upon the ratio $[Cl^-]/[I^-]$. As $[Cl^-]$ increases during the course of the reaction and no variation (within experimental error) of k_3 was observed, we conclude that this pathway is unimportant in these studies.

The chlorite–iodide clock reaction, run under conditions of excess chlorite, has a "spectacularly abrupt fadeout", due to the disappearance of iodine.[7] The reaction responsible for this effect is chlorite–iodine, which had previously been reported to be "quasi instantê".[8] We have shown that this reaction requires about 100 to 800 ms, depending on pH and concentrations. This work, together with the previous studies of the chlorite–iodide reaction[7,8] and an analysis of this reaction in a continuous-flow stirred-tank reactor,[3] should make it possible (at least in the upper pH range where $HClO_2$ is unimportant)[13] to develop a molecular mechanism for the rich variety of phenomena observed in the chlorite–iodide system.

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Comparison of the Coordination Chemistry and Inductive Transfer through the Metal–Metal Bond in Adducts of Dirhodium and Dimolybdenum Carboxylates

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By the study of the thermodynamics of base binding in systems containing metal–metal bonds, significant observations pertaining to the synergistic interaction between the metals can be made that help in understanding the influence that one metal can have upon the chemistry of a second metal. The effectiveness of the metal π^* to ligand π^* back-bonding interaction, which was found to play such an important role in the chemistry of the 1:1 and 2:1 adducts of dirhodium butyrate, is probed as a function of both the ancillary ligand (butyrate vs. perfluorobutyrate) and the metal atom (Rh(II) vs. Mo(II)). Study of the Mo^{IV}_2 system provides strong support for our earlier interpretation of the thermodynamic data for the Rh^{IV}_2 system in terms of π-back-bond stabilization. The change in the base-binding characteristics of the second metal center that accompanies coordination of a base to the primary metal site was also studied as a function of these variables. Results indicate that increasing the electronegativity of the carboxylate group decreases the relative importance of π-back-bonding in the dirhodium system, although such a change has little influence on the inductive transfer to the second metal resulting from coordination of base to the first metal. In addition, it has been shown that the inductive transfer of electrostatic properties of the base is more effective through the shorter Mo–Mo bond than through the longer Rh–Rh bond. On the other hand, the inductive transfer of the base's covalent properties to the second metal center is more effective through the more polarizable Rh–Rh bond than through the quadruple Mo–Mo bond.

Introduction

The understanding and systematic development of a unique reaction chemistry for metal cluster systems require a knowledge of the factors that influence the transmission of electronic effects through metal–metal bonds. Electronic readjustments in the metal–metal bonds of a cluster occur upon coordination of a ligand to one of the metals. These effects not only provide a polarizability mechanism for enhanced ligand binding to the coordinated metal but also influence the subsequent coordination and redox chemistry that occurs at the other interacting metal centers in the cluster. Variations that can be made in the cluster size, the cluster geometry, the metal atoms involved, the electronic nature of the metal–metal bond, and the ancillary ligands provide the potential for a rich and selective chemistry if concepts for the intelligent manipulation of these variables can be developed.

Earlier work from this laboratory[1,2] has focused upon the coordination and redox chemistry of metal-bonded rhodium(II)–rhodium(II) bimetallomers. It was shown[1] that the filled, essentially metal π^* orbitals were very effective at π-back-donation into π-acceptor ligands. This was attributed to a strong interaction between the d_{xz} (and d_{yz}) orbital of one metal with that of a second metal when a direct metal–metal bond exists. The mechanism whereby and extent to which coordination of a base, B, to one metal center influences the acidity of the second metal center could be quantitatively predicted for σ donors with the equation

$$-\Delta H_{2:1} = -\Delta H_{1:1} - kE_B^2 - k'C_B^2 \qquad (1)$$

where E_B and C_B are base parameters from the E and C correlation and k and k' are constant parameters of the cluster that describe the susceptibility of the metal–metal bond to electrostatic and covalent effects.[2] The influence of π back-bonding and σ donation at one center on the ability of the second metal center to undergo these interactions was also determined. The studies demonstrate the utility of thermodynamic studies of base bonding in providing answers to some fundamental questions in cluster chemistry. The systems reported in this article provide information about the influence that the ancillary ligands and the metal atoms themselves have upon the Lewis acid properties of the cluster. Attaining additional data on dirhodium(II) perfluorobutyrate provides information relevant to the former question, and the data on dimolybdenum(II) perfluorobutyrate provide information relevant to the latter.

Experimental Section

1. Synthesis and Purification. Metal Complexes. Rhodium acetate was prepared by literature methods.[3] Conversion to the perfluorobutyrate[4] involved the reflux of a solution of $Rh_2(acetate)_4$ in 30 mL of perfluorobutyric acid and 3 mL of perfluorobutyric anhydride for

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Table I. Thermodynamic Data for the Formation of 1:1 and 2:1 Base Adducts of Dimeric Rhodium(II) Perfluorobutyrate in Toluene Solution

base	K_1	K_2	$-\Delta H_{1:1}$, kcal mol^{-1}	$-\Delta H_{2:1}$, kcal mol^{-1}	$\Delta\bar{\nu}_1$[c]	$\Delta\bar{\nu}_2$[c]
MeCN	$1.43\ (0.23) \times 10^5$	$4.53\ (2.0) \times 10^3$	10.2 (0.8)	7.4 (0.5)	2230	1510
py[a]	$\sim 10^7$		16.3		3220	
N-MeIm[b]	$\sim 10^7$		19.0 (0.4)		3110	1070[d]
Me_2SO	$6.78\ (0.05) \times 10^5$	$6.11\ (0.05) \times 10^3$	10.7 (0.4)	8.1 (0.4)	1560	860
DMA	$5.44\ (0.12) \times 10^4$	$6.37\ (0.19) \times 10^2$	9.5 (0.6)	9.6 (0.8)	1520	850

[a] The experimental $-\Delta H_{1:1}$ value is 15.4 kcal mol^{-1}; a 0.9 kcal mol^{-1} correction for a pyridine–toluene interaction was assumed. No estimate of the error in $-\Delta H_{1:1}$ is available since $-\Delta H_{1:1}$ was determined from only two injections of base. [b] The $-\Delta H_{1:1}$ value was calculated by analyzing the first four injections as a 1:1 equilibria; the 2:1 adduct decomposes. [c] Frequency shifts are obtained from toluene solution and are in units of cm^{-1}. $\bar{\nu}_0$ for $Rh_2(pfb)_4$ occurs at 14 510 cm^{-1} in toluene solvent. $\Delta\bar{\nu}_1 = \bar{\nu}_{1:1} - \bar{\nu}_0$ and $\Delta\bar{\nu}_2 = \bar{\nu}_{2:1} = \bar{\nu}_{1:1}$. [d] Approximate value.

Table II. Solvent-Corrected Enthalpies and Equilibrium Constants for the Formation of 1:1 and 2:1 Base Adducts of Dimeric Rhodium(II) Perfluorobutyrate in Methylene Chloride Solution[a]

base	K_1	K_2	$-\Delta H_{1:1}$, kcal mol^{-1}	$-\Delta H_{2:1}$, kcal mol^{-1}
py[b]	$\sim 10^7$	4.15×10^4	18.4 (0.4)	15.0 (0.4)
N-MeIm[b]	$\sim 10^7$		18.5 (0.9)	
DMA	$2.29\ (0.05) \times 10^5$	$1.52\ (0.01) \times 10^3$	10.9 (0.4)	9.3 (0.3)

[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.[8] [b] ΔH values were calculated from calorimetric data by fixing K_1 at 1×10^7 and fitting $\Delta H_{1:1}$, $\Delta H_{2:1}$, and K_2. The ΔH's change only slightly if K_1 is varied by a factor of 10^2.

15 min under a N_2 atmosphere. Most of the solvent was then distilled off, and the remaining material was cooled to −20 °C for at least 24 h. The resulting dark blue solid was filtered and washed with cold pentane until a clear filtrate was obtained. The solid was recrystallized from benzene, filtered, and washed with cold pentane. The product, a mixture of the water and perfluorobutyric acid adducts, was converted to $Rh_2(pfb)_4$ by drying in vacuo at 100 °C over NaOH for 12 h. Dry rhodium(II) perfluorobutyrate is a bright yellow-green solid, which readily picks up water from the air to form a blue adduct. Since airborne bases are picked up irreversibly by the solid, it must be handled in a clean, inert atmosphere. $Rh_2(pfb)_4$ is not soluble in CCl_4 or aliphatic hydrocarbons, but its solubility in CH_2Cl_2 and aromatic solvents is excellent, $>10^{-2}$ M. Anal. Calcd for $Rh_2C_{16}F_{28}O_8$: C, 18.16. Found: C, 18.3.

Molybdenum acetate was prepared by literature methods[5] $Mo(CO)_6$ was obtained from Alfa Division). Conversion to molybdenum perfluorobutyrate, $Mo(pfb)_4$, was effected by a modified method of that which was used for the preparation of molybdenum trifluoroacetate. A solution of molybdenum acetate (1 g) in perfluorobutyric acid (30 mL) and perfluorobutyric anhydride (3 mL) was degassed and heated to boiling, after which half of the solvent was distilled off. The remaining solid was cooled at −20 °C overnight, filtered, washed with cold pentane, and dried under Ar. The yellow solid was further dried in vacuo at 100 °C over NaOH for 12 h, yielding 2 g of dry molybdenum perfluorobutyrate. Dry molybdenum perfluorobutyrate decomposes slowly in air and should be stored over P_2O_5 in vacuo. $Mo_2(pfb)_4$ is soluble in toluene ($>5.5 \times 10^{-3}$ M) and only slightly soluble in CH_2Cl_2 ($<1 \times 10^{-3}$ M). Anal. Calcd for $Mo_2C_{16}F_{28}O_8$: Mo, 18.38; C, 18.41. Found: Mo, 18.42; C, 18.44.

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 glovebag.

Solvents. Reagent grade toluene was 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_2O_5 (bp 41 °C) and stored over Linde 4-Å molecular sieves. Solvents used in the dimolybdenum perfluorobutyrate study were degassed by three freeze–pump–thaw cycles.

2. Data Collection. Calorimetry. Details of the procedures involved in the calorimetry portion of this work have been described previously.[2]

UV–Vis Spectroscopy. For the obtainment of sample solutions with various concentrations of base yet with a constant concentration of the acid, the appropriate quantity of a base stock solution was added to separate aliquots of a stock solution of the acid and then diluted to 2 mL.[7] Spectra were recorded on a Cary 14 spectrometer.

Cyclic Voltammetry. Cyclic voltammetry was performed as reported previously.[1] The experiments were conducted with use of a PAR Model 173 potentiostat/galvanostat and Model 176 current-to-voltage converter and recorded on a Tektronix 564 storage oscilloscope. The reference electrode was a silver wire suspended in a saturated AgI solution of CH_2Cl_2, which was 0.05 M in Bu_4NI and 0.42 M in Bu_4NBF_4. Electrolyte solutions were 0.42 M Bu_4NBF_4 in CH_2Cl_2. Rhodium carboxylate solutions were 2.5×10^{-3} M, and molybdenum carboxylate solutions were 8×10^{-4} M.

Results

1. Dirhodium(II) Perfluorobutyrate ($Rh_2(pfb)_4$) Thermodynamic Studies. A. Toluene Solutions. Electronic spectral changes upon base binding, similar to those reported earlier,[1,2] were used to determine the equilibrium constants for 1:1 and 2:1 adduct formation. Enthalpies were determined calorimetrically with use of spectroscopic equilibrium constants. A tabulation of the raw spectroscopic and raw calorimetric data is provided in the supplementary material. The thermodynamic parameters that best fit the raw data are shown in Table I. The 2:1 base adducts of pyridine and *N*-methylimidazole could not be studied because of competing dimer decomposition reactions in solution. For these bases the $-\Delta H_{1:1}$ values were determined by analysis of those calorimetric results for which the total base concentration, B_T, was less than the total acid concentration, A_T, using a 1:1 equilibrium constant expression. Good values for $-\Delta H_{1:1}$ could be obtained in this manner.

B. Methylene Chloride Solutions. For the verification of the presence, or absence, of toluene coordination, the thermodynamic parameters were also determined from methylene chloride solutions. A tabulation of the thermodynamic parameters that have been corrected for the base–methylene chloride interaction[8] is presented in Table II. It should be noted that the addition of *N*-methylimidazole to methylene chloride solutions of rhodium(II) perfluorobutyrate resulted in color changes that were not characteristic of 1:1 and 2:1 adduct formation. Therefore, it is believed that *N*-methylimidazole undergoes something other than simple 2:1 equilibria with this acid in methylene chloride solution. Attempts to determine the source of the deviation from simple 2:1 equilibria were unsuccessful.

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Table III. Absorption Maxima for 1:1 and 2:1 Adducts of Dimeric Rhodium(II) Perfluorobutyrate from Methylene Chloride and Toluene Solutions[a]

base	$\bar{\nu}_0$	$\bar{\nu}_{1:1}$	$\bar{\nu}_{2:1}$	$\Delta\bar{\nu}_1$ [b]	$\Delta\bar{\nu}_2$ [b]
	15 720 (14 510)				
MeCN		17 210 (16 740)	18 180 (18 250)	1490 (2230)	970 (1510)
py		18 100 (17 730)	19 420 (...)	2380 (3220)	1320 (...)
N-MeIm		... (17 620)	... (18 690)	... (3110)	... (1070)[c]
Me_2SO		16 500 (16 060)	17 010 (16 920)	780 (1560)	500 (860)
DMA		16 450 (16 030)	16 860 (16 880)	720 (1520)	420 (850)
		av diff[d] 425	av diff[d] 2.7		

[a] Band maxima are presented in the form $\bar{\nu}$ (CH_2Cl_2) ($\bar{\nu}$ (toluene)) in units of cm^{-1}. [b] $\bar{\nu}_0$ for toluene solutions of free $Rh_2(pfb)_4$ is 14 510 cm^{-1}. $\Delta\bar{\nu}_1 = \bar{\nu}_{1:1} - \bar{\nu}_0$, $\Delta\bar{\nu}_2 = \bar{\nu}_{2:1} - \bar{\nu}_{1:1}$. [c] Approximate value. [d] The average difference between $\bar{\nu}$ (CH_2Cl_2) and $\bar{\nu}$ (toluene).

2. Electronic Absorption Spectra of 1:1 and 2:1 Adducts of Dirhodium(II) Perfluorobutyrate. The electronic absorption spectra of the free acid as well as those of the 1:1 and 2:1 adducts provide information regarding solvent interactions with these species. The results are summarized in Table III. Solvent participation is more important for the free acid and 1:1 adduct than for the 2:1 adduct, as might be expected on the basis of availability of unoccupied sites capable of interacting with the solvent.

3. Electrochemical Studies. An electrochemical study of rhodium(II) perfluorobutyrate and its adducts in methylene chloride solution was attempted. The oxidation potentials for this acid and its adducts, however, are at potentials more oxidizing than the solvent–electrolyte cutoff. The inductive effect of the fluorines makes the rhodium centers very difficult to oxidize. This is consistent with the results of Das et al.,[9] on the $Rh_2(O_2CCF_3)_4{\cdot}2DMF$ adduct.

4. Spectral Studies of the Dimolybdenum(II) Perfluorobutyrate–Base Adducts. A spectral titration of $Mo_2(pfb)_4$ with *N*,*N*-dimethylacetamide is illustrated in Figure 1. Similar spectra were recorded for titrations with acetonitrile and pyridine. Since the spectral changes are small and no features that distinguish the 1:1 adduct from the 2:1 adduct can be discerned in the spectrum, the results do not permit accurate determinations of equilibrium constants. Since our primary concern is the enthalpy, fortunately we have been able to show that the uncertainty in *K* does not lead to errors in the enthalpies that mask the differences (Table IV). The titration of *N*-methylimidazole produced a second band at 4480 Å, having a very large molar absorptivity, for solutions in which $B_T/A_T > 1.1$. This unusual behavior is believed to be due to decomposition of the adducts.

The minor influence that coordination has upon the electronic spectrum of $Mo_2(pfb)_4$, which is in constrast to that found for $Rh_2(pfb)_4$, can be rationalized in terms of the electronic configuration. As seen in Figure 2, the lowest energy transition corresponds to a $\delta \rightarrow \delta^*$ transition. This assignment of the visible band is in agreement with Xα–SW calculations.[10] but not with single-crystal polarized spectra.[11] It has also been proposed[10] that this band may correspond to a $\delta \rightarrow \pi^*$ transition. Both transitions are expected to be insensitive to axial coordination. The δ and δ^* molecular orbitals consist primarily of metal d_{xy} atomic orbitals, and the π^* molecular orbital consists primarily of d_{xz} and d_{yz} atomic orbitals. These orbitals are not expected to be as sensitive to coordination of the donors on the *z* axis as is the σ^* orbital of $Rh_2(but)_4$.

5. Calorimetric Studies of Base Coordination to $Mo_2(pfb)_4$. In general, the monotonic nature of calorimetric measurements provides data points that are not well suited for a reliable determination of the equilibrium constants and molar enthalpies for multiequilibria processes. The severity of the problem can be minimized by collecting many data points at both low and high concentrations of the base and by repeating the experiment for each base that is used. With many data points, random errors will tend to be "averaged out" and reproducibility can be verified. For the above reasons, duplicate calorimetric determinations were performed, and for each calorimetric determination, at least nine base injections were made. A tabulation of the raw calorimetric data for the base binding of molybdenum(II) perfluorobutyrate in toluene solutions is presented in the supplementary material. A tabulation of the thermodynamic parameters that best fit the individual calorimetric determinations is presented in Table IV. The first value listed in a given column is from a fit of all the measurements to consecutive 1:1 and 2:1 equilibria. The values in parentheses result from the fitting of those data points for which the total added base concentration was less than the initial acid concentration to a simple 1:1 equilibrium expression, in effect assuming that for these injections $[AB_2] \approx 0$. The advantage of this approach is that the calorimetric data

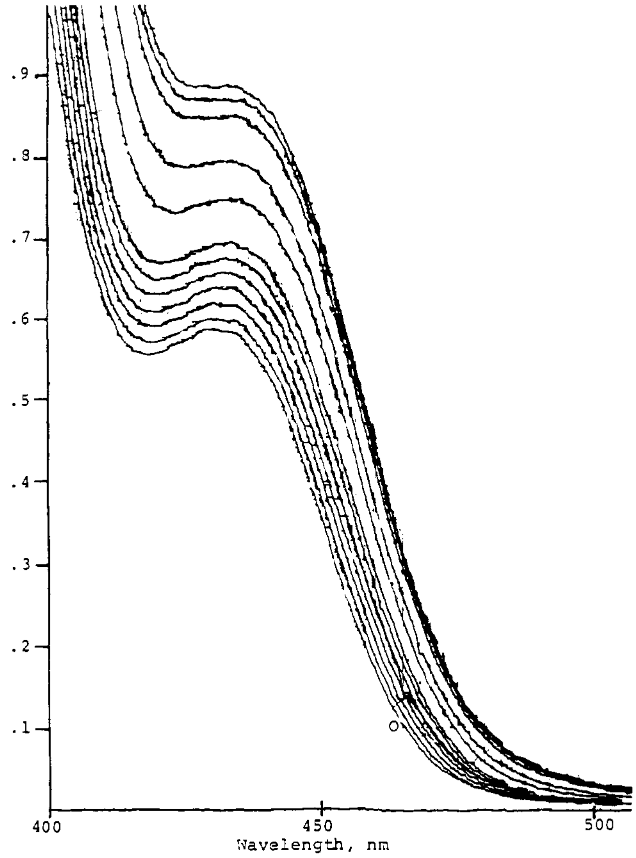

Figure 1. Spectroscopic titration of molybdenum(II) perfluorobutyrate with dimethylacetamide. The spectrum of the free acid is labeled with a "O".

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Table IV. 1:1 and 2:1 Analysis of Molybdenum(II) Perfluorobutyrate Calorimetric Data[a]

base	K_1	K_2	$-\Delta H_{1:1}$, kcal mol^{-1}	$-\Delta H_{2:1}$, kcal mol^{-1} [c]
MeCN[b]	7.5×10 (8.9×10, 9)	3.9×10	5.7 (5.5)	[−1.6]
py	7.5×10^3	1.7×10^2	9.1	6.2
	9.0×10^3 (5.7×10, 3)	3.3×10^2	8.2 (47.4)	4.6
	5.7×10^3 (6.5×10^2, 3)	1.8×10^2	8.7 (12.6)	5.9
THTP[b]	4.4×10 (2.7×10, 10)	7.6	3.5 (5.1)	[1.8]
Me_2SO	2.1×10^4	1.0×10^3	9.0	4.6
	1.7×10^4 (2.8×10^4, 4)	6.76×10^2	9.5 (9.2)	7.3
DMA	2.0×10^5 (9.1×10^7, 4)	6.2×10^2	8.8 (8.8)	6.6
	5.0×10^4 (1.2×10^5, 4)	6.6×10^2	8.8 (8.6)	5.3
bridged ether	5.8×10^2 (5.6×10^2, 3)	3.5×10	6.5 (6.7)	[1.6]

[a] Results from the 1:1 analysis of the data are presented in parentheses. For the K_1 values, the second number in the parentheses indicates the number of data points used in the 1:1 analysis; unless otherwise indicated, the 1:1 analysis was performed with those data points for which $B_T/A_T < 1$. [b] All injections were used for the 1:1 analysis. [c] Brackets refer to unreliable data.

Table V. Entropy Change for Dimeric Molybdenum(II) Perfluorobutyrate Base Binding[a]

base	$-\Delta S_{1:1}$	$-\Delta S_{2:1}$	base	$-\Delta S_{1:1}$	$-\Delta S_{2:1}$
MeCN	10.7 (0.7)		Me_2SO	11.5 (1.3)	7.5 (1.0)
py	14.5 (0.7)	11.2 (0.7)	DMA	6.7 (0.7)	8.1 (0.3)
THTP[b]	10.6 (0.1)		bridged ether	9.3 (0.7)	~2

[a] Values are reported in units of cal mol^{-1} deg^{-1}. The errors were estimated by $\sigma_{\Delta S} = [\partial(\Delta S)/\partial(\Delta H)]\, d(\Delta H)$. The $d(\Delta H)$ term was estimated to be $\simeq \sigma_{\Delta H}$. [b] THTP = tetrahydrothiophene.

Table VI. Solvation-Corrected Enthalpies[a] for Dirhodium(II) Perfluorobutyrate and Butyrate[2]

	$Rh_2(pfb)_4$			$Rh_2(but)_4$	
base	$-\Delta H_{1:1}$	$-\Delta H_{E \text{ and } C}$	$-\Delta H_{2:1}$	$-\Delta H_{1:1}$	$-\Delta H_{2:1}$
MeCN[c]	11.5	6.8	7.4	9.3	8.3
py	18.4	17.0	15.0	16.6	10.5
N-MeIm[c]	20.3	20.3	...	15.4	11.5
Me_2SO[c]	~12	11.7	~8		
DMA	10.9	11.2	9.3		

[a] Enthalpy values are those obtained from methylene chloride solutions in units of kcal mol^{-1} unless noted in footnote *c*. [b] For the 1:1 adduct, with *N*-methylimidazole, dimethyl sulfoxide (an oxygen donor for the acid),[4] and dimethylacetamide $E_A = 5.06$ ($\sigma = 0.28$) and $C_A = 1.74$ ($\sigma = 0.06$). [c] $-\Delta H_{1:1}$ was obtained for $Rh_2(pfb)_4$ by adding 1.3 kcal mol^{-1} (vide infra) for toluene dissociation to the 1:1 enthalpy measured in toluene; no correction was applied to the $-H_{2:1}$ values, for base coordination probably leads to dissociation of more than one benzene and lowers the enthalpy of interaction with benzene.[2]

are fitted to only two parameters (i.e., $-\Delta H$ and K_1), instead of four. The disadvantage, however, is that the extent of complexation of the acid will be limited, and the results will have large marginal to conditional error ratios.[12] However, this method of analysis of the data is only meant to check the consistency (and hence the accuracy) of the data, to insure that the results of the 2:1 analysis of the data are not just an arbitrary fit of the data to a set of parameters. Accurate values for the 1:1 adduct are indicated when agreement between the two analyses is obtained.

For the weakest base, tetrahydrothiophene, the data over the entire range of base concentration gave an adequate fit to a 1:1 equilibrium expression. This indicates that the concentration of AB_2 in this system is always low and the thermodynamic data obtained by fitting the data to a consecutive 1:1 and 2:1 equilibrium expression are of little significance.

When *N*-methylimidazole was used as a base in this experiment, side reactions other than 1:1 and 2:1 adduct formation were encountered. The enthalpy data could not be fit to a combined consecutive 1:1 and 2:1 equilibrium expression. Heat continued to be evolved even after a large excess of base was added.

6. Solvation Contributions to the Measured Enthalpies. The difference in the enthalpies of adduct formation measured in CH_2Cl_2 and toluene indicate coordination of the latter to dirhodium(II) perfluorobutyrate. A correction of −1.3 kcal mol^{-1} to the enthalpies measured in toluene is indicated.

Unlike the rhodium(II) carboxylates, molybdenum(II) perfluorobutyrate is not soluble in methylene chloride; therefore, all conclusions must be based on data obtained from toluene solutions. As is seen in Table V, the entropy changes associated with the base binding of molybdenum(II) perfluorobutyrate in toluene solutions are close to the 12 eu expected.[6e] This fact, as well as the observation that ν_0 is concentration independent, indicates that the metal–oxygen intermolecular interaction that was proposed for supersaturated benzene solutions of rhodium(II) butyrate is not present in this system.[1]

If the enthalpy data for $Mo_2(pfb)_4 \cdot B$ contain a constant enthalpic term resulting from coordination to the free acid, and "*E*, *C*, and *W*" analysis of the data would indicate the magnitude of this enthalpic term.[6d] By a fit of the enthalpy data of Table IV to the *E*, *C*, and *W* equation

$$-\Delta H = E_A E_B + C_A C_B + W$$

a value of $W = 0.4$ kcal mol^{-1} resulted. Since this value is small and since the quality of the fit relative to the error in the measurement was not greatly improved for the *E*, *C*, *W* fit compared to that for the *E*, *C* fit, we conclude that this is a small effect that can be neglected for our purposes.

7. Infrared Studies. The C≡N stretching frequency of free acetonitrile (2265 cm^{-1}) is shifted to slightly higher frequency (2268 cm^{-1}) upon forming a 1:1 adduct with $Mo_2(pfb)_4$. When CO is bubbled through a toluene solution of $Mo_2(pfb)_4$, no detectable IR absorption band for bound CO is observed. Significant quantities of a CO adduct do not form in this system in contrast to the case for dimeric rhodium(II) systems.

Discussion

A qualitative molecular orbital ordering for a d^7–d^7 system is shown in Figure 2. This ordering was proposed earlier in an EPR study[13] of a free radical base adduct and subsequently resulted from SCF–Xα calculations.[14] The interaction of the d orbitals leads to a polarization of the π^* orbital, as shown in Figure 3, that makes it effective at π^* back-bonding into vacant ligand orbitals. The radial extension of the unfilled d orbitals contributes to the pronounced polarization of these orbitals toward the ligand π-acceptor orbitals. Recently, the

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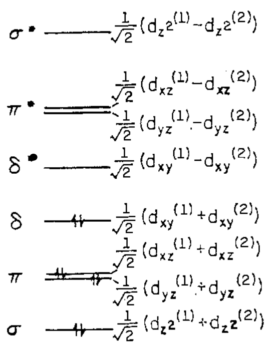

Figure 2. Qualitative MO diagram of rhodium perfluorobutyrate showing combinations of metal 4d orbitals only. This rhodium(II) dimer, being a d^7–d^7 system, had 14 electrons in the metal–metal molecular orbitals.

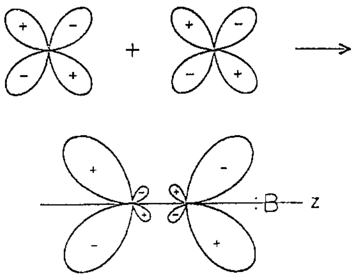

Figure 3. Rhodium d_{xz} (or d_{yz}) orbitals combining to form the corresponding π^* orbitals, which are capable of undergoing π back-bonding to B.

application of this model in our systems has been challenged on the basis of Xα calculations on the $Rh_2(O_2CH)_4{\cdot}2PH_3$ complex.[15] Since our interpretation of the $Rh_2(pfb)_4$ system is based on this π-back-bonding model, we shall discuss the $Mo_2(pfb)_4$ system first, for the results support our position.

Dimolybdenum(II) Perfluorobutyrate. With the MO energy sequence presented in Figure 2, it is predicted that dimeric metal carboxylates possessing eight or fewer electrons in the d-orbital manifold would be incapable of π* back-bonding to donors, for these dimers would not have electron density in the π* orbitals. Molybdenum(II) carboxylates were chosen for study, since they are d^4–d^4 systems. The highest occupied molecular orbital is a δ orbital, and the π* orbitals are empty. As a result, the metal–donor bond should involve a σ interaction. The perfluorobutyrate was chosen because the fluorinated bridging ligands would increase the Lewis acidity and solubility properties of the dimer.[4]

The data for $Mo_2(pfb)_4$ summarized in Table VII, demonstrate that molybdenum(II) perfluorobutyrate is a weaker Lewis acid than either of the rhodium dimers. Most important to the π*-back-bonding model, the data for the 1:1 adducts of $Mo_2(pfb)_4$ give an excellent fit to the *E* and *C* equation for each base that was studied. Thus, as predicted from the d-electron configuration, π* back-bonding is not expected to be significant with this acid and the *E* and *C* model correlates the data. These filled π* orbitals constitute the primary difference in the Rh^{IV}_2 and Mo^{IV}_2 systems, and since the Mo^{IV}_2 systems fit the *E* and *C* equation, it becomes difficult to attribute the failure of the Rh^{IV}_2 system to a lack of confidence[15] in the *E* and *C* analysis. Consequently, convincing support for the π*-back-bonding model results from the thermodynamic bond-strength data.

In the case of a d^5–d^5 or lower electron count configuration, metal–metal bonding will stabilize the d orbitals with symmetry appropriate for π back-bonding into ligands and decrease the tendency for back-bonding to occur in the metal–metal bonded system relative to that for the analogous single metal center. This idea can have important implications in metal cluster chemistry. For example, the decreased tendency of molybdenum clusters to form carbonyl complexes in contrast to the stability of the carbonyl complexes of a single molybdenum atom is rationalized on this basis.

Table VII. Thermodynamic Data for the Formation of 1:1 and 2:1 Base Adducts of Dimeric Molybdenum(II) Perfluorobutyrate in Toluene Solution[a]

base	K_1	K_2	$-\Delta H_{1:1}$	$-\Delta H_{1:1}$-(*E* and *C*)[d]	$-\Delta H_{2:1}$
MeCN	7.5×10	$\sim 3.9 \times 10$	5.7 (0.2)	5.8	small
py[b]	7.1×10^3	2.2×10^2	9.5 (0.2)	9.4	6.5 (0.2)
THTP[c]	2.8×10		5.1 (0.04)	5.1	
Me_2SO	1.9×10^4	7.5×10^2	9.2 (0.4)	9.0	6.1 (0.3)
DMA	1.0×10^5	6.4×10^2	8.8 (0.2)	8.8	6.2 (0.1)
bridged ether	5.8×10^2	$\sim 3.5 \times 10$	6.5 (0.2)	6.8	2

[a] Values are the overall best fit values to the data. Enthalpies are in units of kcal mol^{-1}. [b] Each enthalpy has been corrected for a 0.9 kcal mol^{-1} pyridine–toluene interaction. [c] Analyzed as a 1:1 equilibrium. [d] All of the 1:1 enthalpies in Table VII led to $E_A = 5.92$ ($\sigma = 0.11$) and $C_A = 0.385$ ($\sigma = 0.025$) for molybdenum(II) perfluorobutyrate.

The *E* and *C* fit of the data for the $Mo_2(pfb)_4$ adducts provides fundamental insight concerning the reason for the decreased acidity of this center. A comparison of the *E* and *C* parameters of this acid ($E = 5.92$ and $C = 0.385$ ($C{:}E = 0.065$)) to the *E* and *C* parameters of rhodium(II) perfluorobutyrate (vide infra, $E = 5.06$ and $C = 1.74$ ($C{:}E = 0.34$)) indicates that the principal difference lies in the greatly reduced C_A values. Since both rhodium and molybdenum exist in the +2 oxidation state and have comparable bridging ligands, the partial positive charge on the metal centers should be comparable. Accordingly, the E_A value and the electrostatic interaction (charge–dipole) with various Lewis bases is comparable. However, the dimolybdenum quadruple metal–metal bond is not very polarizable, so a given metal center is not able to accept electron density from the ligand as effectively and distribute it over the whole molecule. A greatly reduced *C* value results. This proposal is supported by X-ray structures[16] of dirhodium and dimolybdenum adducts, which indicate considerable change in the metal–metal bond distance upon adduct formation in the former but not in the latter. Our proposals are also in agreement with the result of SCF–Xα calculations[10] regarding the metal–metal bond strengths in the dimeric rhodium and molybdenum systems and illustrate the effect of the electronic and structural differences on reactivity.

Dirhodium(II) Perfluorobutyrate. Changing a butyrate ligand to a perfluorobutyrate ligand is expected to have minor effects on the orbital ordering in Figure 2 but would lower the energy of the entire manifold as a consequence of the increased partial positive charge on the metal. Such a change is expected to improve the energy match between the π* orbital of the metal complex and the σ-donor orbital of the axial ligand for the dirhodium(II) perfluorobutyrate relative to that of the dirhodium(II) butyrate. This effect, along with the increased partial positive charge on the metal, could lead to greater covalent and electrostatic σ-acceptor properties for the former acid. On the other hand, the acidity of the metal center might be dominated by the metal–metal interaction and would be relatively insensitive to the changes of the ancillary ligands. All other factors being similar, a lower energy for the π* orbitals should decrease the tendency for metal to ligand back-bonding for complexes of $Rh_2(pfb)_4$ compared to that

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for $Rh_2(but)_4$. A study of the acceptor properties of $Rh_2(pfb)_4$ was carried out to tests these predictions. A second important piece of information that can result from thermodynamic data on the 1:1 and 2:1 adducts involves the extent to which the inductive properties of the ancillary ligand moderate the effectiveness of inductive electron density transfer through the metal–metal bond.

The solvation-minimized (vide infra) enthalpies of adduct formation are summarized in Table VI. Like rhodium(II) butyrate, rhodium(II) perfluorobutyrate forms both 1:1 and 2:1 adducts with Lewis bases in solution, as evidenced by the presence of isosbestic points for the $A + B \rightleftarrows AB$ and $AB + B \rightleftarrows AB_2$ equilibria. With 4-picoline *N*-oxide and third-row donors, decomposition or precipitation of the 1:1 adducts prevented their use in the study of rhodium(II) perfluorobutyrate. The enthalpy data (Table VI) indicate that the perfluorobutyrate is a stronger Lewis acid than the butyrate, as expected. Of the bases studied, *N*-methylimidazole, dimethyl sulfoxide (Me_2SO is an oxygen donor for this acid),[4] and dimethylacetamide are believed to be σ donors and hence are suitable to use in characterizing rhodium(II) perfluorobutyrate in terms of the *E* and *C* model. The values 5.06 and 1.74 for E_A and C_A represent the best fit of the data (see Table VI) to the model. By a comparison of these value to those obtained for rhodium(II) butyrate ($E_A = 3.21$, $C_A = 1.32$), the effect of the weaker perfluorobutyrate ancillary ligand is seen to increase both the electrostatic and covalent acceptor properties of the rhodium. The *C*:*E* ratio for this acid (0.34), however, is comparable to that of rhodium(II) butyrate (0.41).

As can be seen in Table VI, the "σ-only" enthalpies predicted by the *E* and *C* equation for *N*-methylimidazole, dimethyl sulfoxide, and dimethylacetamide are all within 0.3 kcal mol^{-1} of the measured enthalpies. The measured enthalpies of the other bases, acetonitrile and pyridine, are 1–4 kcal mol^{-1} larger than the *E* and *C* predicted σ-only values. Attributing the difference to π stabilization (π back-bonding plus synergism in the σ bond), one can compare the amount of π-induced stabilization in the 1:1 adducts of rhodium(II) perfluorobutyrate to that in the 1:1 adducts of rhodium(II) butyrate. For the acetonitrile adduct of rhodium(II) butyrate, approximately 4.7 out of 9.3 kcal mol^{-1} (50%) is attributable to π-induced stabilization,[2] whereas for the rhodium(II) perfluorobutyrate adduct, 4.7 out of 11.5 kcal mol^{-1} (41%) is attributable to π-induced stabilization. Note that although the absolute value of the π-induced stabilization is the same for both acids, the ***relative*** amount of π-induced stabilization (i.e., $(-\Delta H_{1:1} - (-\Delta H_{E\text{ and }C}))/-\Delta H_{1:1}$) in the rhodium(II) perfluorobutyrate adduct is less than that in the rhodium(II) butyrate adduct. The infrared C–N stretching vibration of acetonitrile (2265 cm^{-1}) is lowered to 2258 cm^{-1} in the adduct with $Rh_2(but)_4$ but is increased to 2272 cm^{-1} in the $Rh_2(pfb)_4 \cdot CH_3CN$ adduct. The increased frequency in the latter adduct can be attributed to an increased σ interaction that is not accompanied by increased π back-bonding, leading to a domination of the frequency shift by σ effects.

For the pyridine adducts, the calorimetric results clearly indicate the decreased π-back-bonding capability of rhodium(II) perfluorobutyrate. The $Rh_2(but)_4$–py bond consists of 4.4 out of 16.6 kcal mol^{-1} (26%) π-induced stabilization,[2] whereas the $Rh_2(pfb)_4$–py bond consists of only 1.5 out of 18.4 kcal mol^{-1} (8%).

To further test the π-back-bonding ability of rhodium(II) perfluorobutyrate, carbon monoxide was bubbled through a toluene solution of this dimer. Within 10 s, the solution became bluish purple, indicating either 1:1 or 2:1 adduct formation. The C–O infrared stretching frequency, $\nu_{CO} = 2120$ cm^{-1}, occurs at a higher energy than that for $Rh_2(but)_4(CO)_2$, $\nu_{CO} = 2095$ cm^{-1}, but is still lower than that for free CO, $\nu_{CO} = 2143$ cm^{-1}. This stretching frequency for $Rh_2(pfb)_4 \cdot CO$ could result from a weakened π-back-bonding interaction or a strengthened σ interaction relative to the $Rh_2(but)_4$–CO interaction. It is worthwhile noting that the CO adduct of rhodium(II) perfluorobutyrate decomposes to the free acid and CO (g) while in the IR beam. The rhodium(II) butyrate–CO adduct is stable under these conditions, suggesting that the rhodium(II) perfluorobutyrate is a poorer π donor than rhodium(II) butyrate toward CO.

These results are consistent with the predictions made above from the orbital energy ordering given in Figure 2 and demonstrate a pronounced influence by the ancillary ligands on the acceptor and π-donor properties of a metal–metal bonded system.

Inductive Transfer of Coordination through Metal–Metal Bonds. In an earlier report on the $Rh_2(but)_4$ system,[2] a model was proposed and tested for predicting the enthalpy of coordinating a second donor, B, to the $Rh_2(but)_4B$ adduct. It was proposed that the E_A parameter for the 1:1 adduct, $E_A^{1:1}$, would be given by $E_A^{1:1} = E_A - kE_B$. That is, the electrostatic interaction of a donor with the 1:1 adduct would be diminished from that with the free acid (E_A) in proportion to the dipolar properties of the coordinated base. A similar equation was written for the $C_A^{1:1}$ term of the 1:1 acceptor:

$$C_A^{1:1} = C_A - k'C_B$$

When *k* and *k'* are positive, they reflect (for σ donors) the effectiveness of the metal cluster at transmitting the inductive influence of base coordination to the second metal center. When these expressions are substituted into an *E* and *C* equation for the enthalpy of the 2:1 adduct formation from the 1:1 adduct, the following expression results when the same base is involved in 1:1 and 2:1 adduct formation:

$$-\Delta H_{2:1} = -\Delta H_{1:1} - kE_B^2 - k'C_B^2$$

When the measured enthalpies for the 2:1 $Rh_2(but)_4$ adducts were substituted into eq 1, values of $k = 1.16$ and $k' = 0.0364$ were obtained. Unfortunately the limited date for 2:1 σ-donor adducts do not permit accurate calculation of the *k* and *k'* values of $Rh_2(pfb)_4$. Toluene coordination clouds the interpretation of the $(CH_3)_2SO$ enthalpies. The one reliable set of data bearing on this question is that of 1:1 and 2:1 enthalpies for forming the DMA adducts in CH_2Cl_2. With use of the same *k* and *k'* values as were obtained for $Rh_2(but)_4$, the 2:1 enthalpy for the DMA adduct is calculated as 8.9 kcal mol^{-1} in reasonable agreement with the experimental value of 9.3 kcal mol^{-1}. Thus we conclude that butyrate and perfluorobutyrate ligands have essentially the same influence upon the ability of the metal–metal system to transmit the inductive effect of base coordination from the first metal site to the second.

The *k* and *k'* values determined from $-\Delta H_{2:1}$ for the dimolybdenum adduct provide some significant insights regarding the relationship between the nature of the metal–metal bond and the inductive transfer through it. A least-squares fit of the four bases in Table VII with reported $-\Delta H_{2:1}$ values to eq 1 led to *k* and *k'* values of 1.46 and 0.022 compared to values of 1.16 and 0.036 for the dirhodium system. The electrostatic interaction of the second base is diminished more by coordination of the first base in the dimolybdenum system. This is in keeping with a shorter Mo–Mo bond resulting in a greater electrostatic interaction of the second molybdenum with the lone-pair dipole of the first base coordinated and greater electrostatic repulsion between the polar ligands in the 2:1 adduct. The smaller *k'* value for the dimolybdenum system indicates less effective metal bonding electron density polarization toward the second metal, leading to covalency in the 2:1 interaction that is closer to that in the 1:1 adduct than that in the dirhodium system. This is consistent with less inductive transfer through the stronger metal–metal bond, leading to a higher energy, vacant σ^* orbital.

π Stabilization in the 2:1 Adducts. Equation 1 puts one in the unique position of being able to calculate the σ contribution to the bonding in the 2:1 adduct. Deviations of greater stability in the dirhodium system can be used to probe the influence of coordinating π acceptors on one metal center upon the π back-bonding properties of the second metal. When π- or π^*-back-bond stabilization exists, one can only obtain an estimate on the upper limit of the π stabilization in the second step. This occurs because π back-bonding in the first step enhances σ bonding over that predicted by eq 1. By the assumption that this is not the case, an upper limit of the π stabilization in the second step is calculated. Furthermore, it should be emphasized that although different π-stabilization energies are calculated for the 1:1 and 2:1 steps, both metal–ligand bonds are equivalent in the 2:1 adduct with the sum of these two interactions averaged over the ligands. The $-\Delta H_{2:1}$ value for the second step in the pyridine–$Rh_2(pfb)_4$ system is calculated to be 14.1 kcal mol^{-1} when the k and k' values of $Rh_2(but)_4$ are used. This prediction is in good agreement with the experimental value of 15.0 kcal mol^{-1}, particularly when one considers that π^* back-bonding in the 1:1 adduct is expected to enhance the σ interaction in the 2:1 above that predicted by eq 1. Thus, there is relatively little additional π^* stabilization accompanying the coordination of the second pyridine.

In the acetonitrile system, the $-\Delta H_{2:1}$ for a σ interaction is calculated to be 5.9 kcal mol^{-1}. When compared to the experimental value (7.4 kcal mol^{-1}), this leads to an upper limit for a π^*-stabilization energy of -1.5 kcal mol^{-1}. In contrast to the case for the CH_3CN adducts of the $Rh_2(but)_4$ system (a more effective π-back-donating system with 4.9 kcal mol^{-1} of π^*-back-bonding stabilization), stronger σ coordination to one rhodium center of the stronger acid $Rh_2(pfb)_4$ greatly diminishes the π back-bonding that occurs upon coordination of the second CH_3CN.

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Registry No. $Rh_2(pfb)_4$, 81028-20-8; $Mo_2(pfb)_4$, 24329-24-6; MeCN, 75-05-8; py, 110-86-1; *N*-MeIm, 616-47-7; Me_2SO, 67-68-5; DMA, 127-19-5; THTP, 110-01-0.

Supplementary Material Available: Spectral and calorimetric data for $Rh_2(pfb)_4$ and $Mo_2(pfb)_4$ complexes (15 pages). Ordering information is given on any current masthead page.

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Kinetic Studies of the Reactions of Hydrogen Peroxide with Aqua(nitrilotriacetato)oxovanadate(IV) and Diaquaoxo(2,6-pyridinedicarboxylato)vanadium(IV) in Acidic Aqueous Solution[1]

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The kinetics of the reactions of hydrogen peroxide with aqua(nitrilotriacetato)oxovanadate(IV) (V(IV)–NTA or $VO(nta)(H_2O)^-$) and diaquaoxo(2,6-pyridinedicarboxylato)vanadium(IV) (V(IV)–PDA or $VO(pda)(H_2O)_2$) to form peroxovanadium(V) complexes have been studied spectrophotometrically at an ionic strength of 1.0 mol dm^{-3} ($NaClO_4$) in acidic aqueous solution. The formation rate of the peroxo complexes of V(V)–NTA and V(V)–PDA is first order in vanadium(IV) complexes and hydrogen peroxide and independent of the concentrations of excess ligands (NTA and PDA) and hydrogen ion. The reaction at high pressures up to 1250 kg cm^{-2} was followed by a high-pressure stopped-flow technique. Activation parameters were obtained as follows: for the V(IV)–NTA–H_2O_2 system k_{NTA}(25 °C) = 0.11 ± 0.02 mol^{-1} dm^3 s^{-1}, $\Delta H^{\ddagger} = 45.2 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -112 \pm 10$ J mol^{-1} K^{-1}, $\Delta V^{\ddagger} = -10.5 \pm 0.3$ cm^3 mol^{-1}; for the V(IV)–PDA–H_2O_2 system k_{PDA}(25 °C) = 0.55 ± 0.08 mol^{-1} dm^3 s^{-1}, $\Delta H^{\ddagger} = 36.5 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -125 \pm 15$ J mol^{-1} K^{-1}, $\Delta V^{\ddagger} = -13.0 \pm 0.2$ cm^3 mol^{-1}. The rate-determining step may be the insertion of a hydrogen peroxide molecule into the first coordination sphere of the vanadium(IV) complex. It is followed by rapid electron transfer and peroxo coordination to thus produce the vanadium(V) complex. An associative interchange mechanism is most probably operative. We have studied the complexation equilibrium of the V(IV)–PDA complex: $K_{VO(pda)} = [VO(pda)(H_2O)_2][VO^{2+}]^{-1}[pda^{2-}]^{-1} = 10^{6.77\pm0.15}$ mol^{-1} dm^3 at 25 °C and $I = 1.0$ mol dm^{-3}.

Introduction

Vanadium has been thought for some years to be an essential element in both animals and plants.[2] There have been many reports on the physiological effect of vanadium exogenously added to tissues of animals[3–9] and on the vanadate inhibition of the sodium- and potassium-stimulated adenosine triphosphatase.[10–14] For an understanding of the significant biological role of vanadium and the reaction mechanism of vanadium complexes from the viewpoint of coordination chemistry, kinetic studies on vanadium complexes in aqueous solution are required.

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