complexes with the exception of the iron compounds. The transition-metal ionic radii are all slightly larger than Al^{3+}, and thus the large displacement of aluminum is not the result of purely steric considerations. The structural features for the other Schiff-base aluminum alkyl complexes are expected to be similar to those for $Al(SALEN)C_2H_5$.

Conclusions

Aluminum alkyl complexes with tetradentate Schiff bases of the type $Al(Schiff\ base)C_2H_5$ have been synthesized and found to have stabilities comparable to those of transition-metal complexes. Some of the long-lived solution intermediates prior to insertion have been identified. The reaction of $Al_2(C_2H_5)_6$ with tetradentate Schiff bases occurs stepwise. Two different mechanisms prevail depending on ligand properties. With ACEN, a quasi-stable four-membered Al–O ring is formed initially. This then reacts with excess ligand, producing the inserted $Al(ACEN)C_2H_5$ complex. With the salicylaldehyde-derived ligands, reaction first occurs with one of the hydroxyl protons, producing a half-inserted aluminum diethyl species. This in turn reacts with the remaining hydroxyl proton, releasing a second molecule of ethane and the inserted aluminum ethyl complex. All of the aluminum ethyl Schiff-base complexes exhibit 5-coordinate geometry about the aluminum center. The aluminum–carbon bond in these complexes is more reactive than in the tetraaza macrocycles[6-8] but less reactive than in complexes with mono- and bidentate ligands such as 8-hydroxyquinoline.[21] The bond length of the Al–C bond in SALEN is slightly shorter than for those of the macrocyclic complexes; thus, the lessened stability for $Al(SALEN)C_2H_5$ is probably due to kinetic rather than thermodynamic considerations.

Comparison of the hydrolysis tendencies of trivalent transition-metal alkyl complexes such as well-known Cr(III) and Co(III) species with analogous Al–alkyl complexes leads to some interesting conclusions. First of all, hydrolysis of a metal–carbon bond by a proton should be a straightforward process and to a first approximation be largely dependent upon the polarity of the M–C bond; i.e., the more polar, the more readily it is attacked by H^+. A second contribution to the overall energetics of this process is the energy of the dealkylated metal species remaining and the reorganizational energy required to achieve the ground-state conformation.

For the series of $Al(Schiff\ base)C_2H_5$ complexes examined in this report, the similarity of the coordination spheres of the tetradentate ligands would not be expected to lead to substantial differences in the polarity of the Al–C bond. Yet, a considerable range of rates is observed. These appear to correlate strongly with the degree of flexibility of the tetradentate ligand. The incredible stability of the previously reported macrocyclic aluminum alkyl complexes[7,8] and the surprisingly robust nature of the tetradentate Al–C complexes reported here are probably best accounted for with the following explanation.

Simple protonation of the carbon atom of an aluminum alkyl to produce the corresponding alkane should be a highly thermodynamically and kinetically favored process. However, in the absence of strongly coordinating anions (particularly oxo donors, which are not present in appreciable concentrations in acidic solutions), loss of the alkyl group will leave a four-coordinate square-planar intermediate. However, all known four-coordinate Al^{3+} complexes are approximately tetrahedral. For a third-row metal, the d orbitals are relatively high in energy, such that suitable hybridization schemes for square-planar Al^{3+} coordination are not available. However, if the Schiff base has a flexible backbone allowing facile coordination geometry rearrangements toward tetrahedral or distorted tetrahedral, the overall hydrolysis process may be more energetically favorable. In the case of transition-metal complexes, the greater d-orbital participation in the bonding leads to lower energy square-planar intermediates. Square-pyramidal geometry for Al^{3+} is not as common as for transition metals; there are no known examples of stable square-pyramidal monoalkylaluminum complexes with mono- and bidentate ligands. The bis(acetylacetonate)alkylaluminum complex disproportionates to the mono and tris complex,[22] and work in our laboratory with 8-hydroxyquinoline alkyl complexes also indicates that the bis species is unstable.[21] In these systems, there are few if any constraints on the coordination geometries with a d^0 system such as Al^{3+}; a trigonal-bipyramidal structure is expected to be preferred over a square-pyramidal one. Factors affecting the stability of Al–C bonds should also be applicable to aluminum hydride systems. These are currently under investigation in our laboratories.

Registry No. $Al(SALEN)C_2H_5$, 102630-64-8; $Al(SALOPHEN)C_2H_5$, 102630-65-9; $Al(SALPN)C_2H_5$, 102630-66-0; $Al(ACEN)C_2H_5$, 102630-67-1; $Al(C_2H_5)_3$, 97-93-8; SALEN, 94-93-9; SALOPHEN, 3946-91-6; SALPN, 120-70-7; ACEN, 52751-14-1; $Al_4(SALEN)(C_2H_5)_{10}$, 102648-65-7; $Al(SALEN)(C_2H_5)_2$, 102630-68-2; $Al_2(SALEN)(C_2H_5)_4$, 102630-69-3.

Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen coordinates, and least-squares-plane calculations (3 pages). Ordering information is given on any current masthead page.

---

[21] Dzugan, S. J.; Goedken, V. L., to be submitted for publication.

[22] Kroll, W. R.; Naegele, W. *J. Organomet. Chem.* **1969**, *19*, 439.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Trans Influence across a Rh–Rh Bond. Effect of a Series of Lewis Bases on the Stretching Frequency of Coordinated CO

Carl Bilgrien, Russell S. Drago,* Glenn C. Vogel,[1] and James Stahlbush

Received September 4, 1985

The dependence of ν_{CO} upon σ-donor strength of the Lewis base B in $BRh_2(pfb)_4CO$ adducts, where pfb is perfluorobutyrate, has been probed. The systematic dependence of ν_{CO} upon the strength of the interaction of B with one rhodium center illustrates the ability of the metal–metal bond to transmit the influence of coordination of B to the second metal center and, hence, to the coordinated CO. It is found that ν_{CO} is well described by an *E* and *C* analysis that takes into account the inductive influence of trans base coordination. The deviation observed when B is a π-acceptor base is consistent with an earlier claim that metal–metal bonding in the Rh_2^{4+} unit polarizes the d orbitals with π symmetry, enhancing π-back-bonding interactions with donors that can also function as π acceptors.

The CO ligand is ubiquitous in organometallic chemistry, and considerable effort has been put forth to understand the nature of M—C≡O bonding and the influence of various ligands upon the reactivity and spectroscopic properties of carbonyls. In probing

0020-1669/86/1325-2864$01.50/0

Table I

donor (B)	E_B[a]	C_B[a]	$E_A(1:1)$[b]	$C_A(1:1)$[b]	ν_{CO}, cm^{-1}	
					expt[c]	calcd[d]
	0	0	5.06	1.74	2135.8	2136.0
ethyl acetate	0.975	1.74	3.93	1.68	2130.8	2129.1
acetonitrile	0.886	1.34	4.03	1.69	2129.1	(2129.8)
acetone	0.987	2.33	3.92	1.66	2128.6	2128.7
bridged ether[e]	0.887	4.11	4.03	1.59	2127.0	2127.7
dimethyl sulfoxide	1.34	2.85	3.51	1.64	2126.2	2126.2
triethyl phosphate	1.36	1.81	3.48	1.67	2126.2	2126.7
diethyl sulfide	0.339	7.40	4.67	1.47	2126.1	(2128.4)
dimethylacetamide	1.32	2.58	3.53	1.65	2125.4	2126.5
cage phosphite[f]	0.548	6.41	4.42	1.51	2125.1	(2128.0)
1-methylimidazole	0.934	8.96	3.98	1.41	2124.7	2123.7
piperidine	1.01	9.29	3.89	1.40	2124.2	2123.0
pyridine	1.12	6.89	3.76	1.49	2122.8	(2124.3)
triethylamine	0.991	11.09	3.91	1.34	2121.6	2121.9
4-picoline	1.17	6.80	3.70	1.49	2121.5	(2124.0)
quinuclidine	7.04	13.2	4.24	1.26	2120.8	2121.8

[a] Reference 6. [b] Calculated from eq 2 and 3 for $BRh_2(pfb)_4$. [c] Experimental values for $BRh_2(pfb)_4CO$ were measured and reported to 0.1 cm^{-1}; the upper limit is conservatively estimated as 0.5 cm^{-1}. A 15-cm^{-1} variation of ν_{CO} is observed, which is measured to 3% accuracy. This is comparable to the 2% accuracy in a 10 kcal mol^{-1} variation in an enthalpy fit. [d] Calculated from eq 4 by using $E_A(1:1)$ and $C_A(1:1)$ values. Values in parentheses are for π acceptors whose experimental ν_{CO} values were not used in the correlation. [e] 7-Oxabicyclo[2.2.1]heptane. [f] 4-Ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.1]octane.

the influence of cis- and trans-coordinated ligands, ^{13}C NMR[2] and IR[3] studies of the coordinated carbonyl have probed the relative donor and acceptor properties of coordinated ligands in transition-metal mononuclear carbonyl complexes. In this paper, we examine ligand effects on coordinated CO in a dinuclear complex. Our intentions are twofold: (i) to relate ligand donor strength to carbonyl stretching frequencies across a metal–metal bond with our inductive-transfer model[4] and (ii) to use this relationship to understand the primary orbital interactions responsible for the inductive transfer.

As part of our continuing studies of the transmission of coordination effects across metal–metal bonds,[4,5] we report the variation of the CO stretching frequency, ν_{CO}, with σ-donor strength of coordinated Lewis bases for a series of rhodium dimers of the formula $BRh_2(pfb)_4CO$ where B is a Lewis base and pfb is perfluorobutyrate. In this study, we correlate the changes in ν_{CO} with the *E* and *C* parameters of B.[6] Our strategy involves correlation of experimental stretching frequencies of coordinated CO with predicted changes in the acidity parameters of the second metal center that result from coordination of B to $Rh_2(pfb)_4$ to form the new Lewis acid $BRh_2(pfb)_4$ which will bind CO. The form of the *E* and *C* equation[6] used to describe a nonenthalpic change,[7] $\Delta\chi$, for a given base interacting with a series of acids is given by eq 1a while that for a given acid reacting with a series of bases

$$\Delta\chi + W = E_A E_B^* + C_A C_B^* \tag{1a}$$

is given by eq 1b; here $\Delta\chi$ is a nonenthalpic change such as a

$$\Delta\chi + W = E_A^* E_B + C_A^* C_B \tag{1b}$$

spectral shift or free energy associated with adduct formation. The E_B^* and C_B^* parameters (or E_A^*, C_A^* for constant acid fits) differ from the reported unstarred parameters and contain the conversion factor from kcal mol^{-1} to the units associated with $\Delta\chi$. In this study we use E_A and C_A parameters for $Rh_2(pfb)_4$ and acid parameters $E_A(1:1)$ and $C_A(1:1)$ for the 1:1 base adducts, $BRh_2(pfb)_4$, which react with a second base to form a 2:1 adduct. The $E_A(1:1)$ and $C_A(1:1)$ parameters for the $BRh_2(pfb)_4$ dimers reflect the inductive influence of the coordinated base at one metal site on the acceptor properties of the second according to our inductive-transfer model. In this model,[5] the $E_A(1:1)$ and $C_A(1:1)$ parameters for the Lewis acid $BRh_2(pfb)_4$, a 1:1 adduct itself, interacting with a second base to form a 2:1 adduct are given by

$$E_A(1:1) = E_A - kE_B \tag{2}$$

$$C_A(1:1) = C_A - k'C_B \tag{3}$$

where E_A and C_A are the parameters[5] for unligated $Rh_2(pfb)_4$, E_B and C_B are the parameters for the donor *B*, and *k* and *k′* represent the ability of the metal–metal bond to transmit the inductive influence of the coordinated base, B. Thus, the enthalpy associated with coordination of the second base is given by

$$-\Delta H = (E_A - kE_B)E_{B'} + (C_A - k'C_B)C_{B'} \tag{4a}$$

where A refers to the free acid, B to the first base coordinated, and B′ to the second. For nonenthalpic changes involving a constant base (CO in this study) $-\Delta H$ of eq 4a is replaced by $\Delta\chi + W$ and $E_{B'}$ by $E_{B'}^*$, leading to

$$\Delta\chi + W = (E_A - kE_B)E_{B'}^* + (C_A - k'C_B)C_{B'}^* \tag{4b}$$

The experimental ν_{CO} values obtained when CO is bubbled through methylene chloride solutions of $Rh_2(pfb)_4$ containing enough[8] donor to form $BRh_2(pfb)_4$ are given in Table I. The

---

(1) On sabbatical leave from Ithaca College, Ithaca, New York.

(2) (a) Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027. (b) Connor, J. A.; Jones, E. M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1972**, 2419. (c) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012. (d) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951. (e) Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1983**, *241*, 201.

(3) (a) Bigorgne, M. *J. Inorg. Nucl. Chem.* **1964**, *26*, 107. (b) Angelici, R. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2627. (c) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315. (d) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

(4) Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1982**, *21*, 2196.

(5) (a) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 2897. (b) Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920. (c) Drago, R. S.; Cosmano, R.; Telser, J. *Inorg. Chem.* **1984**, *23*, 4514. (d) Drago, R. S. *Inorg. Chem.* **1982**, *21*, 1697.

(6) The E and C equation $-\Delta H + W = E_A E_B + C_A C_B$ correlates the enthalpies of adduct bond formation to empirical acid (A) and base (B) parameters. *E* and *C* represent the susceptibility of the acid (base) to undergo electrostatic and covalent interactions. *W* is any constant contribution to ΔH associated with a given acid reacting with a series of bases or a given base reacting with a series of acids. In most systems studied to date, $W = 0$. See: (a) Drago, R. S. *Struct. Bonding (Berlin)* **1973**, *15*, 73. (b) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251.

(7) Equation 1a is used to correlate nonenthalpic changes for a given base interacting with a series of acids whose E_A and C_A parameters are known.[6] Similarly, for a given acid interacting with a series of bases, eq 1b is used where the E_B and C_B parameters are obtained from the literature.[6] See: Doan, P. E.; Drago, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 4524.

donor E_B and C_B values are also given along with the $E_A(1:1)$ and $C_A(1:1)$ values for the $BRh_2(pfb)_4$ adduct calculated from eq 2 and 3 with the reported[5] parameters for $Rh_2(pfb)_4$ ($E_A = 5.06$, $C_A = 1.74$, $k = 1.16$, $k' = 0.0364$). Note that the resulting $E_A(1:1)$ and $C_A(1:1)$ values demonstrate the lowered acidity for the second metal center as a result of base coordination at the first rhodium atom. This second metal center is the site for coordinating CO. Because the E and C parameters are rigorously derived from reactions in which only σ interactions are important,[6a] the $E_A(1:1)$ and $C_A(1:1)$ values do not reflect the effect of rhodium to B π-back-bonding in the $BRh_2(pfb)_4$ adduct bond (the term metal to ligand π-back-bonding is used here to also include the proportionately enhanced ligand to metal σ bonding).

When the experimental CO frequencies are substituted for $\Delta\chi$ and the $E_A(1:1)$ and $C_A(1:1)$ values from Table I are used in eq 4b, the least-squares-minimized solution for those systems in which B is not a π-acceptor ligand gives $E_{B'}{}^* = 4.99$, $C_{B'}{}^* = 21.1$, and $W = -2074.1$. These parameters for CO spectral changes allow calculation of CO stretching frequencies for any $BRh_2(pfb)_4CO$ complex when the base is a σ donor whose E_B and C_B parameters are known. The calculated ν_{CO} values for the systems studied in this work are given in Table I, and their excellent agreement with the experimental values demonstrates the "goodness" of the fit. The change in Lewis acidity for the second metal center in $BRh_2(pfb)_4$ adducts for various bases is quantitatively predicted by eq 2 and 3, as seen by the close agreement between the calculated and experimental ν_{CO} values. This supports our claim that this inductive-transfer model can be used to quantify the acceptor strength of metal clusters.

Data for adducts with donors known to act as π acceptors (acetonitrile, cage phosphite, diethyl sulfide, pyridine, and 4-picoline) are not included in the calculation of the CO parameters. The $E_A(1:1)$ and $C_A(1:1)$ numbers for adducts with these five donors do not reflect the reported π-back-bonding from rhodium to the donor because the E_B and C_B values used in eq 2 and 3 reflect σ-only effects. The fact that the largest deviations in predicted and experimental frequencies occur with systems previously reported to π-back-bond lends support to the *synergistic π-back-bond enhancement* previously reported and described in metal–metal-bonded systems.[5d] The deviations of the σ donors are random while those of the π-back-bonding systems are systematically low. Consideration of the values of ν_{CO} when π and σ effects are both operative in the Rh–B bond lends insight into the mechanism of the inductive transfer. The calculated ν_{CO} values for the five π acceptors are given (in parentheses) in Table I; these are the frequencies expected if the Lewis bases, B, utilize only their σ-bonding capabilities in forming the $BRh_2(pfb)_4CO$ adduct. The lower observed ν_{CO} values than calculated from eq 4 manifest the metal to B π-back-bonding contribution for adducts with these five bases.

The effect of σ donation of electron density from the Lewis base, B, to the metal raises the energy of the d-orbital manifold. The rhodium π^* orbitals become more effective at π^*-back-bonding. This coupled with a weaker metal–CO σ bond caused by raising the σ^* molecular orbital energy causes the CO stretching frequency to decrease, as observed. When B is a π-acceptor ligand, the Rh π^* orbital is stabilized by the π^*-back-bonding, but this effect would cause our observed ν_{CO} value to be larger than our calculated value, in contrast to observation. The enhanced ligand to metal σ donation from the base π-back-bonding would raise the energy of the π^* molecular orbital and increase the back-bonding to CO. The σ effect apparently dominates and leads to a decrease in ν_{CO}. The two rhodium atoms in $BRh_2(pfb)_4$ are no longer equivalent, and they will contribute differently to the σ^* MO's of the adduct. If π^*-back-bonding to base B increased the contribution that the uncoordinated rhodium in $BRh_2(pfb)_4$ makes to the π^* MO's, more effective overlap with the π^* orbitals of CO could result upon adduct formation with CO and the observed frequency decrease would also result from this effect. This would constitute a polarization of d-electron density toward the unligated rhodium. The changes in the ν_{CO} frequencies are small and can result from subtle differences in the many perturbations made on the system by base coordination. The key point for our purpose is that σ donors decrease ν_{CO} in a predictable fashion and the π-acceptor bases, B, which are strong donors, cause a decrease larger than expected from a σ-only effect.

It is significant to note that the σ-only E and C analysis has been used to describe the spectral changes in a ligand, CO, that acts as both a σ donor and a π acceptor. The fact that the treatment works indicates that the π-back-bonding into and decreased σ bonding of CO change in a proportional manner when B is varied in the 11 σ-donor adducts.

Experimental Section

Tetrakis(perfluorobutyrato)dirhodium(II), $Rh_2(pfb)_4$. Rhodium(II) acetate, $Rh_2(OAc)_4$, was prepared[9] from $RhCl_3 \cdot 3H_2O$ (Englehard). $Rh_2(pfb)_4$ was prepared from the acetate by ligand exchange. A solution of 2 g of $Rh_2(OAc)_4$ in 30 mL of perfluorobutyric acid and 3.5 mL of perfluorobutyric anhydride was brought to reflux and half the solvent distilled off. The remaining solution was cooled to 25 °C and then to −20 °C for several hours. The dark blue-green $Rh_2(pfb)_4$ compound was filtered, washed with cold pentane, and dried in vacuo. Recrystallization from benzene gave 91% yield. Anal. Calcd for $Rh_2C_{16}O_8F_{28}$: C, 18.17; H, 0.00; F, 50.28. Found: C, 18.63; H, 0.32; F, 49.5.

All bases were reagent grade and purified to insure the exclusion of water, usually by distillation from dessicant. All sample preparations were performed under N_2. Methylene chloride and benzene were purified by standard methods.[10]

IR spectra were recorded with a Nicolet 7000 FTIR calibrated with polystyrene film. Solutions were prepared by bubbling carbon monoxide through methylene chloride solutions 5.0×10^{-3} M in $Rh_2(pfb)_4$ and 4.0×10^{-3} M in base. The solutions were then transferred to a Beckman 0.50 mm path length cell with NaCl windows. One hundred scans were collected, and the contribution from $Rh_2(pfb)_4CO$ was subtracted.

Acknowledgment. The authors gratefully acknowledge the support of this research by the National Science Foundation through Grant M 84-08149. The authors thank Dr. Roger Cramer for helpful discussions.

Registry No. $BRh_2(pfb)_4CO$ (B = ethyl acetate), 102651-22-9; $BRh_2(pfb)_4CO$ (B = acetonitrile), 102651-23-0; $BRh_2(pfb)_4CO$ (B = acetone), 102682-16-6; $BRh_2(pfb)_4CO$ (B = 7-oxabicyclo[2.2.1]heptane), 102651-24-1; $BRh_2(pfb)_4CO$ (B = dimethyl sulfoxide), 102651-25-2; $BRh_2(pfb)_4CO$ (B = triethyl phosphate), 102651-26-3; $BRh_2(pfb)_4CO$ (B = diethyl sulfide), 102651-27-4; $BRh_2(pfb)_4CO$ (B = dimethylacetanide), 102651-28-5; $BRh_2(pfb)_4CO$ (B = 1-phospha-2,6,7-trioxabicyclo[2.2.1]octane, 102651-29-6; $BRh_2(pfb)_4CO$ (B = piperidine), 102651-31-0; $BRh_2(pfb)_4CO$ (B = pyridine), 102651-32-1; $BRh_2(pfb)_4CO$ (B = triethylamine), 102651-33-2; $BRh_2(pfb)_4CO$ (B = 4-picoline), 102651-34-3; $BRh_2(pfb)_4CO$ (B = quinuclidine), 102651-35-4; Rh, 7440-16-6; $BRh_2(pfb)_4CO$ (B = 1-methylimidazole), 102651-30-9.

---

(8) Calorimetric and spectroscopic experiments[5b] with $Rh_2(pfb)_4$ demonstrate well-behaved 1:1 and 2:1 adduct formation with a wide range of donors and no evidence for bridge displacement. Since the IR frequencies for free CO and the CO adduct of $Rh_2(pfb)_4$ are known, new bands must correspond to CO adducts of $BRh_2(pfb)_4CO$.

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

(10) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.