PhCOCl. To **6** (1 g, 2.7 mmol) obtained as noted above, 20 mL of CH_2Cl_2 and 20 mL of PhCOCl are added under N_2 and the solution is refluxed for 3 h. After removal of the solvent in vacuo and chromatographic separation on thick silica gel plates (eluent ether) the brown-red solid **7** is obtained (R_f 0.3) and recrystallized from ether (80%). Some of these crystals were selected for the X-ray crystal structure determination. Anal. Calcd for $C_{19}H_{20}FeN_2O_2S_2$: C, 53.31; H, 4.67; Fe, 13.04; N, 6.54; S, 14.95. Found: C, 53,41; H, 4.62; Fe, 13.00; N, 6.48; S, 14.87.

6. Alkylation of 1 with CH_3I. A THF solution (30 mL) of **1** (0.3 g, 1 mmol) is refluxed with CH_3I (0.06 mL, 1.1 mmol) for 2 h. After this reaction time, TLC indicates that all **1** has reacted. The solvent is removed in vacuo, and the solid residue is dissolved in ether and passed through a short column of alumina; FpI and MeSC(S)NMe_2 are isolated as the only reaction products (respectively 70 and 60%); their identity was verified by ^1H NMR ($CDCl_3$, δ, Me_4Si): FpI, Cp at 5.12; MeSC(S)NMe_2, NMe at 3.60 and SCH_3 at 2.79.

7. Synthesis of $[CpFe(CO)_2(\eta^1\text{-}SC(SMe)(NMe_2))]^+BF_4^-$ from 1 and $Me_3O^+BF_4^-$. To a THF solution (30 mL) of **1** (2.55 g, 8.6 mmol) under N_2 is added $Me_3O^+BF_4^-$ (2.15 g, 10 mmol). After the mixture is stirred 2 h at room temperature, the THF is removed in vacuo; the solid residue is dissolved in 10 mL of CH_2Cl_2, this solution is filtered, and 100 mL of ether is added to precipitate **8**. Recrystallization from acetone yields 1.7 g of large bordeaux red crystals (50%), stable in air (dec pt 141 °C). Anal. Calcd for $C_{11}H_{14}NS_2O_2FeBF_4$: C, 33.11; H, 3.54; N, 3.51; S, 16.07; Fe, 14.14. Found: C, 33.26; H, 3.55; N, 3.49; S, 15.96; Fe, 14.14.

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Quantitative Studies on the Coordination Chemistry of Tetrakis(*n*-butyrato)diruthenium Chloride

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Earlier work on the coordination chemistry of metal carboxylate dimers is extended to the ruthenium system tetrakis(*n*-butyrato)diruthenium chloride, $Ru_2(but)_4Cl$. Calorimetric measurements are made of the enthalpies of adduct formation to $Ru_2(but)_4Cl$ by the Lewis bases acetone, *N*-methylimidazole, tetrahydrothiophene, dimethyl sulfoxide, 4-picoline *N*-oxide, acetonitrile, and pyridine. UV–visible spectroscopy, conductivity measurements, and reactivity studies are performed to validate the calorimetric measurements. A dipyridine adduct of $Ru_2(but)_4Cl$ is reported as the first complex of this type. Comparison of the calorimetric data obtained for $Ru_2(but)_4Cl$ with previous data on analogous systems shows a higher Lewis acidity for $Ru_2(but)_4Cl$. This is attributed to the higher overall charge of the metal dimer unit. A synergistic mechanism is offered to explain how this charge is transmitted to the acceptor Ru atom through the metal–metal bond. This synergism leads to a strong electrostatic base interaction (as indicated by the high E_A value of 7.73). The covalent contribution to the Lewis acidity of this system (indicated by the C_A value of 1.27) is intermediate between the Rh and Mo systems. The covalent contribution to the acidity of these metal–metal-bonded systems depends inversely on the metal–metal bond strength. Higher than predicted enthalpies of adduct formation with pyridine and acetonitrile are observed. These are attributed to a π-back-bonding interaction between the partly filled π^* orbitals of the Ru dimer and empty π^* orbitals on these bases, in agreement with previous results on rhodium(II) dimers.

Introduction

Metal–metal-bonded systems have been widely studied.[1] The nature of the metal–metal bond itself and the coordination chemistry of metal–metal-bonded complexes compared to analogous mononuclear complexes are of great interest. Previous work from this laboratory has concentrated on understanding metal–metal bonding and ligand coordination chemistry of the Rh(II) and Mo(II) carboxylate dimers.[2] Thermodynamic and spectroscopic studies of complexes such as $Rh_2(but)_4$ (but = *n*-butyrate), $Rh_2(pfb)_4$ (pfb = perfluoro-*n*-butyrate), and $Mo_2(pfb)_4$ have led to some interesting conclusions concerning the relationship between structure and reactivity by providing evidence for a synergistic metal–metal interaction. In particular, the rhodium dimers appeared to undergo more than a simple σ-type interaction with certain Lewis bases while the molybdenum dimer showed only σ interactions. This difference in reactivity was attributed to the difference in the populations of their respective molecular orbitals. The rhodium system contains π^* electron density while the molybdenum system does not. Therefore, in those cases involving a Lewis base capable of accepting π^* electron density from the rhodium dimer, π stabilization was observed. This was manifested by the observed Rh–base adduct bond enthalpies being higher than that predicted by the *E* and *C* equation, which considers only σ-type interactions. It is therefore reasonable to expect that if this interpretation is valid, the diruthenium(II,III) carboxylate system would also show instances of π stabilization with the proper bases. A simplified MO scheme for this dimer is shown in Figure 1. This quantitative scheme has been confirmed in calculations by Norman et al.[3] There are a total of 11 d electrons, which

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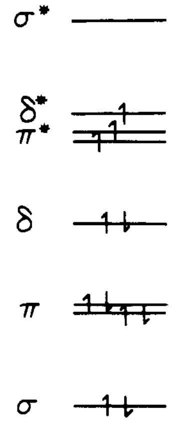


Figure 1. Simplified MO scheme for the metal–metal bond in $Ru_2(but)_4Cl$.

gives a metal–metal bond order of 2.5, in between the Mo–Mo quadruple and Rh–Rh single bonds. The π^* orbitals are populated, though not filled. If the extent of π back-donation depends on the total amount of π^* electron density, one would see a lower apparent π stabilization for the ruthenium dimer as compared to the rhodium dimer. This might not be the case if the energy match between the Ru π^* and base π^* orbitals were not comparable to the Rh system.

The other aspect of the $Ru_2(but)_4Cl$ complex that differs from the rhodium and molybdenum systems is the formal 5+ oxidation state of the metal dimer unit compared to 4+ for rhodium and molybdenum. This oxidation state also leads to formally mixed-valent $Ru^{II}Ru^{III}$ complex. It would be desirable to obtain quantitative information on the coordination chemistry of a mixed-valent cluster since changes in electron delocalization within the cluster could provide a synergistic mechanism and lead to different behavior than observed in clusters studied previously or single metal complexes.

Finally, in addition to helping understand the nature of the metal–metal bond in $Ru_2(but)_4Cl$ as compared to analogous systems, we wished to investigate the chemistry of $Ru_2(but)_4Cl$ for its own sake. The Ru dimer system has not been as widely studied as the Rh or Mo systems and, by virtue of its formally mixed oxidation state nature, should have an interesting chemistry based on the many results obtained for non-metal–metal bonded dimeric Ru complexes.[4,5]

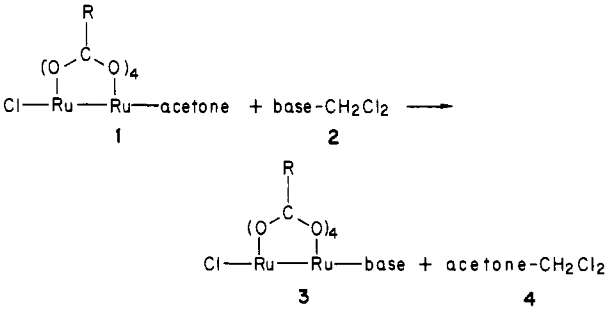
Experimental Section

$Ru_2(but)_4Cl$ was synthesized from $RuCl_3 \cdot 3H_2O$ following the procedure of Stephenson and Wilkinson[6] and recrystallized from butyric acid. Bases and solvents were purified according to established procedure.[2b,c] Electrochemical and calorimetric measurements were performed as reported previously.[2a–c] UV-visible spectroscopy was performed as reported previously[2a,b] with a Cary 14 spectrometer. Conductivity measurements were obtained on a Yellow Springs Instruments Model 31 conductivity bridge calibrated with aqueous KCl. Elemental Analyses were performed by the Microanalytical Laboratory of the University of Illinois.

Results

1. Calorimetry. The measurements of the heats of reaction between the ruthenium carboxylate dimer, acting as a Lewis acid, and various Lewis bases give much information concerning the nature of the reactivity of the dimer. Ideally, measurements of the enthalpies of adduct formation for the various bases binding to the ruthenium dimer should have been made in exactly the same manner as previously done for the rhodium and molybdenum dimers.[2] Unfortunately, $Ru_2(but)_4Cl$ has little solubility in typical solvents of choice such as toluene or methylene chloride. The heptanoate complex was thus synthesized in the hope that a longer carboxylate chain would enhance the solubility of the dimer in nonpolar noncoordinating solvents. This complex did have good solubility in hot toluene or methylene chloride, but it precipitated at ambient temperature. It was then necessary to measure the enthalpies for acid–base adduct formation indirectly. To accomplish this, the butyrate dimer was solubilized with a minimum amount of a weak donor such as acetone. The exchange reaction with a donor strong enough to displace the acetone was then carried out, and the heat evolved in this reaction was measured. The stronger bases used were *N*-methylimidazole, tetrahydrothiophone (THTP), dimethyl sulfoxide (Me_2SO), 4-picoline *N*-oxide, and pyridine.

The base-exchange reaction in CH_2Cl_2 can be described with the reaction (1), where the species involved have been numbered **1**–**4**. The heat evolved by this exchange reaction is the summation of the four individual enthalpies of formation of species **1**–**4**, as shown in eq 2. The enthalpy of formation of



$$\mathrm{Cl{-}Ru{-}Ru{-}acetone}\ (\mathbf{1}) + \text{base-}CH_2Cl_2\ (\mathbf{2}) \longrightarrow \mathrm{Cl{-}Ru{-}Ru{-}base}\ (\mathbf{3}) + \text{acetone-}CH_2Cl_2\ (\mathbf{4}) \qquad (1)$$

$$-\Delta H_{\mathrm{measd}} = \Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 \qquad (2)$$

the Ru–base bond, ΔH_3, is the one of interest. Since methylene chloride is an acidic solvent, it interacts with any free base present. The enthalpies of interaction of the free bases with CH_2Cl_2 (ΔH_2 and ΔH_4) must be determined to convert the measured enthalpy to the solvent-minimized[7] enthalpy of adduct formation. The enthalpies of the hydrogen-bonding interaction between CH_2Cl_2 and a wide range of bases have been successfully incorporated into the *E* and *C* correlation.[7d] Values of $E_A = 1.66$ and $C_A = 0.01$ were obtained for CH_2Cl_2. Combining these E_A and C_A values for CH_2Cl_2 with the tabulated[7b,c] E_B and C_B values for the bases used in this study allows the calculation of ΔH_2. Correcting $\Delta H_{\mathrm{measd}}$ for ΔH_2, the enthalpy of formation of species **2**, gives $-\Delta H_{\mathrm{cor}} = -\Delta H_{\mathrm{measd}} - \Delta H_2$ so eq 2 can be rewritten as

$$-\Delta H_{\mathrm{cor}} = \Delta H_1 - \Delta H_3 - \Delta H_4 \qquad (3)$$

The enthalpies of formation of species **1** and **4** make a constant contribution to the measured enthalpies in every base system studied. This contribution is endothermic for species **1** and exothermic for **4**. Substituting for these constant contributions by letting $W = \Delta H_1 - \Delta H_4$, eq 3 becomes

$$-\Delta H_{\mathrm{cor}} = -\Delta H_3 + W \qquad (4)$$

As reported earlier,[7] a constant contribution to a series of enthalpies can be determined from the *E*, *C* and *W* equation

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

where *W* is the constant contribution. Combining eq 4 and 5 gives

$$-\Delta H_{\mathrm{cor}} = \Delta H_{3(\mathrm{ECW})} + W = E_A E_B + C_A C_B \qquad (6)$$

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Table I. Enthalpies of Base Binding to $Ru_2(but)_4Cl$[a]

base	$-\Delta H_{\text{measd}}$[b]	$-\Delta H_2$[c]	$-\Delta H_{\text{cor}}$[d]	$-\Delta H_{3(\text{ECW})}$[e]
N-methylimidazole	8.0	1.6	9.6	9.7
THTP	3.2	0.7	3.9	3.8
Me_2SO	2.7	2.3	5.0	5.1
4-picoline *N*-oxide	5.9	2.3	8.2	8.0
acetone[f]		1.7		
pyridine	7.2	2.0	9.2	8.3
acetonitrile[g]		1.5		

[a] All values in kcal mol^{-1}. [b] Measured enthalpy for the total reaction. [c] Enthalpy for the base-CH_2Cl_2 interaction. [d] $-\Delta H_{\text{cor}} = -\Delta H_{\text{measd}} - \Delta H_2$. [e] Enthalpies calculated from an *E*, *C* and *W* fit of the first four bases with $E_A = 7.75$ (0.46), $C_A = 1.26$ (0.08), $W = 8.86$ (0.90), and $r^2 = 0.9968$ (standard deviations in parentheses). [f] Acetone enthalpy was determined indirectly (see text). [g] Acetonitrile enthalpy was determined from the exchange reaction with *N*-methylimidazole (see text).

Table II. *E* and *C* Fit of the Experimental Enthalpies[a]

base	$-\Delta H_{\text{exptl}}$[b]	$-\Delta H_{3(\text{EC})}$[c]
N-methylimidazole	18.5	18.6
THTP	12.8	12.6
Me_2SO	13.9	14.0
4-picoline *N*-oxide	17.1	16.8
acetone	10.6	10.6
pyridine	18.1	17.1
acetonitrile	9.7	8.5

[a] All values in kcal mol^{-1}. [b] $-\Delta H_{\text{exptl}} = \Delta H_{\text{cor}} + W$. [c] Calculated enthalpy from an *E* and *C* fit of the first five bases with $E_A = 7.73$ (0.10), $C_A = 1.27$ (0.02), and $r^2 = 0.9982$ (standard deviations in parentheses).

where the subscript ECW indicates that the enthalpy of formation of the Ru–base adduct is derived from the *E*, *C* and *W* equation. Equation 6 shows that one can perform an *E*, *C* and *W* correlation of ΔH_{cor} with the reported[7] E_B and C_B values for the bases studied.

Table I gives the results of this correlation, including the measured enthalpies, the base–CH_2Cl_2 enthalpies, the solvation-corrected measured enthalpies, and the enthalpies obtained from the best fit to the *E*, *C* and *W* equation. Note that acetonitrile was too weak a donor to displace acetone; therefore, once ΔH_{cor} was determined for *N*-methylimidazole, an exchange reaction was carried out in which acetonitrile was displaced from the ruthenium dimer by *N*-methylimidazole to determine the enthalpy for the CH_3CN–$Ru_2(but)_4Cl$ adduct.

The best correlation using the *E*, *C* and *W* equation was obtained with *N*-MeIm, THTP, Me_2SO, and 4-picoline *N*-oxide as the bases. E_A was calculated to be 7.75 (0.46), C_A was 1.26 (0.08), and *W* (the constant contribution from acetone, $\Delta H_1 - \Delta H_4$) was 8.86 (0.90) kcal mol^{-1} (standard deviations in parentheses).

Once *W* is known, it is possible to subtract this contribution from all the other enthalpies. Thus, eq 6 becomes

$$-\Delta H_{\text{cor}} - W = -\Delta H_{3(\text{EC})} = E_A E_B + C_A C_B \qquad (7)$$

where the subscript EC indicates that ΔH_3 is derived using the *E* and *C* equation. This allows one to perform a correlation (without any *W* contribution) to obtain E_A and C_A values for base-free $Ru_2(but)_4Cl$. The results using the enthalpy values for *N*-MeIm, THTP, Me_2SO, 4-picoline *N*-oxide, and acetone are given in Table II. The best *E* and *C* correlation gives values of $E_A = 7.73$ (0.10) and $C_A = 1.27$ (0.02) for $Ru_2(but)_4Cl$. It is important to note that these E_A and C_A values are virtually identical with the E_A and C_A values obtained from the *E*, *C* and *W* correlation (Table I). This indicates that attributing to *W* the effect of acetone solvation is legitimate.

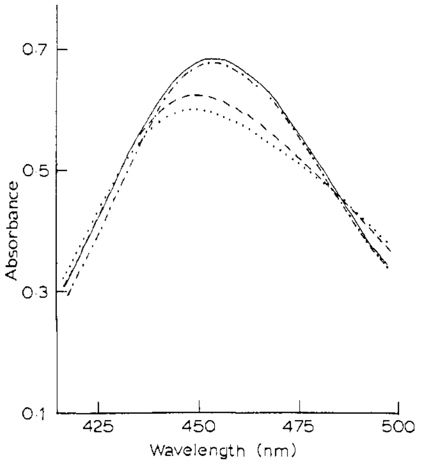

Figure 2. Visible absorption spectrum for $Ru_2(but)_4Cl$ (2.5×10^{-3} M in CH_2Cl_2, 0.1% v/v acetone) with 1 equiv of added base. Bases: acetone (—); 4-picoline *N*-oxide (–·–); pyridine (---); *N*-methylimidazole (···).

This can be further demonstrated in the following manner. Using the tabulated E_B and C_B values for acetone and the E_A and C_A values for $Ru(but)_4Cl$ obtained above, one obtains $-\Delta H$, for acetone–$Ru_2(but)_4Cl$ adduct formation, equal to 10.59 kcal mol^{-1}. Assuming *W* (8.86 kcal mol^{-1}) to be the enthalpy of acetone–$Ru(but)_4Cl$ adduct formation in CH_2Cl_2 and correcting for the acetone–CH_2Cl_2 interaction (−1.7 kcal mol^{-1}) one obtains a solvation-corrected $-\Delta H$ for acetone–$Ru_2(but)_4Cl$ adduct formation of $8.86 - (-1.7) = 10.56$ kcal mol^{-1}, the same value as that obtained independently with the *E* and *C* parameters.

Inclusion of pyridine worsens the fit, and calculation of an enthalpy based on the *E* and *C* numbers reported above gives an enthalpy value that is lower than that found. Acetonitrile and pyridine both give experimental enthalpies that are greater than that predicted by the *E* and *C* equation. This observation indicates that there is some other bonding effect in addition to the σ-only interaction. These two bases also showed large deviations in the rhodium system.

2. Spectrophotometric Titration. The visible region of the spectrum for the ruthenium carboxylate dimer in methylene chloride is typified by a band at ~450 mn. This region is shown in Figure 2. The four curves correspond to the acetone, 4-picoline *N*-oxide, pyridine, and *N*-methylimidazole adducts. As can be seen λ_{max} is virtually independent of base type. With pyridine and *N*-methylimidazole some slight broadening and decrease in intensity is observed. This visible absorption band does not change in either intensity or wavelength as a function of base concentration, unless the base concentration is high enough to cause decomposition of the dimer. This precludes the spectrophotometric determination of the equilibrium constants of base binding, as was done successfully with the rhodium carboxylate system.[2]

There has been some controversy in the past over the assignment of the band. However, recent calculations,[3] resonance Raman studies,[8] and single-crystal-polarized electronic spectra[9] indicate that it is due to a (RuO) $\pi \rightarrow \pi^*$ transition, which would not be expected to be affected by the identity of the axial base since it involves orbitals that are Ru and carboxylate oxygen in character with little metal–metal bond contribution.

3. Cyclic Voltammetry. Unlike the rhodium systems,[2a] no useful information was obtained from cyclic voltammetry. The

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Table III. Comparison of Solvation-Corrected Enthalpies for Adduct Formation between Various Bases and Different Dimeric Systems[a]

acid	base	$-\Delta H_{\mathrm{exptl}}{}^{1:1}$	$-\Delta H_{\mathrm{EC}}{}^{1:1}$	π stablizn	$-\Delta H_{\mathrm{exptl}}{}^{2:1}$	$-\Delta H_{\mathrm{EC}}{}^{2:1\,d}$
$Rh_2(but)_4$[b]	*N*-methylimidazole	15.4	14.9		11.5	11.0
	THTP	1.49[e]	11.5		10.3[e]	9.1
	Me_2SO	10.5[e]	*g*		6.5[e]	*g*
	4-picoline *N*-oxide	11.0	11.0		8.0	8.0
	pyridine	16.6	12.2	4.4	10.5	9.1
	acetonitrile	9.3	4.6	4.7	8.3	3.6
	piperidine	15.0	15.5		10.7	11.2
	caged phosphite	16.8[e]	10.2	6.6	11.3[e]	8.37
$Rh_2(pfb)_4$[c]	*N*-methylimidazole	20.3[f]	20.3			
	THTP	dec				
	Me_2SO	~12[f]	11.7		~8[f]	9.3
	4-picoline *N*-oxide	dec				
	pyridine	18.4	17.0	1.4	15.0	13.9
	acetonitrile	11.5[f]	6.8	4.7	7.4[f]	5.8
	DMA	10.9	11.2		9.3	8.9
$Mo_2(pfb)_4$[c]	*N*-methylimidazole	5.1[f]	5.1			
	THTP	9.0[f]	9.0		6.1[f]	6.2
	Me_2SO					
	4-picoline *N*-oxide	9.5[f]	9.4		6.5[f]	6.5
	pyridine	5.7[f]	5.8		small[f]	4.6
	acetonitrile	8.8[f]	8.8		6.2[f]	6.1
	DMA	6.5[f]	6.8		2[f]	5.3
	bridged ether					
$Ru_2(but)_4Cl$	*N*-methylimidazole	18.5	18.6			
	THTP	12.8	12.6			
	Me_2SO	13.9	14.0			
	4-picoline *N*-oxide	17.1	16.8			
	pyridine	18.1	17.1	1.0		
	acetonitrile	9.7	8.5	1.2		

[a] All enthalpies are in units of kcal mol^{-1} and were measured in methylene chloride solution except as otherwise noted. [b] Values taken from ref 2b. [c] Values taken from ref 2c. [d] Values for $-\Delta H_{\mathrm{EC}}{}^{2:1}$ are for the enthalpy of adduct formation between a 1:1 adduct and a second axial base using the *k,k'* method described in ref 2b, c. [e] Enthalpy measured in benzene solution. [f] Enthalpy measured in toluene solution. [g] ΔH_{EC} cannot be calculated since, for $Rh_2(but)_4$, Me_2SO acts as a sulfur donor and E_B and C_B have been calculated only for Me_2SO acting as an oxygen-donor base.

voltammagram typically consisted of an irreversible reduction–oxidation just above 0.0 V vs. Ag/Ag^+ in CH_2Cl_2. Cotton and Pedersen[10] have reported a quasi-reversible reduction–oxidation at 0 to −0.4 V vs. SCE in various solvents.

4. Conductivity and Reactivity. The Mo and Rh carboxylate dimers studied previously exist as discrete $M_2(O_2CR)_4$ units in both solution and the solid state. In contrast, $Ru_2(but)_4Cl$ exists as a chloro-bridged polymer in the solid state.[11] In solution, a variety of species could exist such as $Ru_2(but)_4{}^+$, $Ru_2(but)_4Cl$, and polymeric units such as $[Ru_2(but)_4Cl]_n$ or $[Ru_2(but)_4Cl_{n-1}]_n{}^+$. If a high concentration of ionic species were present, the analysis based on the calorimetric results would be suspect. Therefore, conductivity measurements on $Ru_2(but)_4Cl$ in several solvents were performed. In methanol a value of 75 for Λ_m was obtained, lower than the previous literature value of 95[6] but high enough to indicate that almost complete dissociation to $Ru_2(but)_4{}^+$ and Cl^- had occurred. However, in ethanol $\Lambda_m = 26$, and in CH_2Cl_2 with ~0.1% acetone $\Lambda_m \simeq 1$. Therefore, considerably less ionization occurred in ethanol, and in CH_2Cl_2 any ionization would be too slight to seriously affect the data. The predominant species present in CH_2Cl_2 solvent containing 0.1% acetone is acetone–$Ru_2(but)_4Cl$, and the enthalpies measured are for the reaction to form B–$Ru_2(but)_4Cl$ as discussed previously. A second potential difficulty with the data is the possibility that dimer decomposition may have occurred, and the measured enthalpies include this contribution. In contrast to Rh and Mo, no complexes of general form $Ru_2(O_2CR)_4BCl$ or $[Ru_2(O_2CR)_4B_2]Cl$ have been isolated. Rather, strong bases such as pyridine or PPh_3 lead to complexes such as $[Ru_3O(O_2CR)_6(py)_3]^+$ and $Ru_3O(O_2CR)_6(PPh_3)_3$.[12] We found that upon exposure to air of a solution of $Ru_2(but)_4Cl$ in CH_2Cl_2 with excess (>10 equiv) pyridine the dark blue-green color of the oxo-bridged trimer rapidly develops. Similar dark blue-green decomposition products are observed with *N*-methylimidazole, 4-picoline *N*-oxide, and triethylamine. By contrast, a red color is observed with primary amine, which most likely results from formation of "ruthenium red" species by analogy with the known[13] complex $[Ru_3O_2(NH_3)_{14}]Cl_6\cdot 4H_2O$. However, when air is rigorously excluded, a dark brown hygroscopic solid can be isolated, which analyzes approximately[14] for $Ru_2(but)_4(py)_2Cl$. This species can be prepared by addition of excess pyridine (5–10 equiv) to $Ru_2(but)_4Cl$ in CH_2Cl_2 followed by removal of solvent and washing with hexane. It gives an EPR spectrum that strongly resembles that of $Ru_2(but)_4Cl$ in various solvents. To our knowledge, this represents the first reported base adduct of the Ru dimer to be isolated. Solutions of $Ru_2(but)_4Cl$ in acetone, acetonitrile, Me_2SO, and THTP show no visible change over prolonged periods. Thus, we believe that in the calorimetric studies only 1:1 adducts are formed and no side reactions occurred. This was confirmed by visible spectroscopy and by preliminary reactivity studies that show that although some strong bases rapidly destroy the metal–metal bonded Ru system, when air is excluded and minimum amounts of bases are used these reactions are minimized. Furthermore, with weaker bases the possibility of side reactions is slight.

Discussion

Several conclusions can be drawn concerning the reactivity of the ruthenium system by comparison of the calorimetric results from this work with those reported earlier. All the

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(14) Anal. Calcd for $Ru_2C_{26}H_{38}N_2O_8Cl$: C, 41.96; H, 5.15; N, 3.76; Cl, 4.76. Found: C, 41.61; H, 5.14; N, 4.01; Cl, 4.36.

Table IV. Comparison of Different Dimer Systems

acid	M_2^{n+}	d^n	BO	E_A	C_A	C_A/E_A
$Rh_2(but)_4$	4	14	1	3.21	1.32	0.411
$Rh_2(pfb)_4$	4	14	1	5.06	1.74	0.344
$Mo_2(pfb)_4$	4	8	4	5.92	0.385	0.065
$Ru_2(but)_4Cl$	5	11	2.5	7.73	1.27	1.64

solvation-corrected enthalpies of adduct formation obtained thus far are compiled in Table III. We note immediately that the ruthenium complex is a stronger Lewis acid than $Rh_2(but)_4$ or $Mo_2(pfb)_4$, which contain metal atoms that bracket ruthenium in the periodic table. When one considers that a chloride ion is occupying one axial coordination site in CH_2Cl_2 solution, comparison of these enthalpies with the enthalpy of the second base addition ($-\Delta H^{2:1}$) in the rhodium and molybdenum systems shows an even greater acidity for $Ru_2(but)_4Cl$. This difference can be attributed to the higher overall oxidation state for the metal dimer unit in the ruthenium system. The following mechanism can be proposed to explain this.

In a symmetrical $Ru_2(but)_4^+$ complex, the two Ru atoms are equivalent and the two make equal contributions to the metal–metal bond MO's shown in Figure 1. As a chloride is brought up to one Ru, this increases the energy of the d orbitals on that Ru atom relative to the other. Thus, the Ru atom with the chloride attached will make a larger contribution to the partly filled and empty antibonding MO's, while the chloride-free Ru atom will have relatively lower energy d orbitals and thus make a larger contribution to the filled bonding MO's. In this manner, less of the metal electron density is associated with the chloride-coordinted Ru atom. Coordination of chloride in effect converts the attached Ru atom from Ru($II^1/_2$) to a formal Ru(III) while the uncoordinated Ru atom becomes Ru(II).

When base coordinates to $Ru_2(but)_4Cl$, it coordinates to the Ru(II) atom. The interaction between the base lone pair and the Ru–Ru σ^* gives a σ bond that is primarily base in character. The antibonding combination of these two orbitals is primarily Ru(II) in character. This interaction with the base raises the d-orbital energies of the Ru(II) center and makes them closer in energy to the Ru(III) atom. Thus, the result of axial base coordination is to make the Ru atoms more equivalent. When the base approaches chloride in base strength, the d-orbital energies of the two Ru atoms will approach each other and the two will make nearly equal contributions to the metal–metal bond MO's. This mechanism allows electron density to be transferred through the metal–metal bond from the Ru(II) to the Ru(III) when base coordinates. This polarization effect, coupled with the inductive electron withdrawl by the Ru(III) from the adjacent Ru(II), results in a synergistic metal–metal interaction that can exist in mixed-valent systems that will enhance the acidity of the low-valent metal center.

It is instructive to compare the enthalpy data for formation of $Ru_2(but)_4Cl$ adducts to the *E* and *C* equation shown in Table III for the individual bases. For donors that do not accept metal π^* electron density in a π-back-bonding interaction, an excellent fit of the experimental data to the *E* and *C* equation is obtained. We have previously reported a mechanism for the synergistic metal–metal interaction in the rhodium system, which leads to π back-bonding from the metal π^* orbitals into vacant low-energy π-acceptor orbitals on bases such as pyridine and acetonitrile. Experimental enthalpies more negative than those predicted by the *E* and *C* equation were explained by this effect, and independent spectroscopic and electrochemical experiments were reported to confirm this explanation. The data for $Mo_2(pfb)_4$, a system with vacant π^* orbitals, fits the *E* and *C* equation well even for the donors pyridine and acetonitrile. Consistent with this pattern, we note that $Ru_2(but)_4Cl$, with half-filled π^* orbitals, shows stabilization from π^* back-bonding as evidenced by experimental enthalpies larger than that predicted by the *E* and *C* equation for adduct formation to pyridine and acetonitrile. The stabilization is less than that found in the rhodium systems, consistent with there being less electron density in the π^* orbital to back-bond. It is therefore reasonable to assume that $Ru_2(but)_4$ would have coordination properties somewhere in between those of $Rh_2(but)_4$ and $Mo_2(but)_4$.

The pertinent *E* and *C* parameters for the Rh, Mo, and Ru dimers that have been studied are given in Table IV. $Ru_2(but)_4Cl$ has a bond order and number of d electrons intermediate between the those of Mo and Rh dimers. However, the dominant feature of the $Ru_2(but)_4Cl$ system is the higher formal charge on the metal core, which leads to an E_A value for ruthenium that is substantially higher than for the others. Comparison of the E_A value of $Rh_2(pfb)_4$ with that for $Rh_2(but)_4$ shows that electron-withdrawing ligands increase the charge on the metal core, and formal oxidation of one of the ruthenium atoms has a similar but more pronounced effect. The C_A parameter, which is related to the acidity of the complex toward covalent interaction, has a value in between the values for the Rh and Mo dimers. Qualitatively, the stronger the metal–metal covalent interaction, the weaker the metal–base covalent interaction, that is, the smaller C_A. The molybdenum dimer has a strong bond with a very high-energy σ^* frontier MO in the axial coordination site while the ruthenium, and to a greater extent, rhodium dimers have weaker bonds with frontier σ^* MO's of favorable energy to interact covalently with axial Lewis bases. Comparison of the polarizability of the metal–metal bond leads to a similar prediction. The more polarizable the metal–metal bond ($Rh_2^{4+} > Ru_2^{5+} > Mo_2^{4+}$), the more effective is a given metal center at accepting electron density from a Lewis base. It would be desirable to compare a neutral $Ru_2(O_2CR)$ with $Ru_2(but)_4Cl$, but such a complex has not been reported despite efforts to achieve its synthesis.[1,7,10] The parameters obtained provide support for several effects previously proposed. Electron-withdrawing ligands enhance the acidity of a metal carboxylate dimer; a stronger, less polarizable metal–metal bond leads to weaker covalent base interactions, and metal dimers with π^* electron density can π back-bond to bases with π-acceptor capabilities.

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Registry No. $Ru_2(but)_4Cl$, 47511-63-7; $Ru_2(but)_4(py)_2Cl$, 93084-63-0; $Ru_2(but)_4Cl$·*N*-methylimidazole, 93084-64-1; $Ru_2(but)_4Cl$·THTP, 93084-65-2; $Ru_2(but)_4Cl·Me_2SO$, 93084-66-3; $Ru_2(but)_4Cl$·4-picoline *N*-oxide, 93084-67-4; $Ru_2(but)_4Cl$·acetone, 93084-68-5; $Ru_2(but)_4Cl$·pyridine, 93084-69-6; $Ru_2(but)_4Cl$·acetonitrile, 93084-70-9; $Rh_2(pfb)_4$·*N*-methylimidazole, 93110-20-4; $Rh_2(pfb)_4·Me_2SO$, 93084-71-0; $Rh_2(pfb)_4·2Me_2SO$, 93084-76-5; $Rh_2(pfb)_4$·pyridine, 93084-72-1; $Rh_2(pfb)_4$·2(pyridine), 93084-75-4; $Rh_2(pfb)_4$·acetonitrile, 93084-73-2; $Rh_2(pfb)_4$·2(acetonitrile), 93084-77-6; $Rh_2(pfb)_4$·DMA, 93084-74-3; $Rh_2(pfb)_4$·2DMA, 93084-78-7; Ru, 7440-18-8.

Supplementary Material Available: Listings of calorimetric data for $Ru_2(but)_4Cl$ (6 pages). Ordering information is given on any current masthead page.