J. Am. Chem. Soc. **1982**, *104*, 888-889

Bond Energies in Two-Ligand Gas-Phase Metal-Ion Complexes Exhibit Trans Influence

Manfred M. Kappes,[1a] Roger W. Jones,[1b] and
Ralph H. Staley*[1c]

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received April 13, 1981

Metal complexes having two or more ligand molecules can exhibit synergistic effects in which the properties and behavior of one ligand show a dependence on the identity of the other ligand or ligands. Such phenomena were first observed in the kinetic behavior of square-planar and octahedral transition-metal complexes and have been generally referred to as the trans effect (or in some cases the cis effect).[2-4] Ground-state properties such as bond distances, vibrational frequencies, and NMR parameters also exhibit such phenomena. For the ground-state properties these phenomena are referred to as trans influence.[2-4] These phenomena should also be manifest in thermodynamic properties, but little data has been available to establish this point.[2-4]

The ideal measure of trans influence in thermodynamic properties would be provided by determination of gas-phase metal–ligand bond strengths, the enthalpy for reaction 1. Reaction 1

$$AMB^+ \rightarrow AM^+ + B, \qquad \Delta H = D(AM^+\text{–}B) \qquad (1)$$

has been written for the case of a unipositive, two-ligand, linear complex, one of the simplest systems which would be expected to exhibit trans influence. Relative bond strengths for two-ligand complexes are given by enthalpy differences for the ligand-exchange reactions 2 and 3. The enthalpy expressions for these

$$AMA^+ + B \overset{K_2}{\rightleftarrows} AMB^+ + A$$

$$\Delta H_2 = D(AM^+\text{–}A) - D(AM^+\text{–}B) \qquad (2)$$

$$AMB^+ + B \overset{K_3}{\rightleftarrows} BMB^+ + A$$

$$\Delta H_3 = D(BM^+\text{–}A) - D(BM^+\text{–}B) \qquad (3)$$

reactions follow from the enthalpy expression for reaction 1. If there were no interaction between the two ligand sites on the metal, then the enthalpies for reactions 2 and 3 would be equal, $\Delta H_2 = \Delta H_3$ (Scheme I). If there is synergistic enhancement of the mixed species AMB^+ compared to the pure species AMA^+ and BMB^+, then this can be measured as a deviation Q of the relative enthalpy for the mixed species, where $Q = (\Delta H_3 - \Delta H_2)/2 = [D(AM^+\text{–}B) + D(BM^+\text{–}A) - D(AM^+\text{–}A) - D(BM^+\text{–}B)]/2$ (Scheme I).

We wish to report measurements, using ion cyclotron resonance (ICR) techniques, of equilibria for the gas-phase reactions 2 and 3 showing synergistic enhancement of the population of the mixed AMB^+ species. The data were measured as part of studies of gas-phase ligand-binding energies to metal cations where the energies of the overall exchange of two B ligands for two A ligands (reaction 4) is used to obtain scales of relative ligand-binding energies. Studies have been completed for Ni^+, Cu^+, and Co^+ with two ligands and are reported separately.[5-7]

$$AMA^+ + 2B \rightleftarrows BMB^+ + 2A$$

$$\Delta H_4 = D(M^+\text{–}2A) - D(M^+\text{–}2B) \qquad (4)$$

Scheme I

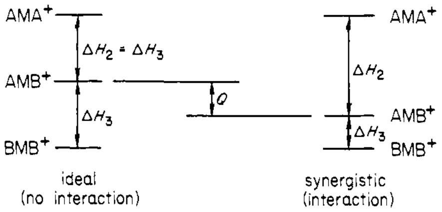


Table I. Stabilization Energies for Intergroup Two-Ligand Gas-Phase Transition-Metal Complexes Showing Synergistic Stabilization[a]

M	A[b]	B[b]	Q[c]	$D(M^+\text{–}2B) - D(M^+\text{–}2A)$
	(A) σ-Base/π-Base Complexes, AMB^+			
Co	EtOH	$EtCH{=}CH_2$	0.75	0.51
Co	Me_2O	$EtCH{=}CH_2$	0.86	0.59
Co	*n*-PrOH	$Me_2C{=}CH_2$	0.75	0.51
Co	$Me_2C{=}CH_2$	EtCHO	0.72	0.54
Ni	$MeCH{=}CH_2$	Me_2O	1.27	1.65
Ni	$Me_2C{=}CH_2$	*n*-PrOH	1.18	0.44
Ni	Me_2O	$EtCH{=}CH_2$	1.18	0.06
Ni	$CH_2{=}C{=}CH_2$	MeOH	1.11	0.81
Cu	$Me_2C{=}CH_2$	*n*-PrCHO	0.72	0.52
Cu	$MeCH{=}CH_2$	Me_2O	1.16	1.46
	(B) σ-Base/S-Base Complexes, AMB^+			
Co	Me_2O	MeSH	0.27	0.12
Co	Me_2S	Me_2CO	0.49	0.07
Co	Et_2O	*n*-BuSH	0.23	0.01
Co	EtSH	*n*-PrCHO	0.34	0.09
Ni	Me_2S	Et_2CO	0.53	0.86
Ni	EtCOMe	Me_2S	0.36	0.83
Cu	Me_2CO	EtSH	0.75	0.53
Cu	*t*-BuCHO	MeSH	0.97	0.73
Cu	Et_2CO	MeNCS	0.30	0.30
	(C) σ-Base/N-Base Complexes, AMB^+			
Co	HCN	*n*-PrCHO	0.20	0.56
Ni	*n*-PrCHO	HCN	0.63	0.11
Ni	NH_3	Et_2CO	0.51	0.54
Cu	HCN	*n*-PrCHO	0.73	0.33
	(D) S-Base/π-Base Complex, AMB^+			
Ni	C_6H_6Cl	EtSH	1.18	0.35
	(E) N-Base/π-Base Complex, AMB^+			
Ni	$EtNH_2$	C_6H_5CN	0.35	1.23

[a] All data in kcal/mol. [b] B is always the stronger ligand and A the weaker ligand. [c] $Q = [D(AM^+\text{–}B) + D(BM^+\text{–}A) - D(AM^+\text{–}A) - D(BM^+\text{–}B)]/2$, see Scheme I.

Instrumentation and procedures for these studies are described in detail elsewhere.[5-9] Briefly, atomic metal cations are produced in the ICR cell by a pulsed YAG laser volatilization/ionization technique. In the presence of various organic molecules, the metal cations react to form metal–ligand complexes. At typical pressures of 3×10^{-6} torr, Ni^+, Cu^+, and Co^+ form complexes with two ligand molecules. Equilibrium constants are obtained from the measured partial pressures of the neutral ligands and the observed abundances of ions as the ligand exchange reactions 2 and 3 approach equilibrium. Equilibrium constants are converted to free energies by the relation $\Delta G = -RT \ln K$. It is assumed that entropy changes are small and tend to cancel so that they may be neglected and the free energy values taken as enthalpies.[10]

---

(1) (a) Institute for Inorganic and Physical Chemistry, University of Bern, CH-3012 Bern, Switzerland. (b) Department of Chemistry, Cornell University, Ithaca, NY 14853. (c) Central Research Department, Experimental Station, DuPont Company, Wilmington, DE 19898.

(2) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; pp 489–498.

(3) Hartley, F. R. *Chem. Soc. Rev.* **1973**, *2*, 163.

(4) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(5) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.*, in press.

(6) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.*, in press.

(7) Jones, R. W.; Staley, R. H. *J. Phys. Chem.*, in press.

(8) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4144.

(9) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794.

(10) The enthalpies are corrected for the statistical factor arising because the mixed species can be formed in two ways as AMB^+ or BMA^+. Other symmetry number[11] and rotational entropy[12] corrections are not made in this work since the geometries for the metal–ligand complexes are not known. The errors introduced should be small since these effects should tend to cancel for the two-ligand complexes studied.

0002-7863/82/1504-0888$01.25/0

Table II. Examples of Stabilization Energies, Q, for Intragroup Two-Ligand Gas-Phase Transition-Metal Complexes Showing Ideal (Statistical) Behavior[a]

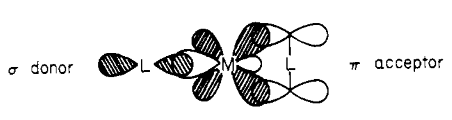
M	A[b]	B[b]	Q[c]	$D(M^+{-}2B) - D(M^+{-}2A)$
(A) σ-Base/σ-Base Complexes, AMB$^+$				
Co	Me_2O	*n*-PrOH	0.01	1.66
Co	Me_2CO	MeCOEt	0.04	1.33
Co	*n*-PrCHO	*i*-PrOH	0.02	0.15
Ni	$EtCO_2Et$	Et_2CO	−0.10	2.30
Ni	MeCHO	EtOH	0.09	0.46
Ni	*t*-BuCHO	Me_2CO	−0.11	1.39
Cu	EtBr	*i*-PrCl	0.03	0.34
Cu	EtCl	CH_2O	0.04	0.53
Cu	EtCHO	*n*-BuOH	−0.05	0.49
Cu	Et_2CO	*n*-$PrCO_2Et$	0.02	0.67
Cu	MeNCO	EtBr	0.08	0.43
Cu	$MeNO_2$	MeOH	0.10	0.01
(B) π-Base/π-Base Complexes, AMB$^+$				
Ni	C_6H_5Cl	C_6H_6	0.14	1.33
Ni	C_2H_2	$CH_2{=}C{=}CH_2$	0.14	0.19
(C) N-Base/N-Base Complexes, AMB$^+$				
Ni	MeCN	$MeNH_2$	0.07	0.14
Ni	EtCN	Me_3N	0.12	1.20

[a] All data in kcal/mol. [b] B is always the stronger ligand and A the weaker ligand. [c] $Q = [D(AM^+{-}B) + D(BM^+{-}A) - D(AM^+{-}A) - D(BM^+{-}B)]/2$, see Scheme I. The mean and standard deviation of the distribution of Q for 85 intragroup equilibria is $\overline{Q} = 0.01 \pm 0.09$ kcal/mol.

Results for a number of ligand pairs show synergistic stabilization of the mixed species. Values of Q for these pairs are given in Table I along with the total enthalpy change for exchange of both ligands, $D(M^+{-}2B) - D(M^+{-}2A)$. The observed values of Q do not correlate with the relative ligand-binding energies, $D(M^+{-}2L)$, or the ligand-binding energy difference for the ligand pair, $D(M^+{-}2B) - D(M^+{-}2A)$. The molecules studied fall into four groups: (1) σ bases (alkyl halides, alcohols, ethers, aldehydes, ketones, esters, isocyanates, and nitro compounds), (2) S bases (alkyl mercaptans and sulfides), (3) N bases (alkyl amines and cyanides), and (4) π bases (olefins and aromatics). Complexes with both ligands from the same group show no special stability for the mixed AMB$^+$ species. A few examples of the results for the intragroup complexes are given in Table II. Altogether 85 intragroup ligand–pair complexes have been studied. The mean and standard deviation for the distribution of Q for these complexes is $\bar{Q} = 0.01 \pm 0.09$ kcal/mol.

The σ-base/π-base pairs show the largest stabilization, $Q \simeq 0.8$, 1.2, and 0.9 kcal/mol for Co$^+$, Ni$^+$, and Cu$^+$ complexes respectively (Table I). Smaller stabilizations are seen for σ-base/S-base, σ-base/N-base, S-base/π-base, and N-base/π-base complexes (Table I).

The observation of synergistic stabilization of the mixed ligand complex for σ-base/π-base and other intergroup pairs constitutes a direct measurement of thermodynamic trans influence in the nearly ideal case of gas-phase two-ligand metal ion complexes. Empirical trans-influence orders predict[2-4] π bases > S bases $\simeq$ N bases > σ bases, consistent with the observed order in the present work. Theories of trans influence are based on the idea that with unlike trans ligands having differing degrees of π bonding a synergistic enhancement is obtained from asymmetric distortion of the metal orbitals involved in bonding. For example, with a pure σ-donor/π-acceptor ligand pair, the empty metal σ-orbital distorts toward the σ-donor ligand and an occupied metal d-orbital distorts toward the empty ligand π-acceptor orbital (structure I).[2-4] With like ligands on both sites, a symmetric structure results, giving no enhancement. Attempts at quantitative theoretical treatment of the effect have met with only very limited success.[2-4]



I

The quantitative thermochemical data provided by the present work for relatively simple systems should facilitate development of more exact theoretical models. Future ICR studies of bond-dissociation energies for two-ligand complexes of Co$^+$, Cu$^+$, Ni$^+$, and other metal cations can be expected to enlarge the data set available for examination of thermodynamic trans influence in the gas phase.

Acknowledgment is made to the National Science Foundation for support of this work by Grant CHE-76-17304.

Registry No. (EtOH)Co(EtCH=CH$_2$)$^+$, 80376-26-7; (Me$_2$O)Co(EtCH=CH$_2$)$^+$, 80376-27-8; (*n*-PrOH)Co(Me$_2$C=CH$_2$)$^+$, 80376-28-9; (Me$_2$C=CH$_2$)Co(EtCHO)$^+$, 80376-29-0; (MeCH=CH$_2$)Ni(Me$_2$O)$^+$, 80376-30-3; (Me$_2$C=CH$_2$)Ni(PrOH)$^+$, 80376-31-4; (Me$_2$O)Ni(EtCH=CH$_2$)$^+$, 80376-32-5; (CH$_2$=C=CH$_2$)Ni(MeOH)$^+$, 80375-75-3; (Me$_2$C=CH$_2$)Cu(*n*-PrCHO)$^+$, 80375-76-4; (MeCH=CH$_2$)Cu(Me$_2$O)$^+$, 80375-77-5; (Me$_2$O)Co(MeSH)$^+$, 80375-78-6; (Me$_2$S)Co(Me$_2$CO)$^+$, 80375-79-7; (Et$_2$O)Co(*n*-BuSH)$^+$, 80375-80-0; (EtSH)Co(*n*-PrCHO)$^+$, 80375-81-1; (Me$_2$S)Ni(Et$_2$CO)$^+$, 80375-82-2; (EtCOMe)Ni(Me$_2$S)$^+$, 80375-83-3; (Me$_2$CO)Cu(EtSH)$^+$, 80375-84-4; (*t*-BuCHO)Cu(MeSH)$^+$, 80375-85-5; (Et$_2$CO)Cu(MeNCS)$^+$, 80375-86-6; (HCN)Co(*n*-PrCHO)$^+$, 80375-87-7; (*n*-PrCHO)Ni(HCN)$^+$, 80375-88-8; (NH$_3$)Ni(Et$_2$CO)$^+$, 80375-89-9; (HCN)Cu(*n*-PrCHO)$^+$, 80375-90-2; (C$_6$H$_6$Cl)Ni(EtSH)$^+$, 80375-91-3; (EtNH$_2$)Ni(C$_6$H$_5$CN)$^+$, 80375-92-4; (Me$_2$O)Co(*n*-PrOH)$^+$, 80375-93-5; (Me$_2$CO)Co(MeCOEt)$^+$, 80375-94-6; (*n*-PrCHO)Co(*i*-PrOH)$^+$, 80387-08-2; (EtCO$_2$Et)Ni(Et$_2$CO)$^+$, 80375-95-7; (MeCHO)Ni(EtOH)$^+$, 80375-96-8; (*t*-BuCHO)Ni(Me$_2$CO)$^+$, 80375-97-9; (EtBr)Cu(*i*-PrCl)$^+$, 80375-98-0; (EtCl)Cu(CH$_2$O)$^+$, 80376-02-9; (EtCHO)Cu(*n*-BuOH)$^+$, 80376-00-7; (Et$_2$CO)Cu(*n*-PrCO$_2$Et)$^+$, 80376-01-8; (MeNCO)Cu(EtBr)$^+$, 80375-99-1; (MeNO$_2$)Cu(MeOH)$^+$, 80376-03-0; (C$_6$H$_5$Cl)Ni(C$_6$H$_6$)$^+$, 80376-04-1; (C$_2$H$_2$)Ni(CH$_2$=C=CH$_2$)$^+$, 80376-05-2; (MeCN)Ni(MeNH$_2$)$^+$, 80376-06-3; (EtCN)Ni(Me$_3$N)$^+$, 80376-07-4.

---

(11) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.

(12) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.

Reactivity of μ-Alkylidene Complexes: Bridge-to-Terminal Alkylidene Ligand Conversion in a Dimolybdenum Complex

Louis Messerle and M. David Curtis*

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

Received October 15, 1981

The synthesis and reactivity of transition-metal complexes which contain μ-alkylidene ligands have attracted considerable interest, in part because these ligands may be key surface intermediates in Fischer–Tropsch reactions for the reductive polymerization of carbon monoxide. These surface alkylidene moieties are postulated[1] to be in bridging positions because few isolable dinuclear complexes with terminal alkylidene or carbene ligands are known;[2] the vast majority contain μ-alkylidene ligands.

We reported recently the synthesis of reactive μ-alkylidene complexes by the thermal decomposition of μ-diazoalkane complexes, which are generated by the addition of diazoalkanes to a metal–metal triple bond.[3] Coordinatively saturated μ-alkylidene complexes can also be obtained from the addition of diazoalkanes to formal metal–metal double bonds.[4-6] Here, we report the first

---

(1) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181–6182.

(2) Examples: Casey, C. P. *Chem. Commun.* **1970**, 1220–1221. Casey, C. P.; Cyr, C. R. *J. Organomet. Chem.* **1973**, *57*, C69–C71.

(3) (a) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789–7791. (b) This transformation can also be affected photochemically: Messerle, L.; Curtis, M. D., unpublished results.

0002-7863/82/1504-0889$01.25/0