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 $D^\circ(V^+-C_2H_3)$ 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 $D^\circ(MCH_3^+)$ to $D^\circ(MCH_2^+)$ 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 $D^\circ(MCH^+)$ 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.

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(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].

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(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.

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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 = η^5-$CH_3C_5H_4$) (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.

Scheme I

$$\mathrm{Cp_2Mo_2(CO)_6} \xrightarrow{h\nu} \mathrm{2}\underset{17}{\mathrm{CpMo(CO)_3}}$$

$$\underset{\mathbf{17}}{\mathrm{CpMo(CO)_3}} + \mathrm{L} \rightarrow \underset{17}{\mathrm{CpMo(CO)_2L}} + \mathrm{CO}$$

$$\underset{17}{\mathrm{CpMo(CO)_2L}} + \mathrm{L} \rightarrow \underset{19}{\mathrm{CpMo(CO)_2L_2}}$$

$$\underset{19}{\mathrm{CpMo(CO)_2L_2}} + \mathrm{Cp_2Mo_2(CO)_6} \rightarrow \underset{18}{\mathrm{CpMo(CO)_2L_2^+}} + \mathrm{Cp_2Mo_2(CO)_6^-}$$

$$\mathrm{Cp_2Mo_2(CO)_6^-} \rightarrow \underset{18}{\mathrm{CpMo(CO)_3^-}} + \underset{17}{\mathrm{CpMo(CO)_3}}$$

Scheme II

$$\mathrm{Cp_2Mo_2(CO)_6} \xrightarrow{h\nu} \mathrm{2}\underset{17}{\mathrm{CpMo(CO)_3}}$$

$$\underset{17}{\mathrm{CpMo(CO)_3}} + \mathrm{L} \rightarrow \underset{17}{\mathrm{CpMo(CO)_2L}} + \mathrm{CO}$$

$$\underset{17}{\mathrm{CpMo(CO)_2L}} + \mathrm{L} \rightarrow \underset{17}{\mathrm{CpMo(CO)L_2}} + \mathrm{CO}$$

$$\underset{17}{\mathrm{CpMo(CO)L_2}} + \mathrm{Cp_2Mo_2(CO)_6} \rightarrow \underset{16}{\mathrm{CpMo(CO)L_2^+}} + \mathrm{Cp_2Mo_2(CO)_6^-}$$

$$\mathrm{CpMo(CO)L_2^+} + \mathrm{CO} \rightarrow \underset{18}{\mathrm{CpMo(CO)_2L_2^+}}$$

$$\mathrm{Cp_2Mo_2(CO)_6^-} \rightarrow \underset{18}{\mathrm{CpMo(CO)_3^-}} + \underset{17}{\mathrm{CpMo(CO)_3}}$$

According to Scheme II, after the 17-electron $\mathrm{CpMo(CO)L_2}$ complex transfers an electron to $\mathrm{Cp_2Mo_2(CO)_6}$, the resulting $\mathrm{CpMo(CO)L_2^+}$ intermediate acquires a CO ligand to form the product $\mathrm{CpMo(CO)_2L_2^+}$. In the presence of L, one might also expect some $\mathrm{CpMo(CO)L_3^+}$ complex to form (eq 2). To test for

$$\mathrm{CpMo(CO)L_2^+} + \mathrm{L} \rightarrow \mathrm{CpMo(CO)L_3^+} \qquad (2)$$

the formation of $\mathrm{CpMo(CO)L_3^+}$, we irradiated (λ >405 nm) $\mathrm{Cp_2Mo_2(CO)_6}$ (1.5×10^{-2} M) in benzene with the tridentate ligand triphos (5×10^{-2} M) (triphos = bis(2-(diphenylphosphino)ethyl)phenylphosphine).[3] If the reaction follows the pathway in Scheme II, the expected cationic product would be $\mathrm{CpMo(CO)(triphos\text{-}}P,P',P''\mathrm{)^+}$; the pathway in Scheme I would yield the bidentate triphos complex $\mathrm{CpMo(CO)_2(triphos\text{-}}P,P'\mathrm{)^+}$. (Triphos was selected as the ligand because the reaction of $\mathrm{CpMo(CO)L_2^+}$ with L will be a ring closure step. Such steps are generally fast[4] and should be competitive with the reaction of $\mathrm{CpMo(CO)L_2^+}$ with CO.) As in the disproportionation reactions of $\mathrm{Cp_2Mo_2(CO)_6}$ with bidentate phosphines, the photoreaction with triphos was very efficient: the quantum yield for the disappearance of $\mathrm{Cp_2Mo_2(CO)_6}$ is 80 ± 20 ($I = 9 \times 10^{-8}$ einstein/min; λ = 405 nm). The only products were $\mathrm{CpMo(CO)_3^-}$ and $\mathrm{CpMo(CO)_2(triphos\text{-}}P,P'\mathrm{)^+}$.[5] The exclusive formation of $\mathrm{CpMo(CO)_2(triphos\text{-}}P,P'\mathrm{)^+}$ is explained only by the pathway involving 19-electron intermediates.

Complexes of the type $\mathrm{CpMo(CO)L_3^+}$ are rare, presumably because of steric crowding between the three L's. Thus, it might be argued that the $\mathrm{CpM(CO)(triphos\text{-}}P,P',P''\mathrm{)^+}$ complex cannot exist. However, we point out that $\mathrm{CpMo(CO)(triphos\text{-}}P,P',P''\mathrm{)^+}$ can by synthesized; irradiation (λ = 366 nm) of a solution of $\mathrm{CpMo(CO)_2(triphos\text{-}}P,P'\mathrm{)^+}$ leads to the formation of $\mathrm{CpMo(CO)(triphos\text{-}}P,P',P''\mathrm{)^+}$.[6] The quantum yield of reaction 3 is 1,

$$\mathrm{CpMo(CO)_2(triphos\text{-}}P,P'\mathrm{)^+} \xrightarrow{366\ \mathrm{nm}} \mathrm{CpMo(CO)(triphos\text{-}}P,P',P''\mathrm{)^+} + \mathrm{CO} \qquad (3)$$

under either 1 atom of CO or 1 atm of argon. When the logical assumption is made that Mo–CO bond dissociation is the primary photoprocess, the unit quantum yield indicates that CO cannot significantly compete with the third phosphorus group for the vacant coordination site in $\mathrm{CpMo(CO)(triphos\text{-}}P,P'\mathrm{)^+}$. This result taken together with the exclusive formation of $\mathrm{CpMo(CO)_2(triphos\text{-}}P,P'\mathrm{)^+}$ is consistent only with Scheme I.

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[3] Photolysis and anaerobic techniques used were the same as those described previously; see ref 1.

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[5] $\mathrm{CpMo(CO)_2(triphos\text{-}}P,P'\mathrm{)^+}$ was identified by its carbonyl region infrared and its ^{31}P NMR spectra: $\nu(\mathrm{C{\equiv}O})$ 1966 and 1901 cm^{-1} as compared with $\mathrm{CpMo(CO)_2(diphos\text{-}}P,P'\mathrm{)^+}$ (diphos = 1,2-bis(diphenylphosphino)ethane) $\nu(\mathrm{C{\equiv}O})$ 1970 and 1904 cm^{-1}; $\delta(^{31}\mathrm{P})$ 69.9 and 84.6 (coordinated central and terminal phosphorus atoms) and −10.8 ("dangling" terminal phosphorus atom) (1:1:1). $\delta(^{31}\mathrm{P})$ values for free triphos are −11.9 (terminal phosphorus atom) and −15.7 (central phosphorus atom). Chemical shifts are relative to 85% $\mathrm{H_3PO_4}$; positive shifts are downfield. These chemical shifts are typical of chelated phosphorus atoms in five-membered metallocycles, though somewhat more positive than those with more electron-rich metal centers. See: Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: Berlin, Heidelberg, 1979, pp 133–138.

[6] $\mathrm{CpMo(CO)(triphos\text{-}}P,P',P''\mathrm{)^+}$ was identified by its carbonyl region infrared spectrum, $\nu(\mathrm{C{\equiv}O})$ 1858 cm^{-1}, as compared with reasonably similar known complexes such as $\mathrm{CpMo(CO)(CH_3CN)(PPh_3)_2^+}$, $\nu(\mathrm{C{\equiv}O})$ 1860 cm^{-1}.[7] The ^{31}P NMR spectrum of the complex has resonances at δ 90.28 (terminal phosphorus atoms) and 108.0 (central phosphorus atom) (2:1).

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Metathesis of Acetylenes by Molybdenum(VI) Alkylidyne Complexes[1]

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The first reported homogeneous system for the metathesis of acetylenes involved $\mathrm{Mo(CO)_6}$ as the catalyst precursor.[2] This system has been improved and studied in some detail.[3] More recently a relatively active catalyst based on $\mathrm{MoO_2(acac)_2}$ has been reported.[4] However, in no case has the active catalyst been detected. On the basis of the fact that tungsten(VI) alkyidyne complexes[5] will rapidly metathesize dialkylacetylenes,[6] we postulated that molybdenum-based systems also involve molybdenum (VI) alkylidyne complexes as the active species. We set out to test this theory.

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