

Figure 2. Observed and calculated ${}^{31}\text{P}\{^1\text{H}\}$ spectra¹⁰ for the stereochemically rigid species, **3**.

coupling to phosphorus, ruling out a metal hydride. The fluxional process involving the phosphorus ligands has almost no effect on the ring proton resonances; there is little change going from +30 to -140 °C. In addition, ${}^1\text{H}\{^{31}\text{P}\}$ NMR experiments indicate ${}^{31}\text{P}$ coupling only to the two allylic hydrogens at 5.00 ppm (~1 Hz) and homonuclear ${}^1\text{H}$ decoupling experiments indicate coupling of the high-field resonance to three of the ring protons. The ${}^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was normal with allylic resonances at 95.73 (1) and 67.20 (2) ppm and the remaining ring carbon atoms at 27.17 (2), 21.25 (1), and 22.49 (2) ppm.

The extreme high-field shift of the two ring protons coupled with the observation of normal chemical shifts for the two carbon atoms to which they are attached can be explained on the basis of a nonbonded interaction of the ring protons with the metal center. Though we were not able to freeze out any dynamic process involving the cyclooctenyl group, we believe that the metal-hydrogen interactions involve one hydrogen at a time. Since it would take only a small conformational change to exchange hydrogen atoms, this failure to freeze out the exchange is not unexpected.¹² The coordinative unsaturation of the complex, unusual, if not unprecedented, for systems of this type, is apparently slightly relieved by the metal-hydrogen interaction. When **1** is reacted with DCl in methanol-*d*₁, one deuterium is incorporated into the complex (as indicated by FDMS¹⁰ peak at 538) in one of the two positions indicated in **2** (as indicated by ${}^1\text{H}$ NMR). There is no further deuterium incorporation even on stirring in DCl/MeOD for 4 h. Thus, the protonation, which takes place through a hydrido intermediate resulting in exclusive endo attack, is an irreversible process. This is in contrast to the cyclohexadiene iron tricarbonyl system where multiple deuterium incorporation is observed.⁵

Steric effects may account for the lack of further reaction of **2** after protonation by coordinating acids. The starting cyclooctadiene complex can be protonated with methanolic HCl and isolated as the chloride salt (though the material does not crystallize well). The cyclooctenyl complex, **2**, does not react with additional trimethyl phosphite, even in large excess; thus, a tetrakis phosphite species similar to that observed in the π -allyl system⁸ is not observed. It does, however, react with sterically less demanding¹³ molecules such as CO and *t*-BuNC, to give the 18-electron systems. *fac*- $[\text{Fe}(\text{P}(\text{OMe})_3)_3\text{L}(\text{C}_8\text{H}_{13})][\text{BF}_4]^{14}$ (**3**, L = CO; **4**, L = *t*-BuNC). The complexes are yellow, as expected for saturated species. The NMR spectra of these complexes have no unusual features; the proton

resonance which is shifted to high field in **2** is now in the normal aliphatic range for both complexes. The ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra are AB₂¹⁵ spin systems (Figure 2) as expected for stereochemically rigid octahedral complexes. The infrared spectra show absorptions for ν_{CO} at 1982 and ν_{NC} at 2140 cm^{-1} for **3** and **4** respectively.

Since the submission of this report, we have been able to prepare and characterize the cyclohexenyl and cycloheptenyl analogues of **2**. Preliminary ${}^{31}\text{P}\{^1\text{H}\}$ NMR studies indicate a progressive change in spin system type (ABC \rightarrow AB₂ \rightarrow A₃) with increasing temperature for these new systems. Examination of the ${}^{31}\text{P}\{^1\text{H}\}$ spectrum of **2** at -150 °C reveals features (relative to the -140 °C spectrum) which we now know to be characteristic of rapid exchange ($k \approx 10^4$) of the two hydrogen atoms at the metal coordination site. We estimate that at -150 °C ΔG^\ddagger is <5 kcal/mol for this process. These results confirm our interpretation of the dynamics of the metal-hydrogen interaction. Protonation of acyclic diene complexes gives species which display related behavior.

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- (11) Shifts in parts per million Me₄Si (integration; t = triplet, q = quartet, and br = broad).
- (12) This is in contrast to the protonated cyclohexadienyl iron tricarbonyl complex⁶ where the exchange process is frozen out at -80 °C. In that system a stronger interaction involving C-H cleavage was postulated, but we feel this is not the case. Substitution of one carbonyl by a phosphorus ligand was shown to lower the barrier for the exchange process: M. Brookhart, private communication.
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- (14) FDMS gives a peak at 565 for **3** and at 620 for **4**.
- (15) ${}^{31}\text{P}\{^1\text{H}\}$ NMR: **3**, AB₂, δ_A -150.0, δ_B -163.6 ppm ($J_{\text{AB}} = 171$ Hz); **4**, AB₂, δ_A -159.9, δ_B -169.7 ppm ($J_{\text{AB}} = 161$ Hz).
- (16) Contribution No. 2519.

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Binding and Activation of Enzymic Substrates by Metal Complexes. 4. Structural Evidence for Acetylene as a Four-Electron Donor in $\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{S}_2\text{CNET}_2)_2$

Sir:

Recently, the reactions of $\text{Mo}(\text{CO})_2\text{L}_2$ (L = S_2CNET_2 , $\text{S}_2\text{P}(i\text{-Pr})_2$) with C_2H_2 and its substituted analogues to give products of two forms, $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')\text{L}_2$ and $\text{Mo}(\text{RC}_2\text{R}')_2\text{L}_2$, were described.^{1,2} Their spectral data were interpreted in terms of the complexes being 18-electron systems with $\text{RC}_2\text{R}'$ acting as a four-electron donor in the former type and a three-electron donor in the latter. X-ray structural

Table I. Comparison of Spectral Data for $M(\text{CO})(\text{C}_2\text{H}_2)(\text{S}_2\text{CNEt}_2)_2$ ($M = \text{Mo}, \text{W}$)

Spectrum	M = Mo	M = W
IR ^a	$\nu(\text{C}=\text{O})$ 1960 No assignable $\nu(\text{C}\equiv\text{C})$	$\nu(\text{C}\equiv\text{O})$ 1960 No assignable $\nu(\text{C}\equiv\text{C})$
Vis ^b	615 (121) 400 (sh, 1910), 372 (2100)	698 (90) 360 (3440)
NMR ^c	$\delta(\text{C}_2\text{H}_2)$ 12.3	$\delta(\text{C}_2\text{H}_2)$ 13.1

^a KBr pellets; values in reciprocal centimeters. ^b 1,2-Dichloroethane solution; values in nanometers with molar absorptivity in parentheses. ^c CDCl_3 solution; values in parts per million from Me_4Si .

determinations have been completed³ on three of these compounds, $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNEt}_2)_2$, $\text{Mo}(\text{CO})(\text{HC}_2\text{Ph})(\text{S}_2\text{CNEt}_2)_2$, and $\text{Mo}(\text{PhC}_2\text{Ph})_2(\text{S}_2\text{CNEt}_2)_2$, but all attempts to obtain crystals of the unsubstituted acetylene complex, $\text{Mo}(\text{CO})(\text{C}_2\text{H}_2)_2$, suitable for structural analysis were unsuccessful. Because of our continuing interest in the modes of binding and activation of small molecules, we have prepared the complexes $\text{W}(\text{CO})(\text{C}_2\text{H}_2)_2(\text{L})_2$ ($\text{L} = \text{S}_2\text{CNMe}_2, \text{S}_2\text{CNEt}_2$) which, by nature of comparative spectral data (vide infra), appear to be extremely similar structurally to their molybdenum analogue. Herein, we report the preparation and x-ray structure of $\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{S}_2\text{CNEt}_2)_2$ (**1**) which, to our knowledge, is the first mononuclear complex containing coordinated C_2H_2 to be so characterized.

A solution of the complex⁴ $\text{W}(\text{CO})_2(\text{PPh}_3)(\text{S}_2\text{CNEt}_2)_2$ (0.75 g) in CH_2Cl_2 (50 mL) was stirred for 30 min under an atmosphere of pure C_2H_2 during which time the color of the reaction mixture changed from orange-red to deep green. After evaporation to dryness under vacuum and trituration of the residue with diethyl ether, the product **1** (0.37 g, 74%) was obtained as a green solid which was isolated by filtration, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{N}_2\text{OS}_4\text{W}$: C, 29.2; H, 4.12; N, 5.24. Found: C, 30.0; H, 3.85; N, 5.18. The spectral (IR, visible, and NMR) data for **1** and its molybdenum analogue are presented in Table I. The spectra are very similar and indicate similar structures for the two complexes both in solution and in the solid state. The extreme downfield shift in the NMR spectrum for the acetylenic protons is most unusual and, as postulated previously,^{1,2} is indicative of C_2H_2 behaving as a formal four-electron donor to tungsten. Recently, a similar shift has been observed⁵ for the acetylenic protons of $(\text{C}_5\text{H}_5)\text{W}(\text{CO})(\text{CH}_3)(\text{C}_2\text{H}_2)$.

Crystals of **1** were obtained from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ solution.⁶ Some 6000 intensities were measured in the range $4^\circ < 2\theta < 60^\circ$ with a Philips PW1100 diffractometer, using $\text{Mo K}\alpha$ radiation. Background time was equal to scan time, with an ω scan speed of $2^\circ/\text{minute}$ and an ω scan width of 0.8° ; 3305 reflections were used in structure resolution and refinement. All computations were conducted as previously described.⁷ The heavy atoms were given anisotropic temperature factors to yield, after introduction and refinement of the hydrogen atoms positions, $R = 0.038$.⁶

The geometry of the molecule is shown in Figure 1. It is similar to that encountered in the other carbonyl acetylene complexes³ with the $\text{C}=\text{O}$ and $\text{C}\equiv\text{C}$ bonds being nearly coplanar and essentially parallel. The geometry about the metal may be regarded as pseudooctahedral but is probably better described as pentagonal-bipyramidal, with sulfur atoms S_3 and S_2 occupying the apexes and the carbonyl carbon, both acetylenic carbons and the two remaining ligating sulfur atoms constituting the equatorial plane. The bond lengths of the inner coordination sphere and the H-C-C angles of the coordinated acetylene are listed in the figure legend. The longest W-S bond is trans to the acetylenic bond. The acetylenic carbons assume sp^2 hybridization upon coordination to the metal.

Carbonyl acetylene complexes of molybdenum and tungsten

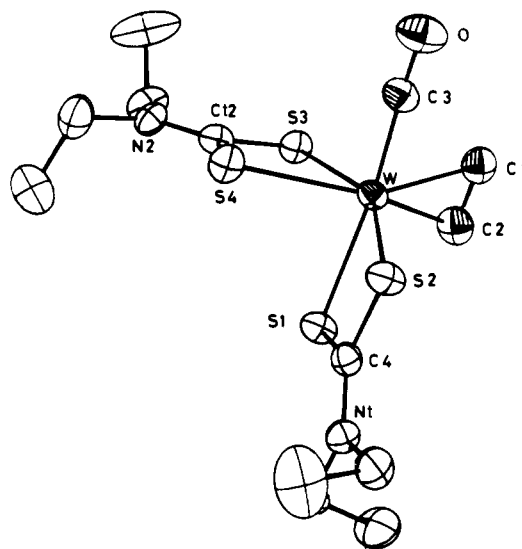


Figure 1. Perspective view of **1**. Main bond lengths (ångströms) follow: W-C_1 , 2.038 (8); W-C_2 , 2.015 (9); $\text{C}_1\text{-C}_2$, 1.29 (1); W-C_3 , 1.936 (7); $\text{C}_3\text{-O}$, 1.16 (1); W-S_1 , 2.557 (1); W-S_2 , 2.399 (1); W-S_3 , 2.550 (1); W-S_4 , 2.588 (2). Other distances are similar to previously reported values. Angles (degrees) of interest follow: $\text{H-C}_1\text{-C}_2$, 136.1 (4.4); $\text{H-C}_2\text{-C}_1$, 130.2 (6.2).

have been regarded as 16-electron^{3,5,8,9} or 18-electron^{1,2} species while oxo acetylene complexes of these metals⁸⁻¹¹ are generally agreed to be 18-electron systems. The available structural data^{3,9-11} indicate that, although little variation is evident in the acetylenic C-C bond lengths ($1.28 \pm 0.02 \text{ \AA}$) in these two classes of compounds, a significant difference is observed in the metal-acetylenic carbon bond lengths. Thus the average M-C bond ($2.11 \pm 0.01 \text{ \AA}$) in the structurally characterized⁹⁻¹¹ oxo acetylene complexes is nearly 0.1 \AA longer than the average W-C bond ($2.03 \pm 0.01 \text{ \AA}$) in **1**.¹² This observation, in light of the spectral evidence, is best rationalized if both are considered as 18-electron species with **1** having a four-electron donor acetylene and the oxo acetylene complexes having a two-electron donating acetylenic ligand.

Simple molecular symmetry arguments also support this concept. Complex **1** is diamagnetic and is formally tungsten(II), i.e., a spin-paired $5d^4$ electronic configuration. In the pseudooctahedral coordination sphere around tungsten, the d^2sp^3 hybrid orbitals are involved in σ bonding with the four sulfur atoms, the carbonyl carbon (on the z axis), and the acetylene molecule (on the x axis). The carbonyl ligand will bind most strongly along the z axis if the metal d_{xz} and d_{yz} orbitals contain the two electron pairs, maximizing π back-bonding into both π antibonding orbitals of the carbon monoxide. The metal d_{xy} orbital will then be empty and able to accept π -electron density from the acetylene (in addition to that donated to the d^2sp^3 octahedral hybrid) but *only* if the acetylene orients itself parallel to the W-C-O (z) direction on the x axis. This is, in fact, the observed geometry of **1** which is, therefore, consistent with donation from *both* of the filled acetylene $1\pi_u$ bonding orbitals, i.e., with acetylene acting as a formal four-electron donor. In this orientation, the empty $1\pi_g$ acetylene antibonding orbitals can compete¹³ with the 2π antibonding orbitals on carbon monoxide for metal-to-ligand back-bonding through interaction with the metal d_{xz} (π type) and d_{yz} (δ type) orbitals and, if successful, will weaken the tungsten-carbonyl bonding. Such competition is reflected in both the tungsten and molybdenum complexes by the increase in $\nu(\text{CO})$ compared with those observed in the dicarbonyl starting materials.¹⁴ The valence bond representation of this molecule would approach that of a dicarbene and thus be similar to the scheme recently proposed¹⁵ to account for the

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 mononuclear 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.

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Reversible Binding of Acetylene by $OMo(S_2CNEt_2)_2$

Sir:

The reactions of $OMo(S_2CNEt_2)_2$ (**1**) with diazenes,¹ activated acetylenes,^{1,2} hydrazoic acid,³ and various oxo transfer reagents^{4,5} have been described in recent publications. Because Mo(IV) has been proposed^{1,6-8} 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.

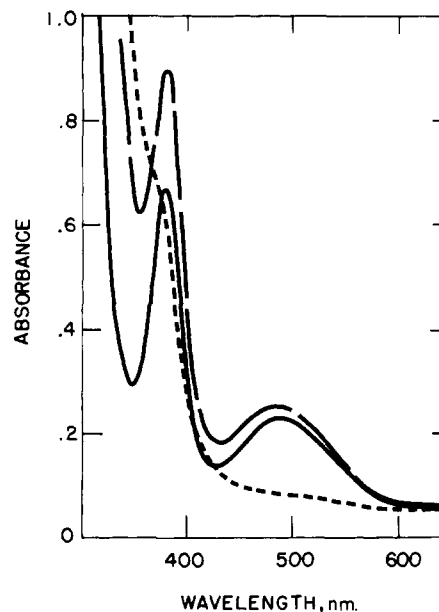


Figure 1. Visible spectral changes for the reaction of $OMo(S_2CNEt_2)_2$ with C_2H_2 in CH_2Cl_2 : before addition of C_2H_2 (—); after addition of C_2H_2 (---); after pumping on reaction mixture (— · —). Final spectrum is more intense than initial owing to loss of solvent during removal of C_2H_2 .

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, $OMo(S_2CNEt_2)_2(HC\equiv CCO_2Me)$, 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 S_2CNEt_2 approaches a value of 2:8, which is consistent with **2** being the 1:1 adduct, $OMo(S_2CNEt_2)_2(C_2H_2)$, 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 ($\Delta\nu = 7$ 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 S_2 ,¹⁴ and ditoluoylacetylene.²

