geometrical aspects of the product of a remarkable isocyanide coupling reaction.

Both the structural and molecular orbital symmetry evidence presented herein are consistent with the spectral evidence. Together, they show that it is possible for an acetylene molecule to donate more than two electrons to the metal ion in a monunuclear complex. We emphasize that the acetylenic carbon–carbon bond length is a poor indicator for the number of electrons donated from acetylene to metal, a better indication being metal–carbon distance. Studies of the chemistry of these carbonyl acetylene complexes of molybdenum and tungsten and their oxo acetylene analogues are underway and should give further insight into the effect of the number of electrons donated by the acetylene on the properties and reactivity of the complexes.

References and Notes

(1) J. W. McDonald, J. L. Corbin, and W. E. Newton, *J. Am. Chem. Soc.*, **97**, 1970 (1975).
(2) J. W. McDonald, W. E. Newton, C. T. C. Creedy, and J. L. Corbin, *J. Organomet. Chem.*, **92**, C25 (1975).
(3) L. Ricard, C. Martin, and R. Weiss, paper presented at the XVII International Conference on Coordination Chemistry, Hamburg, 1976.
(4) G. J.-J. Chen, R. O. Yelton, and J. W. McDonald, *Inorg. Chim. Acta*, **22**, 249 (1977).
(5) H. G. Alt, *J. Organomet. Chem.*, **127**, 349 (1977).
(6) Crystal data: $C_{13}H_{22}N_2OS_4W$, M = 533.8; monoclinic; a = 12.052 (2) Å, b = 15.311 (3) Å, c = 10.366 (2) Å, β = 90.11 (1) °; V = 1912.8 Å³; Z = 4; ρ_{calcd} = 1.853, ρ_{obsd} = 1.84; space group $P2_1/n$; R = $\Sigma||F_o|| - ||F_c||/\Sigma|F_o|$ for $F_o^2 > 3\sigma(F_o^2)$.
(7) L. Ricard, J. Estiene, and R. Weiss, *Inorg. Chem.*, **12**, 2183 (1973).
(8) P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 241 (1976).
(9) J. A. K. Howard, R. F. D. Stansfield, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 246 (1976).
(10) W. E. Newton, J. L. Corbin, J. W. McDonald, L. Ricard, and R. Weiss, unpublished work.
(11) N. G. Bokiy, Yu. V. Gatilov, Yu. T. Struchkov, and N. A. Ustynyuk, *J. Organomet. Chem.*, **54**, 213 (1973).
(12) This difference could be due in part to the variations in metal, acetylenic substituents, and ligands on the compounds being compared. However the significance of the bond length difference is substantiated by a comparison of the Mo–acetylenic bond distances in $XMo(C_5H_5)(C_6F_5)(CF_3C_2CF_3)$ as found in ref 9 where the average Mo–C bond is ~0.06 Å longer when X = O than when X = CO.
(13) In C_s symmetry, the 5σ and 2π orbitals of CO and the 1π_g orbitals of C_2H_2 have the same representation. Orbital are labeled according to R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).
(14) The carbon–oxygen stretching modes are observed at 1930 and 1835 cm⁻¹ in $W(CO)_2(PPh_3)(S_2CNEt_2)_2$ and at 1950 and 1870 cm⁻¹ in *cis*-Mo$(CO)_2(S_2CNEt_2)_2$. These modes in this latter complex are lowered by only 5 and 10 cm⁻¹, respectively, on the binding of triphenylphosphine.⁴
(15) C. T. Lam, P. W. R. Corfield, and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 617 (1977).

Louis Ricard, Raymond Weiss*

Laboratoire de Cristallochimie associé au C.N.R.S.
Institut Le Bel Université Louis Pasteur
67070 Strasbourg-Cédex, France

W. E. Newton, Grace J.-J. Chen, John W. McDonald*

Contribution No. 606
Charles F. Kettering Research Laboratory
Yellow Springs, Ohio 45387
Received September 12, 1977

Reversible Binding of Acetylene by OMo(S₂CNEt₂)₂

Sir:

The reactions of OMo(S₂CNEt₂)₂ (**1**) with diazenes,¹ activated acetylenes,¹,² hydrazoic acid,³ and various oxo transfer reagents⁴,⁵ have been described in recent publications. Because Mo(IV) has been proposed¹,⁶⁻⁸ to constitute the active site of nitrogenase, we have continued to investigate the chemistry of **1** and herein report the binding of unsubstituted acetylene (a known⁹ substrate of nitrogenase) to this complex.
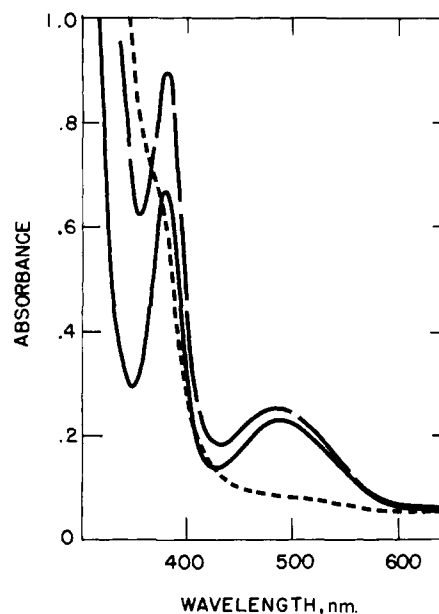

Figure 1. Visible spectral changes for the reaction of OMo(S₂CNEt₂)₂ with C_2H_2 in CH_2Cl_2: before addition of C_2H_2 (—); after addition of C_2H_2 (- - -); after pumping on reaction mixture (- -). Final spectrum is more intense than initial owing to loss of solvent during removal of C_2H_2.

Exposure of nonaqueous (1,2-dichloroethane, CH_2Cl_2, DMF) solutions of **1** to 1 atm of C_2H_2 results in the visible spectral change shown in Figure 1, clearly indicating the formation of a new species, **2**. In contrast, C_2H_4 effects no spectral change under identical conditions. The binding of C_2H_2 is reversible, as evidenced by the return of the spectrum of **1** when the reaction mixture is subjected to pumping. This reversibility has thus far thwarted our attempts to isolate the adduct. However, it has been possible to characterize **2** by spectroscopic means.

The NMR spectra of equilibrium mixtures of **1** and **2** in CD_2Cl_2 have been examined at 100 MHz as a function of the pressure of C_2H_2 (1 atm or less) and the temperature. A resonance centered at about δ 3.9 at ambient temperature is due to the overlapped signals from the methylene protons of both **1** and **2** while the resonance near 1.4 is similarly due to the methyl protons of these compounds. A single resonance at δ 8.73, which is due to coordinated C_2H_2,¹⁰ contrasts markedly with the resonance at 2.04 which arises from the free C_2H_2 in solution. It is noteworthy that the spectrum of the isolable² complex, OMo(S₂CNEt₂)₂(HC≡CCO₂Me), contains a resonance at δ 8.78 due to the single acetylenic proton. As the pressure increases to 1 atm, the ratio of the intensities of the bound acetylenic protons and the methylene protons of S₂CNEt₂ approaches a value of 2:8, which is consistent with **2** being the 1:1 adduct, OMo(S₂CNEt₂)₂(C_2H_2), whose formation is shown in eq 1. When these solutions are cooled to −55 °C, the single resonance at δ 8.73 disappears and two new peaks at 8.74 and 8.81 (Δν = 7 Hz) are found instead. These peaks are particularly well resolved and are of approximately equal intensity.¹² The observed spectra are consistent with a structure in which C_2H_2 is bound cis to the oxo group but inconsistent with coordination of C_2H_2 trans to the oxo group since magnetic equivalence would then result. Furthermore, maximum bonding interactions should occur when C_2H_2 is bound not only in a cis position but in a plane perpendicular to the oxo group. Similar geometries have been found in the structurally characterized adducts of **1** with (NC)₂C=C(CN)₂,¹³ S₂,¹⁴ and ditoluoylacetylene.²

$$OMo(S_2CNEt_2)_2 + C_2H_2 \rightleftharpoons OMo(S_2CNEt_2)_2(C_2H_2) \quad (1)$$
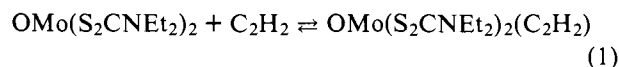
The IR spectrum of a solution of **1** and **2** in CH_2Cl_2 saturated with C_2H_2 is also consistent with eq 1. That spectrum contains bands at 965 ($\nu_{Mo=O}$ of **1**) and 935 cm^{-1} ($\nu_{Mo=O}$ of **2**) in approximately a 1:3 ratio and a band at 1684 cm^{-1} ($\nu_{C\equiv C}$ of bound C_2H_2 in **2**).[10] The latter is 290 cm^{-1} lower than the corresponding stretching frequency of free C_2H_2 (1974 cm^{-1}) and is indicative of significant weakening of the triple bond on coordination. The features of the IR spectrum attributable to **2** may be compared with the corresponding absorptions in the IR spectrum of $OMo(S_2CNEt_2)_2(HC\equiv CCO_2Me)$($\nu_{Mo=O}$ 925 and $\nu_{C\equiv C}$ 1790 cm^{-1}).[2]

Further substantiation of the stoichiometry of the reaction between **1** and C_2H_2 in CH_2Cl_2 was provided by examining the variation in molar absorptivity at 490 nm that accompanies changing the pressure of C_2H_2 over the solution at 25 °C. The relationship between the apparent molar absorptivity (ϵ_{app}), the molar absorptivities of **1** and **2** (ϵ_1 and ϵ_2, respectively), the pressure of C_2H_2, and the equilibrium constant (K) for eq 1 is shown in eq 2. The values of ϵ_{app} were obtained at five different pressures of C_2H_2 (determined by gas chromatography) ranging from 0.04 to 0.30 atm. The plot of ϵ_{app} vs. ($\epsilon_1 - \epsilon_{app})/P_{C_2H_2}$ was linear and yielded $K = 16$ atm^{-1} and $\epsilon_2 = 46$ cm^{-1} M^{-1}.

$$\epsilon_{app} = [(\epsilon_1 - \epsilon_{app})/KP_{C_2H_2}] + \epsilon_2 \qquad (2)$$

Addition of $NaBH_4$ (0.2 mmol) to DMF (4.0 mL) solutions of **2** (0.056 mmol) containing H_2O (1.0 mL) yields ethylene (0.020 mmol), butadiene (0.006 mmol), and H_2 (0.163 mmol) after 4 h at 30 °C.[15] These products are identical with those obtained[16-17] in various ratios for the reduction of C_2H_2 by $NaBH_4$ in aqueous systems using "molybdothiol catalysts", and by these catalysts alone under extremely alkaline conditions.[16] Addition of acids (HCl, CF_3CO_2H) to DMF solutions of **2** yields no detectable ethylene or butadiene. Similar acidification of solutions of the Mo(II) complexes, Mo(CO)-$(C_2H_2)L_2$ ((L = S_2CNEt_2, $S_2P(i-Pr)_2$), gave significant amounts of C_2H_4.[11,18]

Evidence has been presented previously which suggests that the substrate-activating, molybdenum-containing site of oxidases cycles molybdenum between oxidation states VI and IV during catalysis.[19] Our observations that the oxomolybdenum(IV) core binds the nitrogenase substrate acetylene but is unaffected by ethylene adds credence to the suggestion that molybdenum-containing reductases (particularly nitrogenase) may use these same oxidation states, but in reverse,[1,6-8,19] Further, the evidence presented herein may be relevant to and support the mechanism of acetylene reduction in the "molybdothiol" systems,[6,16] where, although no intermediates have been isolated, molybdenum(IV) has been implicated in the catalytically active entity.

References and Notes

(1) P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **94**, 9640 (1972).
(2) W. E. Newton, J. L. Corbin, J. W. McDonald, L. Ricard, and R. Weiss, unpublished work.
(3) E. A. Maatta and R. A. D. Wentworth, *Inorg. Chem.*, in press.
(4) P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 2552 (1975).
(5) G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).
(6) E. L. Moorehead, B. J. Weathers, E. A. Ufkes, P. R. Robinson, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **99**, 6089 (1977), and references therein.
(7) R. A. D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976).
(8) W. E. Newton, J. L. Corbin, and J. W. McDonald, *Proc. Int. Conf. N₂ Fixation, 1st, 1976*, 53 (1976).
(9) R. Schollhorn and R. H. Burris, *Proc. Natl. Acad. Sci., U.S.A.*, **58**, 213 (1967); M. J. Dilworth, *Biochim. Biophys. Acta*, **127**, 285 (1966).
(10) These values may be compared with those for $(C_5H_5)_2Mo(C_2H_2)$ of δ 7.68 and 1613 cm⁻¹ reported in K. L. Tang Wong, J. L. Thomas, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **96**, 3694 (1974), and with δ 12.3 and no observable $\nu_{C\equiv C}$ in $Mo(CO)(C_2H_2)(S_2CNEt_2)_2$ in ref 11.
(11) J. W. McDonald, W. E. Newton, C. T. C. Creedy, and J. L. Corbin, *J. Orga-*
(12) These resonances are presumably the central lines of an AB quartet whose wing lines have yet to be detected. Further details of the spectrum at low temperature will be given in a subsequent publication.
(13) L. Ricard and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **10**, 217 (1974).
(14) J. Dirand, L. Ricard, and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **11**, 661 (1975).
(15) The product yields were determined by standard gas chromatography techniques. Only the gas phase of the reaction mixture was sampled and therefore the total yields of ethylene, butadiene, and hydrogen may be substantially greater depending on their solubilities in DMF.
(16) G. N. Schrauzer and P. A. Doemeny, *J. Am. Chem. Soc.*, **93**, 1608 (1971); P. R. Robinson, E. L. Moorehead, B. J. Weathers, E. A. Ufkes, T. M. Vickrey, and G. N. Schrauzer, *ibid.*, **99**, 3657 (1977).
(17) J. L. Corbin, N. Pariyadath, and E. I. Stiefel, *J. Am. Chem. Soc.*, **98**, 7862 (1976).
(18) J. W. McDonald, J. L. Corbin, and W. E. Newton, *J. Am. Chem. Soc.*, **97**, 1970 (1975).
(19) See E. I. Stiefel, W. E. Newton, G. D. Watt, K. L. Hadfield, and W. A. Bulen, *Adv. Chem. Ser.*, **No. 162**, 353 (1977), for a concise summary of this evidence.
(20) Support from NSF Grant No. MPS 75-08188 is gratefully acknowledged.

E. A. Maatta, R. A. D. Wentworth*[20]

Contribution No. 3075 from the Department of Chemistry
Indiana University, Bloomington, Indiana 47401

W. E. Newton, John W. McDonald,* Gerald D. Watt

Contribution No. 607
Charles F. Kettering Research Laboratory
*Yellow Springs, Ohio 45387*

On the Mechanism of the Thermal Cope Rearrangement of Allyl-Substituted Cyclopropenes

Sir:

Recently, Doering[1] and Dewar[2,3] have drawn attention to the possibility of a two-step mechanism for the Cope rearrangement, in which formation of the new C–C bond precedes rupture of the old one, so that the reaction involves a biradical intermediate. At this time we wish to report on a study dealing with the thermal Cope rearrangement of allyl-substituted cyclopropenes. Our results suggest that the Cope rearrangement of this system does not proceed via a pericyclic process but rather involves the formation of an intermediate analogous to the 1,4-cyclohexylene biradical.

Thermolysis of 1,2-diphenyl-3-allyl-3-methylcyclopropene[4] (**1**) at 150 °C for 48 h produced an equilibrium mixture of recovered starting material (37%), 1,3-diphenyl-2-methyl-3-allylcyclopropene (**2**, 11%) and 1,2-diphenyl-6-methyltricyclo[2.2.0,0^{2,6}]hexane (**3**, 53%). The same distribution of

1 (37%)   2 (11%)

3 (53%)
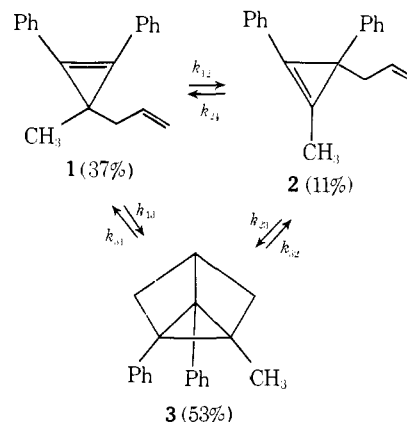
products was obtained by heating either **2** or **3** at 150 °C for 48 h. The rates and the corresponding Arrhenius parameters,