Scheme I

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

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

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

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

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

Scheme II

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

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

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

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

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

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

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.

(4) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Chemistry"; Wiley: New York, 1958; p 223.

(5) $\mathrm{CpMo(CO)_2(triphos}\text{-}P,P'\mathrm{)^+}$ was identified by its carbonyl region infrared and its ^{31}P NMR spectra: ν(C≡O) 1966 and 1901 cm^{-1} as compared with $\mathrm{CpMo(CO)_2(diphos}\text{-}P,P'\mathrm{)^+}$ (diphos = 1,2-bis(diphenylphosphino)ethane) ν(C≡O) 1970 and 1904 cm^{-1}; δ(^{31}P) 69.9 and 84.6 (coordinated central and terminal phosphorus atoms) and −10.8 ("dangling" terminal phosphorus atom) (1:1:1). δ(^{31}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, ν(C≡O) 1858 cm^{-1}, as compared with reasonably similar known complexes such as $\mathrm{CpMo(CO)(CH_3CN)(PPh_3)_2^+}$, ν(C≡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).

(7) Treichel, P. M.; Barnett, K. W.; Shubkin, R. L. *J. Organomet. Chem.* **1967**, *7*, 449–459.

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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(1) Multiple Metal–Carbon Bonds. 34. For part 33, see: Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476.

(2) Mortreux, A.; Delgrange, J. C.; Blanchard, M.; Lubochinsky, B. *J. Mol. Catal.* **1977**, *2*, 73.

(3) Devarajan, S.; Walton, O. R. M.; Leigh, G. J. *J. Ogranomet. Chem.* **1979**, *181*, 99.

(4) Bencheick, A.; Petit, M.; Mortreux, A.; Petit, F. *J. Mol. Catal.* **1982**, *15*, 93.

(5) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645.

0002-7863/84/1506-4067$01.50/0

One of the most active types of tungsten alkylidyne complexes for the metathesis of dialkylacetylenes is $W(CR)(OCMe_3)_3$.[6] The analogous molybdenum complex can be prepared in a series of reactions virtually identical with those used to prepare $W(CCMe_3)(OCMe_3)_3$; i.e., $Mo(CCMe_3)(CH_2CMe_3)_3$[7] is treated with 3 equiv of HCl in the presence of 1,2-dimethoxyethane (dme) to give blue *mer*-$Mo(CCMe_3)(dme)Cl_3$,[8a] which is then treated with $LiOCMe_3$ in ether to give white, pentane-soluble, air- and water-sensitive, sublimable $Mo(CCMe_3)(OCMe_3)_3$ (**1**) in high yield.[8b] $Mo(CCMe_3)(O\text{-}i\text{-}Pr)_3$ (**2**) and $Mo(CCMe_3)(OCH_2CMe_3)_3$ (**3**) were prepared similarly. To our surprise *pure* **1** does *not* react with 3-heptyne,[9] 2-butyne, or diphenylacetylene, while **2** and **3** polymerize 3-heptyne. Some initial and catalytic metathesis products of 3-heptyne are observed, but eventually are consumed, presumably to give polymers. The mechanism of the polymerization reaction is unknown. One possibility is that an intermediate molybdenacyclobutadiene complex readily reacts with more acetylene to give a "molybdenabenzene" complex and that subsequent relatively rapid "ring expansions" ultimately yield polymer. These results suggest that bulky alkoxides are required to prevent polymerization and that Mo is not electrophilic enough in $Mo(CCMe_3)(OCMe_3)_3$ compared to W in $W(CCMe_3)(OCMe_3)_3$ to attract the acetylene through the bulky ligand system. Therefore, we turned to more electron-withdrawing fluoro-*tert*-butoxide and 2,6-disubstituted phenoxide ligand systems.

$Mo(CCMe_3)(dme)Cl_3$ reacts with 3 equiv of $MOCMe_x(CF_3)_{3-x}$ (M = Li or K) in ether or dichloromethane to give white $Mo(CCMe_3)[OCMe_2(CF_3)]_3$ (**4**), orange-red *mer*-$Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme)$ (**5**), or purple *mer*-$Mo(CCMe_3)[OC(CF_3)_3]_3(dme)$ (**6**).[10] Only **5** loses dme upon sublimation in vacuo (60 °C, 0.1 μm) to give yellow $Mo(CCMe_3)[OCMe(CF_3)_2]_3$ (**7**);[11] **6** sublimes with dme intact. *All* of these complexes react readily with dialkylacetylenes to give the expected *tert*-butyl-containing cleavage product(s) and the expected new alkyidyne complex(es) in high yield and will metathesize 3-heptyne.[12] No significant amount of acetylene polymer is formed in any case, and we were not able to detect intermediate molybdenacyclobutadiene complexes by ^1H NMR at 25 °C in any case. The new alkylidyne complexes are analogous in every way to the parent neopentylidyne complexes. Two exemplary reactions are shown in eq 1 and 2.

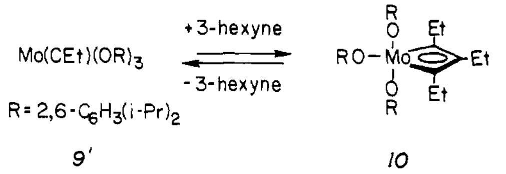
$$Mo(CCMe_3)[OCMe_2(CF_3)]_3 \xrightarrow[-Me_3CC\equiv CPr]{\text{4-octyne}} Mo(CPr)[OCMe_2(CF_3)]_3 \quad (1)$$

$$Mo(CCMe_3)[OCMe(CF_3)_2]_3(dme) \xrightarrow[-Me_3CC\equiv CMe]{\text{+2-butyne}} Mo(CMe)[OMe(CF_3)_2]_3(dme) \quad (2)$$

$Mo(CCMe_3)(dme)Cl_3$ reacts with 3 equiv of $LiOCH(CF_3)_3$ in dichloromethane to give *mer*-$Mo(CCMe_3)[OCH(CF_3)_2]_3(dme)$ (**8**).[13] Like **6**, **8** sublimes (60 °C, 0.1 μm) with dme intact. **8** also reacts readily with dialkylacetylenes to give new alkylidyne complexes (e.g., eq 3) Again we see no evidence for molybdenacyclobutadiene intermediates or formation of polymeric acetylenes.

$$Mo(CCMe_3)[OCH(CF_3)_2]_3(dme) \xrightarrow[-Me_3CC\equiv CEt]{\text{+3-hexyne}} Mo(CEt)[OCH(CF_3)_2]_3(dme) \quad (3)$$

$Mo(CCMe_3)(dme)Cl_3$ reacts with 3 equiv of $LiO(2,6\text{-}C_6H_3\text{-}(i\text{-}Pr)_2$ in ether to give $Mo(CCMe_3)[O(2,6\text{-}C_6H_3(i\text{-}Pr)_2)]_3$ (**9**) in high yield.[14] It too reacts rapidly with 3-hexyne or 4-octyne to give the expected *tert*-butylacetylene and will readily metathesize 3-heptyne. The interesting feature is that in ether **9** reacts with an excess of 3-hexyne to give red crystals of what appears to be a molybdenacyclobutadiene complex (**10**). When **10** is redissolved in C_6D_6, a 1:1 mixture of $Mo(CEt)[O(2,6\text{-}C_6H_3(i\text{-}Pr)_2)]_3$ (**9′**) and 3-hexyne is formed. If more 3-hexyne is added to **9′**, a mixture of **10** and **9′** is observed by ^1H and ^{13}C NMR.[15] These data suggest the equilibrium shown in eq 4. We expect **10** to be



(4)

roughly a trigonal bipyramidal complex with the MoC_3 ring in the equatorial plane, as has recently been shown to be the case for the analogous tungsten complex.[16] The ready loss of 3-hexyne from **10** can be interpreted in terms of a generally lower electrophilicity of Mo compared to W, as we postulated initially above.

We feel that the principles of acetylene metathesis are now well in hand and that d^0 alkylidyne complexes are likely to be the active catalysts in most, if not all, systems. How a molybdenum(VI) alkylidyne complex is formed from $Mo(CO)_6$[2,3] is hardly obvious. However, it is worth noting in this context that ethylidyne cluster complexes containing Mo(IV) *have* been isolated from the reaction of acetic acid with $Mo(CO)_6$;[17] disproportionation or oxidation in the presence of the appropriate potential ligand (e.g., phenol) could generate molybdenum(VI) alkylidyne complexes. Finally, it is interesting to note that phenols[2-4] and fluoroalcohols[2] are required "co-catalysts" in the $Mo(CO)_6$-based systems, further evidence that molybdenum(VI) alkylidyne complexes closely related to those we have reported here are the active catalysts.

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(6) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (b) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75.

(7) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. $Mo(CCMe_3)(CH_2CMe_3)_3$ is now prepared in 35 ± 5% yield reproducibly. MoO_2Cl_2 (10 g in 100 mL of THF) was added slowly to 6 equiv of Me_3CCH_2MgCl (1 M in ether) at −78 °C. After addition was complete, the mixture was warmed to 25 °C and filtered. All solvents were removed in vacuo and the residue was extracted with pentane. The pentane was removed in vacuo and the pale yellow product sublimed at 70 °C and 0.001 μm onto a 0 °C probe.

(8) (a) A solution of HCl in ether (1.65 M, 30 mL, 49.5 mmol) was slowly added to an ether solution of $Mo(CCMe_3)(CH_2CMe_3)_3$ (6.00 g, 15.9 mmol) and 1,2-dimethoxyethane (4.9 mL, 47.1 mmol). The mixture was warmed to 25 °C and stirred for 1 h to give a blue solution. The solution was filtered and concentrated in vacuo to give a total of 4.20 g (73%) of blue *mer*-$Mo(CCMe_3)Cl_3(dme)$ in three crops. Anal. Calcd for $MoC_9H_{19}O_2Cl_3$: C, 29.90; H, 5.30. Found: C, 29.69; H, 5.18 $\delta(CCMe_3)$ 341.3 in C_6D_6. (b) Anal. Calcd for $MoC_{17}H_{36}O_3$: C, 53.12; H, 9.44. Found: C, 52.72; H, 9.30. $\delta(CCMe_3)$ 296.1 in C_6D_6.

(9) Some samples of **1** will metathesize 3-heptyne slowly, but activity stops after an hour or two, and little if any of the expected *tert*-butyl-containing acetylenes are found. We propose that impurities are the active species.

(10) LiOR in ether for **4**; KOR in ether for **5**; KOR in dichloromethane for **6**. $\delta(CCMe_3)$ 309.7 for **4**, 318.8 for **5**, both in C_6D_6.

(11) Calcd for $MoC_{17}H_{18}O_3F_{18}$: C, 28.83; H, 2.56. Found: C, 28.40; H, 2.61.

(12) The slowest to metathesize 20 equiv of 3-heptyne in ether to equilibrium (**4**) requires ~30 min. The fastest (**6**) requires ≲1 min. ($T \approx 25$ °C in all cases.)

(13) Calcd for $MoC_{18}H_{22}O_5F_{18}$: C, 28.59; H, 2.93. Found: C, 28.25; H, 2.85.

(14) Calcd for $MoC_{41}H_{60}O_3$: C, 70.67; H, 8.68. Found: C, 70.46; H, 8.70. $\delta(CCMe_3)$ 337.2 in C_6D_6.

(15) In a ^{13}C NMR spectrum of a mixture of **10** and **9′** $\delta(CEt)$ for **9′** is 327.9 (cf. 337.2 ppm in **9**) and $\delta(C_\alpha Et)$ in **10** is 259.8 (cf. 244.9 ppm in $W(C_3Et_3)[O(2,6\text{-}C_6H_3(i\text{-}Pr)_2)]_3$[16]). These reaction mixtures are extremely clean.

(16) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics*, in press.

(17) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem.* **1981**, *103*, 5779.