Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. We thank Professor John Shapley for suggesting the investigation of CO rate dependence and Professor Sheldon Shore for drawing our attention to the measurements of the solubility of CO in THF.

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(24) Present address: Department of Chemistry, University of California, Los Angeles, CA 90024.

Department of Chemistry
University of Notre Dame
Notre Dame, Indiana 46556

Ananda K. Bandyopadhyay
Rajesh Khattar[24]
Thomas P. Fehlner*

Received August 28, 1989

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

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

M	$D°(M^+$–$CH_2)$ this work	$D°(M^+$–$CH_2)$ literature	promotion energy[b] sd^{n-1}	promotion energy[b] 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.

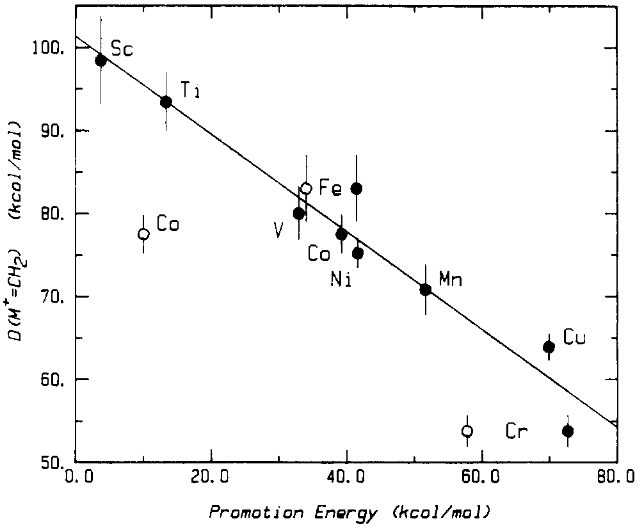

Figure 1. Bond dissociation energies for first-row transition-metal ions to methylidene vs atomic metal ion promotion energy to an sd^{n-1} spin-decoupled state (closed circles). For M = Co, Cr, and Fe, the open circles represent the atomic metal ion promotion energy to a spin-decoupled d^n state. The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

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

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

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

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.

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Figure 1 compares $D°(M^+-CH_2)$ values to $E_p(sd^{n-1})$ for the first-row transition metals. The slope of the linear regression fit is nearly identical with those previously reported for MH^+ and MCH_3^+.[6] The excellent fit to the data indicates that the promotion energy–bond strength correlation extends to double bonds as well as single bonds of transition metals. The maximum or intrinsic $M^+{=}CH_2$ bond strength is ~101 kcal/mol, such that the intrinsic $M^+{-}C$ π-bond strength is ~45 kcal/mol. The intrinsic double-bond value corresponds nicely with the lone metal–methylidene bond energy known for a *saturated* metal center, $D°[(CO)_5Mn^+{=}CH_2] = 96 \pm 7$ kcal/mol.[16] Preliminary data indicate that a parallel correlation also holds for M^+-CH triple bonds,[6] with an intrinsic $M^+{\equiv}CH$ BDE of ~130 kcal/mol. It is interesting to note that the ratio of the *intrinsic* M^+–C single-, double-, and triple-bond strengths, 1.0:1.68:2.20, is nearly identical with that for C–C single, double, and triple bonds (as represented by $CH_3{-}CH_3$, $CH_2{=}CH_2$, and $CH{\equiv}CH$), 1.0:1.65:2.21.

In their theoretical paper, Carter and Goddard[2] suggest that the M^+-CH_2 BDEs should correspond to the *lower* value of the sd^{n-1} and d^n promotion energies, shown in boldface in Table I. For M = Co and Cr, however, it is clearly the higher $E_p(sd^{n-1})$ value that best matches the periodic trend (Figure 1). In contrast, the $E_p(d^n)$ data point for M = Fe is in better agreement with the best fit than the $E_p(sd^{n-1})$ value, although the latter value is within 2 standard deviations of the line. Overall, this suggests that the bonding character for $M^+{=}CH_2$ bonds involves substantial 4s character. Conversely, the slope of the line in Figure 1 is not unity, which could mean that s–d hybridization may be important in the bonding.

On the basis of the deviation of $D°(FeCH_2^+)$ from the line, a comparison of the bonding in this molecule to neighboring species would be a particularly interesting topic for detailed theoretical characterization. Theoretical studies of $CuCH_2^+$ should also be fruitful since Figure 1 suggests this species could have a covalent M–C double bond, but a comparable bond strength can conceivably arise from a dative interaction where $CH_2(^1A_1)$ donates a pair of electrons into the empty 4s orbital of ground-state $Cu^+(3d^{10})$. Indeed, very recent results of Planelles et al.[17] conclude that the ground state of $CuCH_2^+$ has the latter electronic structure although a $Cu{=}CH_2^+$ species (correlating to excited $Cu^+(^3D,4s^13d^9) + CH_2(^3B_1)$) was not explicitly considered.

Acknowledgment. This work was supported by the National Science Foundation.

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Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

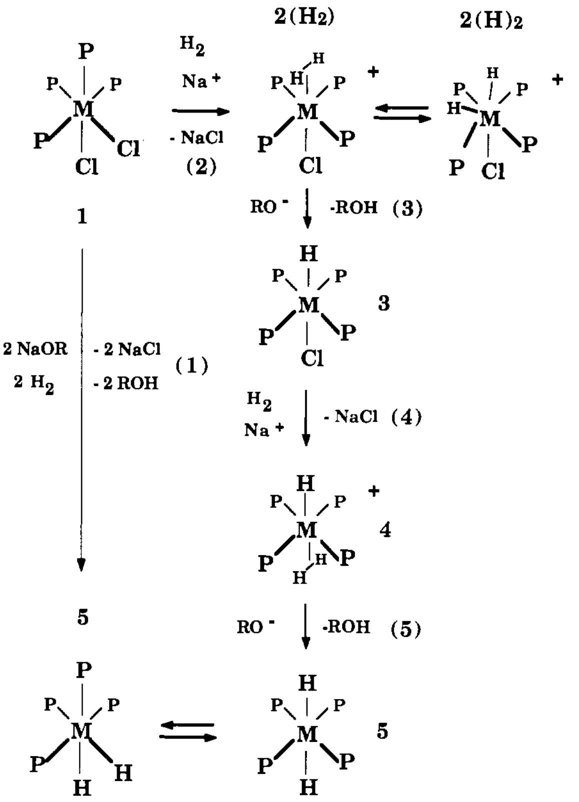
P. B. Armentrout*[,19]
L. S. Sunderlin
Ellen R. Fisher

Received September 6, 1989

From *cis*-Dichloride Complexes to Dihydride Complexes of the Iron Group Metals via Two Successive η^2-Dihydrogen Intermediates

The properties of the iron group hydride complexes of the type $[M(H_2)(H)L_2]^+$ (M = Fe, Ru, Os; L = di(tertiary phosphine)[1]) are being studied to understand the bonding and reactivity of the unusual η^2-dihydrogen ligand.[2] There is also interest in the use of the neutral complexes $MXHL_2$ (X = H,[3] alkyl[4]) for the activation of C–H bonds. We describe here how the heterolytic cleavage of dihydrogen provides a convenient route to the complexes of $MH_2(PR_2CH_2CH_2PR_2)_2$ (R = Et, M = Fe, Os; R = Ph, M = Ru, Os) as well as MH_2(*rac*-tetraphos-1) (M = Ru, Os), some of which are quite difficult to prepare by using standard hydride reagents, $LiAlH_4$ or $NaBH_4$. The conditions for the reactions are surprisingly mild (1 atm, 20 °C), especially for the d^6 Os complexes. The preparative methods developed from the following observations: (a) *cis*-β-$OsCl_2$(*meso*-tetraphos-1) is converted directly to $[Os(H_2)(H)$(*meso*-tetraphos-1)$]BPh_4$ when it is treated with $NaBPh_4$ in THF under 1 atm H_2;[1d] (b) $[Fe(H_2)(H)L_2]^+$ complexes can be deprotonated to give dihydrides (eq 5, Scheme I);[1a,5] (c) coordinated H_2 is generally considered to be more acidic than a hydride ligand in the same molecule.[2a,b] This is the first example of two successive heterolytic cleavages

Scheme I[a]



[a] The substituents on the phosphine ligands have been left out for clarity. The stereochemistries of 2 are tentative.

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