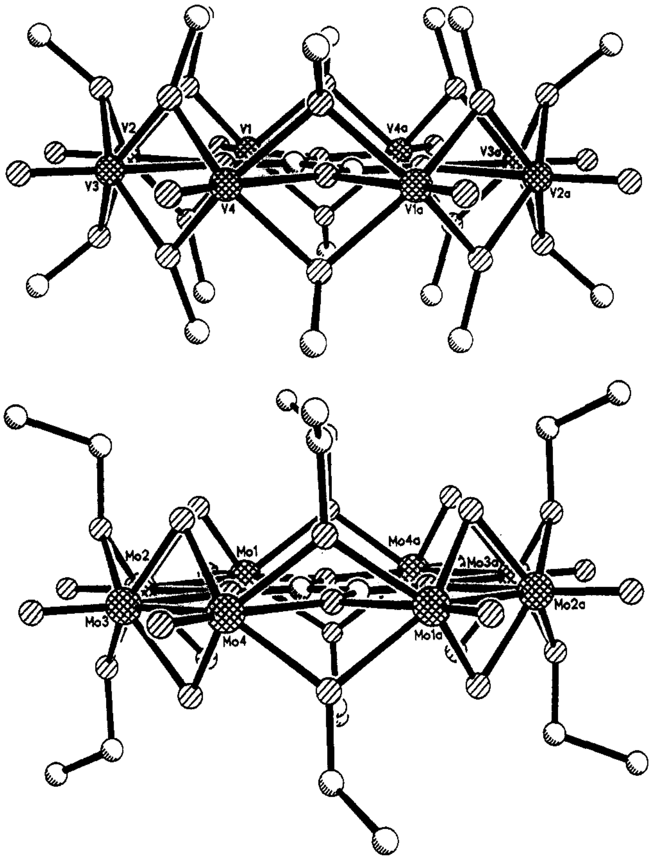

Figure 2. Schematic representations of the structures of $[V_8O_8(OCH_3)_{16}(C_2O_4)]^{2-}$ (top) and $[Mo_8O_{16}(OC_2H_5)_8(C_2O_4)]^{2-}$ (bottom)[14] illustrating exclusively alkoxy bridging in the former and the alternating bis(alkoxy)/dioxo bridging of the latter.

croconic acid, $H_2C_5O_5$, and with various organohydrazines.[13]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE8815299 to J.Z.).

Supplementary Material Available: Tables of experimental details for the X-ray diffraction studies, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (17 pages); tables of observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

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(13) Polyoxomolybdate complexes of squaric acid have been described recently: Chen, Q.; Ma, L.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 5944; Chen, Q.; Liu, S.; Zubieta, J. *Angew. Chem.*, in press.

(14) Crystal data for $[(n\text{-}C_4H_9)_4N]_2[Mo_8O_{16}(OC_2H_5)_8(C_2O_4)]$, $C_{50}H_{112}N_2O_{28}Mo_8$: monoclinic space group $P2_1/n$, $a = 12.054$ (1) Å, $b = 12.322$ (2) Å, $c = 26.075$ (4) Å, $\beta = 100.20$ (1)°, $V = 3811.7$ (12) Å^3, $Z = 2$, $D_{calc} = 1.70$ g cm^{-3}. Structure solution and refinement based on 3576 reflections with $I_0 \geq 3\sigma(I_0)$ (Mo Kα, $\lambda = 0.71073$ Å) converged at a final discrepancy value of 0.0564.

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Skeletal Rearrangement of $[Rh_2Fe_4(CO)_{16}B]^-$. An Example of an Associative Cluster Isomerization

The mechanisms for the interchange of fragments in molecules of all types have fascinated chemists for a long time. Perhaps because of this, the challenge of understanding the complexities of cluster rearrangements has not lacked champions beginning with the work of Lipscomb in 1960.[1] Recently, on the basis of continuing developments in the understanding of the electronic structure of clusters, there has been an increase in the number of reports proposing a variety of mechanistic rules to rationalize and predict the ease of rearrangement for various cluster shapes both for main-group and transition-metal cluster systems.[2] In one study, particularly relevant here, it was suggested that, among other criteria, large barriers are to be associated with mechanisms involving intermediates having skeletal electron counts different from that of the rearranging cluster.[3] Nearly all these theoretical studies restrict discussion to unimolecular pathways. This, plus the fact that examples of kinetically characterized transition-metal cluster framework isomerizations are rare,[4-7] leads us to report the kinetics of the facile isomerization of the octahedral, closed boride $[Rh_2Fe_4(CO)_{16}B]^-$. For octahedral closed clusters, high barriers are suggested by the theoretical studies. Our results show that in transition-metal cluster systems the presence of adventitious Lewis bases, e.g., CO, can open efficient bimolecular rearrangement pathways presumably by the stabilization of intermediates of higher skeletal electron count.[8]

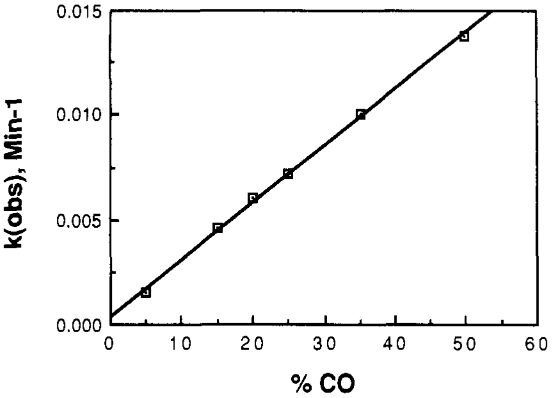

Figure 1. Plot of the pseudo-first-order rate constant for the isomerization of the sodium salt of $[1,2\text{-}\{Rh(CO)_2\}_2\text{-}3,4,5,6\text{-}\{Fe(CO)_3\}_4B]^-$ to $[1,6\text{-}\{Rh(CO)_2\}_2\text{-}2,3,4,5\text{-}\{Fe(CO)_3\}_4B]^-$ in THF at 22 °C vs the volume percent CO in N_2 with a total pressure of 1 atm. The line is a least-squares fit corresponding to the equation $k(\text{obs,m}^{-1}) = 4.03 \times 10^{-4} + 2.71 \times 10^{-4}[\%\ CO]$: $R = 1.00$.

As reported earlier[9] the preparation of the trans or $[1,6\text{-}\{Rh(CO)_2\}_2\text{-}2,3,4,5\text{-}\{Fe(CO)_3\}_4B]^-$ isomer of the boride proceeds through an intermediate proposed to be the cis or $[1,2\text{-}\{Rh(CO)_2\}_2\text{-}3,4,5,6\text{-}\{Fe(CO)_3\}_4B]^-$ isomer.[10] In contrast to the former, the latter has not been isolated or crystallographically characterized in the solid state but the spectroscopic parameters are structurally definitive.[11] Hence, we have now investigated the

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kinetics of reaction 1 in order to explore the mechanism for this

$$cis\text{-}[Rh_2Fe_4(CO)_{16}B]^- \rightarrow trans\text{-}[Rh_2Fe_4(CO)_{16}B]^- \quad (1)$$

framework isomerization. ^{11}B NMR spectroscopy was used to monitor the appearance of the trans isomer and the disappearance of the cis isomer.[12] Under presumably pure N_2 and with THF as a solvent the reaction of the sodium salt was first order in the cluster. The apparent activation parameters under these conditions are $E_a = 17.6$ kcal/mol and $A = 7 \times 10^8$ s^{-1}.[13] The latter parameter is too small for a unimolecular rearrangement reaction and caused us to search for mechanistic complexities.[14]

The first-order rate constant, k_1, in Et_2O is greater than that in THF or glyme. However, k_1 is independent of the identity of the cation (Li, Na, K), suggesting that solvation is not playing a major role. Careful purging of the system during preparation of the cis isomer gave lower rates of isomerization into the trans structure ($\approx\times\ ^1/_2$) while replacing the N_2 atmosphere with CO yielded a half-life for conversion of the cis to trans isomer approaching the limit of the analysis method. Thus, we were led to measure the first-order rate constant in THF as a function of CO concentration with the results shown in Figure 1.[15] The rate of reaction 1 is given by eq 2 where $k_2 = 4.2 \times 10^{-2}$ M^{-1} s^{-1}. At

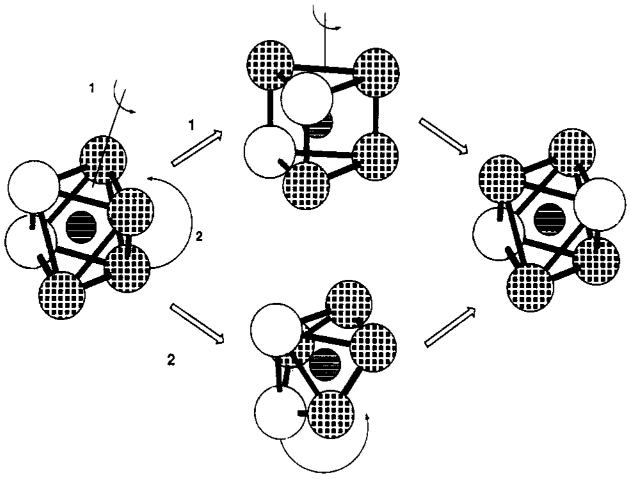
$$\text{rate} = k_2[\text{CO}][\text{cluster}] \quad (2)$$

22 °C the CO independent rate is judged to be zero within experimental error.[16] This CO dependence accounts for the apparently inconsistent behavior reported above. The enhanced rate in Et_2O arises from the fact that the solubility of CO is greater in Et_2O[17] than in THF.[15] The low value of the frequency factor for the pseudo-first-order rate constant is due to the fact that the process is actually second order. Using Figure 1 to estimate the CO concentration for the variable-temperature measurements leads to an A value of $\approx 10^{11}$ M^{-1} s^{-1} for the second-order reaction. This is a typical value for a low-barrier acid–base reaction. Thus, the stoichiometric mechanism for reaction 1 is associative in nature, i.e.

$$cis\text{-}[Rh_2Fe_4(CO)_{16}B]^- + CO \rightarrow trans\text{-}[Rh_2Fe_4(CO)_{16}B]^- + CO \quad (3)$$

The rate of reaction 1 is not increased in the presence of NEt_3, showing that CO most likely promotes the reaction by coordination to the metal framework. This was corroborated by demonstrating that PMe_2Ph promotes the isomerization but is less efficient than CO in doing so.[18] The addition of a Lewis base to a cluster adds two electrons to the skeletal electron count. In metal clusters, this may[19] or may not[20] lead to an opening of the cluster framework; however, addition of two additional skeletal electrons will certainly serve to stabilize more open structures. Hence, the most recent proposal of a capped-square-pyramidal intermediate with the same skeletal electron count as an octahedron[3] is judged improbable as there is no obvious role for an added CO ligand to play.

Scheme I



The intermediates for two of the most frequently proposed pathways for rearrangement of a six-atom closo cluster (see Scheme I) have higher skeletal electron counts than an octahedral cluster.[21] The pathway via a trigonal-prismatic intermediate has always been appealing from the point of view of simplicity and symmetry; however, it is well-known experimentally[22] as well theoretically[23] that a trigonal-prismatic cluster requires two more electron pairs than an octahedron. This suggests that two CO ligands would be required to fully stabilize this intermediate. The rate-determining step might well be the addition of the first CO, and, thus, one cannot rule out this pathway on the basis of the observed first-order dependence on [CO]. However, addition of two CO's introduces a steric problem, and one can argue that addition of a second CO might well have a slower rate than that of the first. Hence, this route is less probable than an alternate pathway involving a pentagonal-pyramidal intermediate. Such an intermediate is a nido six-atom cluster requiring only one additional electron pair for stability. Several arrangements of the Rh and Fe atoms are possible, and only one such possibility is illustrated in Scheme I. Here one added CO ligand satisfies the electronic requirements of the intermediate, and the opening of the cluster provides sufficient room for good binding. As this is the simplest mechanism that will explain existing observations, we favor it.

Clearly nature does not recognize the niceties of restrictions in mechanistic type—restrictions often adopted, if not required, in theoretical approaches in order to make a complex problem tractable. But in a negative way, our observations confirm the proposed skeletal-electron-counting selection rule.[3] As a unimolecular pathway has an intrinsic advantage over a bimolecular one, the fact that low levels of CO provide an effective rearrangement pathway suggests that any mechanism going through an intermediate of increased electron count is unfavorable in the absence of suitable Lewis bases. On the other hand, this observation does not provide any information on the relative magnitudes of the barriers for competing unimolecular pathways.

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(11) The large low-field chemical shift (δ 205) is consistent with a boron atom directly bonded to six transition-metal atoms (Rath, N. P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 5345). The narrow line width (12 Hz) in the ^{11}B NMR spectrum and correspondingly long relaxation time (470 ms) demonstrate a highly symmetrical environment, i.e., octahedral (Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Vol. 2, p 50). The observed triplet with $J_{BRh} = 23.3$ Hz shows direct bonding of the boron atom to two rhodium atoms.

(12) In a typical run, 0.08 mmol of freshly prepared cis-$[Rh_2Fe_4(CO)_{16}B]^-$ complex in 2.0 mL of solvent was transferred to a 10 mm NMR tube containing N_2 or N_2/CO gas mixture. The loss of the signal at δ 205 and the formation of the signal at 211 were monitored in a NT-300 spectrometer at a chosen temperature. The total integral of the two signals with respect to a standard reference ($[B_3H_8]^-$) was constant with time showing no loss of boron during the isomerization process. Plots of ln $[I_{205}/(I_{205} + I_{211})]$ vs time yielded good straight lines at up to 75% conversion, and the slopes are the first-order rate constants.

(13) The temperature range was 273 to 328 K.

(14) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.

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(16) At 25 °C with 10% CO the fraction of reaction carried by a unimolecular pathway is $\leq$7 times that for the bimolecular pathway. As the activation energy for a unimolecular path is generally higher than that for a bimolecular one, the bimolecular mechanism will be even more predominant at lower temperatures.

(17) The solubility of CO in Et_2O is 0.0163 M atm^{-1} at 295 K: Linke, W. F., Ed. *Solubilities of Inorganic and Metal Organic Compounds*; 4th ed.; Van Nostrand: New York, 1958; Vol. 1, p 456.

(18) The second-order rate constant for PMe_2Ph is 1.1×10^{-2} M^{-1} s^{-1} at 22 °C for the sodium salt in THF with purging.

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Intrinsic Transition-Metal–Carbon Double-Bond Dissociation Energies: Periodic Trends in $M^+–CH_2$ Bond Strengths

Transition-metal methylidenes have long been postulated as intermediates in a variety of reactions such as metal alkyl decomposition, polymerization of olefins, olefin homologation and metathesis, and cyclopropane formation from olefins.[1] Consequently, the bond dissociation energies (BDEs) of transition-metal alkylidenes are of fundamental interest in surface chemistry, organometallic chemistry and catalysis. Few condensed-phase M=C BDEs are known, however, so it is instructive to evaluate gas-phase values to find *intrinsic* bond strengths that are useful as maximum values for the condensed phase. In addition, it has been shown that the gas-phase values serve as a good basis for estimating BDEs in coordinatively saturated complexes.[2] In this communication, we report recent results for $M^+{=}CH_2$ BDEs for the entire first row of the transition metals and attempt to clarify the periodic trends in these values.

One means of analyzing the periodic trends in singly bonded transition-metal species, e.g. $M^+–H$, has been to correlate the BDEs of these species with the metal ion promotion energy (E_p).[3,4] E_p is best defined as the energy necessary to take a metal atom in its ground state to an electron configuration where there is one electron in the valence s orbital that is spin-decoupled from the remaining metal d electrons.[4,5] The intrinsic or maximum ML^+ BDE results when $E_p = 0$, since no energy is required to place the metal in the most suitable state for bonding. Similar correlations also exist for E_p vs M–H, $M–CH_3$, and $M^+–CH_3$ BDEs,[5–7] leading to an intrinsic bond energy of ~56 kcal/mol for first-row transition-metal single bonds.[6]

Similar correlations for multiply bonded transition-metal species were not evident from early data.[3] More recently,[6] the beginnings of such a correlation could be seen although incomplete data prevented any definitive analysis. Therefore, we have recently investigated MCH_2^+ BDEs for the first-row transition metals, providing the first experimental measurements for M = Sc,[8] Ti,[9] V,[10] and Cu[11] and changing those for M = Cr,[12] Mn,[13] Fe,[14] Co, and Ni.[11] This thermochemistry is measured by examining reactions 1–3 as a function of translational energy. Reaction 1 is

$$M^+ + CH_4 \rightarrow MCH_2^+ + H_2 \qquad (1)$$

$$M^+ + c\text{-}C_3H_6 \rightarrow MCH_2^+ + C_2H_4 \qquad (2)$$

$$M^+ + c\text{-}C_2H_4O \rightarrow MCH_2^+ + CH_2O \qquad (3)$$

used for M = Sc–Cr, and reactions 2 and 3 are used for M = Cr–Cu. Threshold energies for these endothermic reactions are determined and related to the metal methylidene BDEs. Detailed descriptions of our experimental apparatus[15] and methods of interpretation have been published.[8–10,12] The derived MCH_2^+ bond energies, as well as M^+ double-bond promotion energies taken from Carter and Goddard,[2] are listed in Table I.

Table I. Transition-Metal Methylidene Bond Energies[a]

	$D°(M^+–CH_2)$		promotion energy[b]	
M	this work	literature	sd^{n-1}	d^n
Sc	98.4 ± 5.3[c]		**3.7**	19.5
Ti	93.4 ± 3.5[d]		**13.3**	22.5
V	80.0 ± 3.2[e]	76 ± 2[f]	**32.9**	37.5
Cr	53.8 ± 1.9[g]	65 ± 7,[h] 49.6[i]	72.7	**57.8**
Mn	70.6 ± 3.0[j]	94 ± 7,[h] 58.4[k]	**51.6**	85.7
Fe	83.0 ± 4.0[l]	96 ± 5,[h] 82 ± 5[m]	41.4	**34.0**
Co	77.5 ± 2.3[n]	85 ± 7,[h,o] 84 ± 5[m]	39.2	**10.0**
Ni	75.2 ± 1.8[n]	86 ± 6[h,p]	**41.6**	
Cu	63.9 ± 1.6[n]	48[q]	69.9[r]	

[a] All values in kcal/mol at 298 K. [b] Values from ref 2, except where noted. [c] Reference 8. [d] Reference 9. [e] Reference 10. [f] Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 1806–1819. [g] Reference 12. [h] Reference 3. [i] Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1984**, *88*, 1485. [j] Reference 13. [k] Brusich, M. J.; Goddard, W. A. Cited in ref 2. [l] Reference 14. [m] Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 2537–2540. [n] Reference 11. [o] Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819–2826. [p] Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1829–1833. [q] Reference 17. [r] Average excitation energy of the $^1D(sd^9)$ and $^3D(sd^9)$ states.

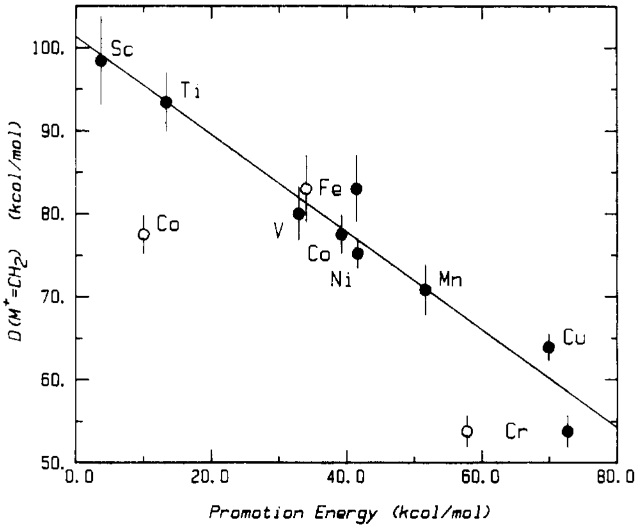

Figure 1. Bond dissociation energies for first-row transition-metal ions to methylidene vs atomic metal ion promotion energy to an sd^{n-1} spin-decoupled state (closed circles). For M = Co, Cr, and Fe, the open circles represent the atomic metal ion promotion energy to a spin-decoupled d^n state. The line is a linear regression fit to the closed circles.

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