

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 comparable¹¹ 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 reasonable 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 $D^0(V^+-C_2H_3)$ 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 obeying electron pairs datively. Other transition metals probably obey similar correlations. Comparisons of $D^0(MCH_3^+)$ to $D^0(MCH_2^+)$ 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 $D^0(MCH^+)$ 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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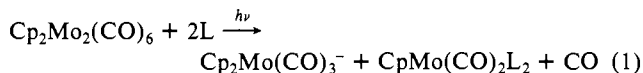
Nineteen-Electron Species as Intermediates in the Photochemical Disproportionation of $(\eta^5-C_5H_5)_2Mo_2(CO)_6$

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In a recent paper, we showed that the photochemical disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex ($Cp = \eta^5-C_5H_5$) (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 in-



volving 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.

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

(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.

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