orbitals is also consistent with the strong π-accepting character of PF_3. PRDDO calculations on the model complex $Cr(NH_3)_5(PF_3)$ yield Cr d-orbital populations of 1.74 e for d_{xz} and d_{yz} and 1.98 e for d_{xy}. The enhanced depopulation of the d_π orbitals in this complex relative to $Cr(NH_3)_5(PH_3)$ demonstrates the greater π-accepting ability of PF_3 relative to PH_3 even without d orbitals on phosphorus. There are several reasons for the enhanced π-accepting ability via σ^* orbitals of PF_3 compared to PH_3 and PH_3 relative to NH_3. First, highly polar bonds, such as those between phosphorus and fluorine, characteristically have low-lying σ^* orbitals and are thus better π acceptors. Similarly, the P–H σ^* orbitals in PH_3 lie at lower energies than those of NH_3.[17] Second, because the σ P–F bond is highly polar toward F, the σ^* orbital must necessarily be highly polar toward P, therefore increasing the σ^*–metal d_π overlap. The second argument also holds to a lesser extent for P–H as compared to N–H bonds: e.g., the N–H σ^* orbital will be polar toward H and therefore not overlap well with the metal. Finally, the phosphine σ^* orbitals are composed of 3s and 3p orbitals, which overlap more effectively with metal 3d orbitals than the 2s and 2p orbitals utilized by amines. Of course, a quantitative calculation of the π-accepting ability of ligands such as PF_3 will probably require d orbitals, but our results show that *d orbitals on phosphorus are not necessary for a qualitative understanding of π back-bonding effects in these systems.*

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(17) When a polarized double-ζ basis set is used, the eigenvalues and symmetries of the three LUMO's of free PH_3 are 0.177 au(e) and 0.250 au(a). For NH_3, the corresponding values are 0.236 au(e) and 0.357 au(a).

Bond Energy–Bond Order Relations in Transition-Metal Bonds: Vanadium

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One of the strengths of organic chemistry has been the extensive tabulation and correlation of bond strengths, bond lengths, and bond orders. This enables the prediction of the stability of unknown species and the estimation of the thermochemistry of postulated reaction mechanisms. Presently, transition-metal chemistry does not enjoy a similar power. While bond lengths are often known and bond orders can be estimated, bond strengths, particularly of individual bonds, are virtually unknown. Consequently, the energetics of even a simple series of single, double, and triple bonds between a metal and a ligand remain undocumented. In this paper, we present the first such results for the bond energies of vanadium ions to hydrogen, oxygen, and a number of carbon ligands.

The technique employed to determine bond energies is guided ion beam mass spectrometry. In this method, a mass- and energy-selected ion beam, here V^+, is reacted with a neutral gas. The interaction occurs inside an octopole ion trap[1] which "guides" the ion beam and product ions into the analyzer and detector. The trap eliminates many of the experimental difficulties common to conventional ion beam experiments and dramatically increases the sensitivity. The data are analyzed to yield reaction cross sections as a function of kinetic energy. Details of the technique and methods of analysis can be found elsewhere.[2,3] In this study, the vanadium ions are produced by surface ionization of $VOCl_3$ (Puratronic, 99.995% pure, used as received except for multiple freeze–pump–thaw cycles) on a resistively heated rhenium filament. At the filament temperature used, ~2200 K, the V^+ ions are calculated to be primarily in the ^5D ($(3d)^4$) ground state, >81%, and the first excited state, ^5F ($(4s)^1(3d)^3$), <19%.[4] The presence of the ^5F state is estimated to influence the bond energies cited here by no more than 0.06 eV (1.5 kcal/mol).[5]

Table I. Vanadium Ion–Ligand Bond Energies Derived from Reaction 1 and the Carbon Bond Used for Comparison in Figure 1

			correlation for Figure 1	
A	$D°(V^+–A)$, kcal/mol[a]	AB	$H_nC–A$	$D°(H_nC–A)$, kcal/mol[b]
H	50.0 (2)[c]	H_2	$CH_3–H$	104
C	88 (5)	CO	C–C	145
CH	115 (5)	C_2H_6	HC–CH	230
CH_2	80 (8)	C_2H_4	$H_2C–CH_2$	173
CH_3	50.5 (3)	C_2H_6	$H_3C–CH_3$	90
O	131 (5)[d]	CO	C–O	257
C_2	140 (12)	C_2H_2		
C_2H	109 (12)	C_2H_2, C_2H_4		
C_2H_2	>42	C_2H_4		
C_2H_3	75 (12)	C_2H_4		
C_2H_4	>33	C_2H_6		

[a] All values from this work except as noted. Uncertainties in parentheses. [b] Wagman, D. D. et al. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. [c] Elkind, J. L.; Aristov, N.; Ervin, K. M.; Armentrout, P. B., unpublished work. [d] This value agrees with that derived from appearance potential measurements on $VOCl_3$, 129 ± 5 kcal/mol (Flesch, G. D.; Svec, H. J. *Inorg. Chem.* **1975**, *14*, 1817) as well as unpublished studies of the reactions of V^+ and VO^+ with other oxygen-containing species.

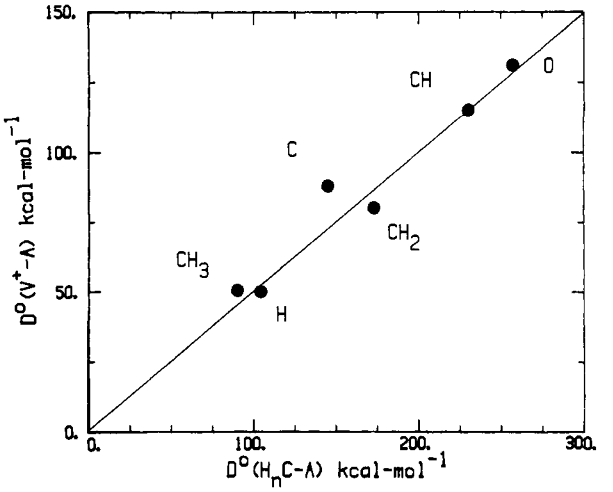

Figure 1. Bond dissociation energies from Table I for V^+–A vs. H_nC–A where A is the group indicated. The line is the least-squares best fit to the data.

Bond dissociation energies (BDEs) are derived from the cross-section data by measuring the endothermicity, E_0, of reaction 1, which is taken to equal the difference in energy of the bond

$$V^+ + AB \rightarrow VA^+ + B \qquad (1)$$

broken, $D°(AB)$, which is generally known, and the bond formed, $D°(V^+–A)$, the quantity of interest. Full details of the reactions of V^+ with H_2, CO, and the C_2 hydrocarbons and the analysis of these results will be published elsewhere.[6] Table I lists these

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(1) Teloy, E.; Gerlich, D. *Chem. Phys.* **1974**, *4*, 417.

(2) Ervin, K. M.; Aristov, N.; Loh, S. K.; Armentrout, P. B. *J. Phys. Chem.* **1983**, *87*, 3593. Ervin, K. M.; Armentrout, P. B., *J. Chem. Phys.*, submitted for publication.

(3) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

(4) Moore, C. E. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, *34*.

(5) This is 19% of the excitation energy of the ^5F state, 0.32 eV.[4]

(6) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.*, submitted for publication.

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reactions and the derived bond strengths. To get a feeling for the trends in these bond energies, a comparison with analogous bonds to carbon (Table I) is shown in Figure 1. The fact that the points generally lie along a line demonstrates the intuitively reasonable result that bond order–bond strength correlations hold for metal–ligand bonds.[7] It is interesting to note that the slope of the line in Figure 1 calculated by using linear regression analysis is 0.50. This may be a reflection of the difference in the ability of the two species to share electrons. Both the electronegativity (V = 1.5; C = 2.5)[8] and the ionization potential (V = 6.74 eV; C = 11.26 eV)[4] of vanadium are about one-half (0.6) that of carbon.

The points in Figure 1 may be seen to fall into three separate groups corresponding to single, double, and triple bonds. Quite naturally, both VH^+ and VCH_3^+ appear to have single bonds. Therefore, they are expected to have quartet ground states since only one of the four V^+ electrons is involved in bonding.[9] The fact that these ions have nearly the same bond energy differs from results for other transition-metal ions.[10,11] There, the metal–methyl ion BDE is found to be 5–10 kcal/mol higher than that of the metal–hydride ion BDE. It has been argued, however, that these BDEs should, in fact, be comparable[11] leading to the prediction that the *neutral* metal–hydride BDEs should exceed those of the metal–methyl by ~10 kcal/mol. This has long been the common wisdom in organometallic chemistry. Several reasons may explain the discrepancy between our results and the earlier beam work. Metals to the left side of the periodic table may have weaker methyl bond energies than those to the right, where much of the previous data is located. Alternatively, the improved sensitivity of the present apparatus may allow a more accurate interpretation of the threshold behavior of the beam results. Since the beam technique is still in its infancy, this latter possibility will become clearer with time.

In the double-bond region of Figure 1 are found the carbon atom and methylene ligands. Both species have triplet ground states, ^3P and $^3B_1$, respectively, which easily permit double-bond formation with the metal σ and 3d π orbitals of V^+. Thus, the ground states of both VC^+ and VCH_2^+ should be low-spin triplets. If one of the unpaired electrons occupies the other metal 3d π orbital, it can donate into the empty 2p on the carbon atom. Since the methylene ligand has no such empty orbital, this may explain why the VC^+ bond is stronger than the VCH_2^+ bond.

The triple-bond region finds the methylidyne ($^2\Pi$) and oxide (^3P) ligands. The VCH^+ species seems an obvious candidate for a triple bond and would be expected to have a doublet ground state by virtue of a lone unpaired electron on the metal. It is not so apparent why VO^+ should have a triple bond since an oxygen atom has only two unpaired electrons. By analogy with the bonding in CO, a triple bond can be formed if the O atom donates four electrons and the V^+ donates two. This leaves two nonbonding electrons on V^+. In the isoelectronic TiO, this leads to a $^3\Delta$ ground state; however, there are also low-lying $^1\Delta$ and $^1\Sigma^+$ states.[12] This bonding scheme seems resonable since it predicts the experimentally observed relative BDEs of the first-row transition-metal-oxide ions. Specifically, besides VO^+, ScO^+ and TiO^+[13] have strong bonds since the metal ions have at least two electrons for binding and an empty (accepting) 3d orbital. The metals Cr^+ through Ni^+ do not meet these criteria and thus their oxides have weaker bonds.[14]

Although speculative, the correlation of Figure 1 may be further extended to the $VC_2H_n^+$ bond energies. For example, to place $D°(V^+–C_2H_3)$ in Figure 1, it must be considered a double bond. This may indicate significant interaction between V^+ and the π cloud of the vinyl ligand. Similarly, VC_2H^+ and VC_2^+ appear to have triple bonds, again indicating significant π interactions.

The vanadium ion is nearly an ideal case for the correlation noted here. A $(3d)^4$ ground-state configuration allows formation of single, double, and triple bonds while also being capable of accepting electron pairs datively. Other transition metals probably obey similar correlations. Comparisons of $D°(MCH_3^+)$ to $D°(MCH_2^+)$ for M = Cr, Mn, Fe, Co, and Ni[10] tend to indicate that the carbene species are doubly bonded.[15] Recent calculations on $CrCH_2^+$ confirm this.[16] Data on $D°(MCH^+)$ are not available for other metals. The utility of these correlations is striking. Not only can reasonable bond strengths be predicted from educated guesses of the bond order, but detailed bonding interactions of transition-metal species can also be elucidated. Work is under way to test these concepts further with other metal ions, neutral metals, and ligated species.

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(7) While simple, such a result is not necessarily obvious. For example, Fox et al. (Fox; Ray; Rubesin; Schaefer *J. Chem. Phys.* **1980**, *73*, 3246) have calculated that $AlCH_3$, $AlCH_2$, and AlCH all have essentially single bonds. The multiply bonded states lie higher in energy. Bond energies are calculated to be 68, 77, and 88 kcal/mol, respectively. Metal–metal bonds in transition-metal dimers also do not seem to show bond energy–bond order correlations.

(8) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

(9) This is consistent with the $^4\Phi$ ground state calculated for the isoelectronic molecule, TiH [Scott, P. R.; Richards, W. G. *J. Phys. B* **1974**, *7*, 500, L347].

(10) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

(11) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L., submitted for publication.

(12) Scott, P. R.; Richards, W. G. *Mol. Spectrosc.* (*Chem. Soc., London*) **1976**, *4*, 70.

(13) Murad, E. J. *Geophys. Res.* **1978**, *83*, 5525.

(14) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.

(15) For these five metals, the average value for the ratio of the methylene BDE to the methyl BDE is 1.53 ± 0.22 while for vanadium, the value is 1.57 ± 0.18.

(16) Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1984**, *88*, 1485.

Nineteen-Electron Species as Intermediates in the Photochemical Disproportionation of $(\eta^5\text{-}CH_3C_5H_4)_2Mo_2(CO)_6$

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In a recent paper, we showed that the photochemical disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex ($Cp = \eta^5\text{-}CH_3C_5H_4$) (eq 1) proceed via a chain mechanism.[1,2] Scheme I shows the proposed mechanism. Our previous paper[1a] demonstrated the requirement that two phosphines coordinate to the photogenerated molybdenum radical before electron transfer occurred, and, therefore, we postulated the formation of a 19-electron intermediate. However, an alternative mechanism involving a more orthodox 17-electron species can be invoked (Scheme II). The mechanism in Scheme II differs from ours in that the attack of L on $CpMo(CO)_2L$ leads to substitution of L for CO rather than formation of the 19-electron adduct $CpMo(CO)_2L_2$. In this communication, we present evidence which shows that the pathway involving the 19-electron species is indeed the one operating in the disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex.

$$Cp_2Mo_2(CO)_6 + 2L \xrightarrow{h\nu} Cp_2Mo(CO)_3^- + CpMo(CO)_2L_2 + CO \quad (1)$$

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(1) (a) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem .Soc.* **1983**, *105*, 6032–6037. (b) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 527.

(2) The methylcyclopentadienyl complexes were used in our previous and present studies because they are more soluble in the solvents employed.