–ligand π-back-bonding stabilization is a very sensitive function of distance. In many organometallic systems, it is often proposed that involvement of a metal's π system in π back-bonding to a given ligand weakens the tendency of the metal to under π back-bonding to another ligand; that is, π-orbital saturation occurs. This apparently is not occurring in the acetonitrile 2:1 adduct of Rh_2But_4 and it most probably is not the cause for decreased π stabilization in many other organometallic systems. Literature reports of π-orbital saturation should be reexamined to determine whether or not this previously unrecognized σ-inductive weakening of π^* back-bonding is a possible reason for observed trends.

Solvent Effects in the Benzene and CH_2Cl_2 Data. The solvation correction procedures provide some very interesting insights regarding the solution behavior of this system. In earlier studies[14] from this laboratory, investigation of the enthalpy of adduct formation in several solvents led to procedures for correcting enthalpy data that were obtained in polar acidic or basic solvents to the solvation-minimized data one would measure in poorly solvating solvents such as CCl_4 and alkanes. Subtle specific interactions in solution were indicated in systems that failed to obey these correction procedures.

The values that are most readily comparable (C_6H_6 vs. CH_2Cl_2) are the $\Delta\Delta H_T$ values (Table V) because variable contributions from benzene coordination (eq 1) are absent. The values for acetonitrile, pyridine, and *N*-methylimidazole are similar in these two solvents as expected. The piperidine value deviates, and we shall discuss the reason for this in a later section. If the values reported previously[1] for 4-picoline *N*-oxide were employed, this sytem would also deviate. This donor caused problems earlier[15] when the measured enthalpy of formation for the pyridine *N*-oxide adduct of $VO(hfac)_2$ in benzene was found to be 0.8 kcal·mol^{-1} less than the *E*- and *C*-predicted enthalpy. It is possible that 4-picoline *N*-oxide and pyridine *N*-oxide interact with benzene in the same way that pyridine does,[16] resulting in a low measured enthalpy of adduct formation in benzene solutions for these bases. Accordingly, the enthalpy of adduct formation of 4-picoline *N*-oxide with *m*-fluorophenol was measured in benzene solution. A value of 8.4 kcal·mol^{-1},[17] in good agreement with the solvent-minimized value of 8.5 kcal·mol^{-1}, was obtained indicating the absence of a significant specific interaction of benzene with 4-picoline *N*-oxide. Both *N*-oxides are extremely hygroscopic, and they must be handled in the complete absence of water. Previous workers did not take great precautions so it is likely that the bases that were used were wet,[1,18] resulting in less negative enthalpies of formation.

Table VI. Entropy Change for Dimeric Rhodium(II) Butyrate Base Binding[a]

base	benzene[b]		methylene chloride[c]	
	$-\Delta S_{1:1}$	$-\Delta S_{2:1}$	$-\Delta S_{1:1}$	$-\Delta S_{2:1}$
MeCN	2.4 (0.9)	21.5 (1.5)	12.5 (2.0)	18.3 (5.3)
py	0.3 (0.9)	17.8 (1.2)	17.1 (0.8)	10.4 (0.8)
N-MeIm	0.7 (≥2.3)	13.0 (4.9)	9.8 (≥1.2)	18.2 (≥1.6)
pip	3.4 (≥1.0)	20.4 (2.7)	8.0 (≥0.7)	16.0 (≥0.8)
THTP	4.1 (1.1)	15.2 (1.3)		
caged phosphite	7.2 (0.8)	18.0 (0.7)		
4-pic-*N*-O	−7.7 (0.9)	10.4 (4.9)	6.7 (1.2)	8.9 (1.7)
Me_2SO	0.8 (2.5)	9.4 (1.5)		

[a] Values are calculated from $\Delta S = \Delta H/T + R \ln k$ reported in units of cal·mol^{-1}·deg^{-1}. The errors were estimated by $\sigma_{\Delta S} = (\partial(\Delta S)/\partial(\Delta H))\mathrm{d}(\Delta H) + (\partial(\Delta S)/\partial(K))\mathrm{d}K$; $\mathrm{d}(\Delta H)$ and $\mathrm{d}K$ were estimated from the corresponding standard deviations. For those bases for which $\mathrm{d}K$ is unknown, a lower limit of $\sigma_{\Delta S}$ is obtained from the ΔH term. [b] Benzene solution data from Table I were used to calculate the $-\Delta S$ values. [c] Methylene chloride solution data from Table II were used to calculate the $-\Delta S$ values.

The interpretation of the $\Delta\Delta H_{1:1}$ and $\Delta\Delta H_{2:1}$ data in these two solvents is complicated by variation of the position of the equilibrium in eq 1 for various bases. The enthalpy data, in methylene chloride solutions, for adding the first base are greater than those in benzene by 3–6 kcal·mol^{-1} for all bases studied. However, excluding piperidine, the enthalpy of adduct formation for the second base addition is roughly comparable between the two solvents. Therefore, the greatest contribution to the anomalous interaction in benzene is associated with the formation of the 1:1 adduct, and not with the formation of the 2:1 adduct.

A similar conclusion is reached through an analysis of the entropy change associated with base binding, Table VI. The $-\Delta S_{2:1}$ values in benzene, the $-\Delta S_{1:1}$ values measured in methylene chloride, and the $-\Delta S_{2:1}$ values measured in methylene chloride correspond to simple base addition and are all reasonably close to a $-\Delta S$ value[6e] of 12 eu. The $-\Delta S_{1:1}$ value for caged phosphite is an exception; the region is not certain. Thus, these entropy values, like the enthalpy values, indicate anomalies associated with the formation of the 1:1 adduct in benzene solutions.

In a previous report,[1] the equilibrium in eq 1 was proposed to explain this behavior. If both benzenes are displaced when one base coordinates or if coordination of the first base weakens the interaction to the remaining benzene, a lower enthalpy, $\Delta H_{1:1}$, and entropy, $\Delta S_{1:1}$, would be measured than one would obtain in the absence of benzene coordination. The solvent dependence of the visible spectra of the acid and its adducts provides important insights regarding these alternatives and another important solution interaction. As seen in Table VII,

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(14) (a) W. Partheimer, T. D. Epley, and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 3886 (1968); (b) R. S. Drago, M. S. Nozari, and G. C. Vogel, *ibid.*, **94**, 90 (1972).

(15) R. S. Drago, T. C. Kuechler, and M. Kroeger, *Inorg. Chem.*, **18**, 2337 (1979).

(16) M. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **94**, 6877 (1972).

(17) This enthalpy has been corrected for a 1.2 kcal·mol^{-1} *m*-fluorophenol–benzene interaction.[14b] The raw calorimetric data are presented in the supplementary material.

(18) With use of the *E* and *C* equation the 4-picoline *N*-oxide–water interaction is predicted to be 4.9 kcal·mol^{-1}, and the water–benzene interaction is predicted to be 0.73 kcal·mol^{-1}; thus, hydrated 4-picoline *N*-oxide would be expected to yield molar enthalpies about 4 kcal·mol^{-1} lower than that for dry 4-picoline *N*-oxide. If the base is only partially hydrated, the deviation would be less, as was seen for the dirhodium(II) butyrate and vanadyl studies. The use of 4-picoline *N*-oxide that was stored in a closed jar over partially hydrated P_2O_5 for 3 months gave a heat in CH_2Cl_2 that was *2 kcal·mol^{-1} less* than that for which the base was stored in an inert-atmosphere box for the same period of time. The entropy data of Table IV support this conclusion. The strong base–water interaction is broken up upon adduct formation and is expected to lower the $-\Delta S$ value for both steps of the base adduct formation reaction. This is seen in Table IV where both $-\Delta S_{1:1}$ and $-\Delta S_{2:1}$ are substantially less than the averages $-\Delta S_{1:1}$ and $-\Delta S_{2:1}$ values. For these reasons the enthalpies reported in Table I are those calculated by the solvation-correction procedure.

Table VII. Absorption maxima for 1:1 and 2:1 Adducts of Dimeric Rhodium(II) Butyrate from Methylene Chloride and Benzene Solutions[a, b]

base[f]	$\bar{\nu}_{1:1}$	$\bar{\nu}_{2:1}$	$\Delta\bar{\nu}_1$[c]	$\Delta\bar{\nu}_2$[c]
MeCN	16 610 (16 260)	17 990 (18 080)	1470 (1280)	1210 (1840)
py	17 610 (17 120)	19 300 (19 300)	2470 (2140)	1700 (2180)
N-MeIm	17 510 (17 040)	18 960 (18 940)	2370 (2050)	1440 (1900)
pip	17 470 (17 120)	18 830 (18 900)	2330 (2140)	1360 (1780)
4-pic-*N*-O	16 000 (15 530)[d]	16 810 (16 690)	860 (550)	810 (1170)
	av diff[e] 426	av diff[e] −40		

[a] Benzene solution data are from ref 1, except for $\bar{\nu}_0$ which was remeasured in a saturated benzene solution. [b] Band maxima are presented in the form $\bar{\nu}(CH_2Cl_2)$ ($\bar{\nu}$(benzene)) in units of cm^{-1}. [c] $\bar{\nu}_0$ for saturated solutions of Rh_2But_4 is 14 980 cm^{-1}; $\Delta\bar{\nu}_1 = \bar{\nu}_{1:1} - \bar{\nu}_0$, $\Delta\bar{\nu}_2 = \bar{\nu}_{2:1} - \bar{\nu}_{1:1}$. [d] The frequency of this band maximum is not accurately known. [e] The average difference between $\bar{\nu}(CH_2Cl_2)$ and $\bar{\nu}$(benzene) in cm^{-1}. [f] $\bar{\nu}_0$(free acid) = 15 410 (14 980) cm^{-1}.

the $\bar{\nu}_{1:1}$ values obtained from benzene solutions are all less than the corresponding values obtained from methylene chloride solutions. The deviations between the $\bar{\nu}_{2:1}$ values in these two solvents are about those expected from the accuracy of determining a band maximum in this wavelength domain. Since the 2:1 adducts do not demonstrate such a pronounced solvent dependence, it is likely that the variation in the 1:1 adducts is due to benzene solvent coordination involving π-electron donation to the axial sites. Further, it has been found that the absorption maximum of *supersaturated* benzene solutions of rhodium(II) butyrate, $\bar{\nu}_0$ = 15 340 cm^{-1}, broadens, decreases in intensity, and shifts to a lower energy over a period of hours as solid rhodium(II) butyrate precipitates out of solution. The spectrum of a saturated benzene solution of rhodium(II) butyrate has an absorption maximum at 14 980 cm^{-1}. The high $\bar{\nu}_0$ value obtained from supersaturated solutions likely results from a carboxylate oxygen–rhodium intermolecular bridging interaction (aggregation) in the supersaturated solutions. Aggregation raises the level of the σ^* orbital of the acid, resulting in a $\pi^* \rightarrow \sigma^*$ transition that is higher in energy than would be present in the absence of this interaction. Aggregation may still be present in the saturated solutions (vide infra) but to a lesser extent than in the supersaturated solutions, as indicated by the lowered $\bar{\nu}_0$ value. Similar oxygen–metal interactions have been reported in the solid state.[19]

The above effect is also consistent with calorimetric and spectrophotometric results. When a strong base coordinates to dirhodium(II) butyrate, the aggregate will break up. This decreases the observed $-\Delta H_{1:1}$ and $-\Delta S_{1:1}$ values from what one would obtain in the absence of this intermolecular interaction. A more exothermic reaction results in methylene chloride solutions because in supersaturated benzene solutions intermolecular acid interactions exist along with benzene solvation. The nearly constant deviation of the $-\Delta H_{1:1}$ values in benzene from those in CH_2Cl_2 is expected since the degree of supersaturation and solvation is about the same for each solution.[1] The fact that the $-H_T$ values in CH_2Cl_2 and benzene differ by essentially the same amount as the $-\Delta H_{1:1}$ values indicates that the 1:1 adduct is not aggregated. There probably is some weak benzene solvation of the 1:1 adduct as indicated by the solvent dependence of the $\pi^* \rightarrow \sigma^*$ transition for the free acid and the 1:1 adducts (see Table VII).

Even though it is not possible at this point to determine the extent to which aggregation and benzene coordination individually contribute to the measured enthalpy, these studies enable us to determine solvent-minimized enthalpy values. From the above discussion it is concluded that the calorimetric data obtained from methylene chloride solutions represent solvent-minimized data and that the calorimetric data obtained from benzene solutions, with the exception of piperidine, can be corrected for the above complicating interactions by the addition of a constant, 3.9 kcal·mol^{-1}, to the $-\Delta H_{1:1}$ values.

As mentioned earlier, the $\Delta\Delta H_T$ value listed in Table V for piperidine deviates from 3.9 kcal·mol^{-1} by more than can be expected from random experimental errors. For $\Delta\Delta H_{1:1}$ the difference is 2.1 kcal·mol^{-1} less than the expected value, and for $\Delta\Delta H_T$ the difference is an *additional* 1.8 kcal·mol^{-1} less. This indicates that there is an additional enthalpic term associated with the coordination of each mole of base to the acid. It is expected and has been demonstrated previously[20] that the N–H proton is more acidic in the "ammonium" form of the adduct than in free piperidine. As a result, it is likely that the N–H proton of the rhodium(II) butyrate–piperidine adduct is involved in a hydrogen-bonding interaction with the solvent, benzene. This interaction, which is not present in methylene chloride, would lead to a large value for the enthalpy of adduct formation measured in benzene solutions. Experimental support for this hypothesis has been obtained from the infrared N–H stretching vibration of the 1:1 adduct: $\nu_{N-H(benzene)}$ = 3260 cm^{-1} and $\nu_{N-H(CH_2Cl_2)}$ = 3270 cm^{-1}. The ν_{N-H} value for piperidine occurs at 3338 cm^{-1} in both benzene and methylene chloride. The N–H stretching frequency in the adduct is lowered relative to the value obtained in CH_2Cl_2 as a result of the hydrogen-bonding interaction with benzene. A previous study[21] of the hydrogen bonding of base adducts of pyrrole indicates that a 10-cm^{-1} shift in ν_{N-H} roughly corresponds to a 2 kcal·mol^{-1} interaction.

This analysis of solvent effects has not only provided some interesting detail regarding solvent effects in benzene but also establishes the solvent-minimized data (Table III) necessary to characterize Rh_2But_4 as a Lewis acid.

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Registry No. $Rh_2(But)_4$, 56281-34-6; $Rh_2(But)_4$·MeCN, 78063-98-6; $Rh_2(But)_4$·2MeCN, 78088-85-4; $Rh_2(But)_4$·py, 78063-99-7; $Rh_2(But)_4$·2py, 59993-30-5; $Rh_2(But)_4$·*N*-MeIm, 78064-00-3; $Rh_2(But)_4$·2*N*-MeIm, 78064-01-4; $Rh_2(But)_4$·pip, 78064-02-5; $Rh_2(But)_4$·2pip, 78064-03-6; $Rh_2(But)_4$·THTP, 78064-04-7; $Rh_2(But)_4$·2THTP, 78064-05-8; $Rh_2(But)_4$·(caged phosphite), 78064-06-9; $Rh_2(But)_4$·2(caged phosphite), 78064-07-0; $Rh_2(But)_4$·4-pic-*N*-O, 78064-08-1; $Rh_2(But)_4$·2(4-pic-*N*-O), 78064-09-2; $Rh_2(But)_4$·Me_2SO, 78065-16-4; $Rh_2(But)_4$·2Me_2SO, 59978-36-8; Rh, 7440-16-6.

Supplementary Material Available: Spectral and calorimetric data for Rh_2But_4 complexes (5 pages). Ordering information is given on any current masthead page.

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