

the axial ligands (His and Met) in cytochrome c^{14} are retained upon reduction of the iron center.

Acknowledgment. We thank Steve Mayo for Figure 1. R. J. C. acknowledges a postdoctoral fellowship from the Natural Sciences and Engineering Research Council of Canada. This research was supported by National Science Foundation Grant CHE82-18502.

(14) Takano, T.; Dickerson, R. E. *J. Mol. Biol.* **1981**, *153*, 79-94; 95-115.

Protonation of Molybdenum(II) and Tungsten(II) Bis(alkyne) Complexes: Formation of η^4 -C₄R₄H Ligands

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Received February 22, 1985

Protonation of a metal-bound alkyne carbon in $M(R^1C_2R^2)_2(S_2CNR_2)_2$ complexes¹ ($M = Mo$ or W , $R^1 = R^2 = Ph$, $R = Et$; $M = Mo$, $R^1 = Ph$, $R^2 = H$, $R = Me$) with HBf_4 induces an oxidative coupling of the C_2 moieties to form an η^4 -C₄R₄H ligand. Stoichiometric addition of HBf_4 to $M(PhC_2Ph)_2(S_2CNEt_2)_2$ ($M = Mo, W$) in CH_2Cl_2 followed by precipitation and trituration with Et_2O yields $[M(\eta^4-C_4Ph_4H)(S_2CNEt_2)_2][BF_4]$.² The carbene carbon (C_1) resonates at low field (W , 270.0 ppm, $^1J_{WC} = 84$ Hz; Mo , 279.8 ppm) while the protonated carbon (C_4) is found at much higher field in the ^{13}C NMR spectrum (W , 76.9 ppm, $^1J_{CH} = 154$ Hz; Mo , 83.5 ppm, $^1J_{CH} = 157$ Hz). The two intervening carbons of the MC_4 ring are also bound to the metal and exhibit shifts between 114 and 122 ppm for both metals. Both 1H and ^{13}C NMR indicate that $Mo(PhC_2H)_2(S_2CNMe_2)_2$ adds acid at a terminal acetylenic carbon and undergoes head-to-tail coupling to yield $[Mo(\eta^4-C(Ph)C(H)C(Ph)CH_2)(S_2CNMe_2)_2]^+$, with a phenyl substituent on the carbene carbon, as the only isolated isomer.³

Reaction of $[W(\eta^4-C_4Ph_4H)(S_2CNEt_2)_2][BF_4]$ with aqueous NEt_3 in CH_2Cl_2 results in substitution of one dithiocarbamate by an oxide ligand to form a neutral $W(O)(\eta^4-C_4Ph_4H)(S_2CNEt_2)$

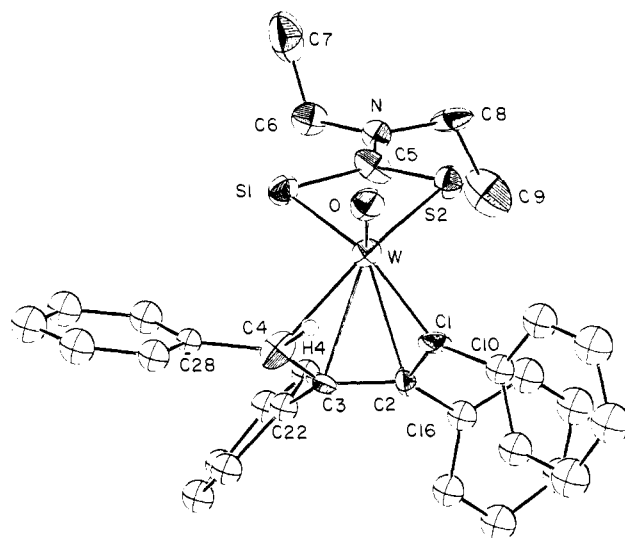
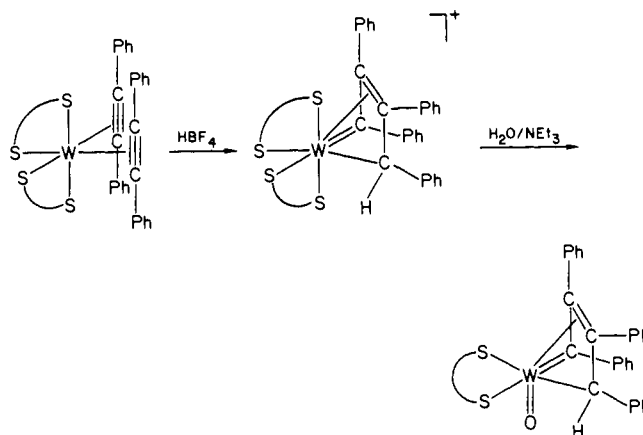


Figure 1. ORTEP diagram showing the atomic labeling scheme for $W(O)(\eta^4-C_4Ph_4H)(S_2CNEt_2)$. The position of H4 is a calculated one, and it is drawn in only to assist in visualizing the C_4Ph_4H ligand. The thermal ellipsoids are drawn at the 40% probability level.

Scheme I



complex (see Scheme I). Purification of the crude product by chromatography on Florisil separated two isomers: **a**, eluted with CH_2Cl_2 , dark orange, unique 1H at 4.05; **b**, eluted with Et_2O/CH_2Cl_2 (1/100), dark gold, unique 1H at 5.77 ppm. Both isomers exhibit NMR spectra characteristic of the η^4 -C₄Ph₄H ligand and an intense $W=O$ infrared absorption.⁴ The chemical shift difference of 1.7 ppm for the unique proton of the C_4Ph_4H ligand in the two isomers is comparable to differences seen for syn and anti positions of π -allyl or π -butadiene ligands.⁵ The anti position of the terminal proton in isomer **a** (vide infra) was anticipated from the higher 1H chemical shift relative to the analogous proton in isomer **b**, and we tentatively assign a syn proton location to the C_4Ph_4H ligand in **b**. Isomer **a** can be cleanly converted to **b** by heating in wet acetonitrile for several hours at 54 °C.

(1) Molybdenum reagents were synthesized by literature methods.^{1a,b} The tungsten bisalkyne reagent was synthesized by reflux of $W(CO)_2(PhC_2Ph)(S_2CNEt_2)_2$ ^{1c,d} with excess diphenylacetylene in methanol for 8 h followed by alumina chromatography with toluene as eluant and recrystallization from a methylene chloride/hexanes solvent mixture. (a) Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842. (b) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25. (c) Ricard, L. Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W.; *J. Am. Chem. Soc.* **1978**, *100*, 1318. (d) We used an alternate synthetic route: Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745.

(2) $[W(\eta^4-C_4Ph_4H)(S_2CNEt_2)_2][BF_4]$: 1H NMR ($CDCl_3$) δ 7.62-6.52 (m, 20, C_6H_5), 4.27-3.73 (m, 8, CH_2), 4.14 (s, 1, $CHPh$), 1.55 (m, 6, CH_3), 1.38, 1.24 (t, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 270.0 (s, $^1J_{WC} = 84$ Hz, $=CPh$), 200.4, 199.4 (s, S_2CNEt_2), 136.5-125.8 (C_6H_5), 121.1, 114.4 (s, $=CPhCPhCPhCPh$), 76.9 (d, $^1J_{CH} = 154$ Hz, $CHPh$), 48.0, 47.0 (t, $^1J_{CH} = 140$ Hz, CH_2), 12.5, 12.8, 13.4 (q, $^1J_{CH} = 129$ Hz, CH_3); IR (CH_2Cl_2) ν_{CN} 1530 cm^{-1} ; $[Mo(\eta^4-C_4Ph_4H)(S_2CNEt_2)_2][BF_4]$: 1H NMR (CD_2Cl_2) δ 7.73-6.53 (m, 20, C_6H_5), 4.71 (s, 1, $CHPh$), 4.21-3.36 (m, 8, CH_2), 1.47 (t, 6, CH_3), 1.35-1.12 (m, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 279.8 (s, $=CPh$), 199.7, 197.6 (s, S_2CNEt_2), 135.9-127.6 (C_6H_5), 122.1, 113.7 (s, $=CPhCPhCPhCPh$), 83.5 (d, $^1J_{CH} = 157$ Hz, $CHPh$), 47.4, 46.7 (t, $^1J_{CH} = 140$ Hz, CH_2), 13.5, 12.7 (q, $^1J_{CH} = 130$ Hz, CH_3); IR (CH_2Cl_2) ν_{CN} 1524 cm^{-1} .

(3) $[Mo(\eta^4-C(Ph)C(H)C(Ph)CH_2)(S_2CNEt_2)_2][BF_4]$: 1H NMR ($CDCl_3$) δ 7.61-7.20 (m, 10, C_6H_5), 7.4 (approximate chemical shift estimated from homonuclear decoupling experiments, $=CPhCPhCPhCPh$), 4.58, 3.25 (dd, 2, $^2J = 4$, $^4J = 1$ Hz, $=CPhCPhCPhCPh$), 3.74 (s, 6, CH_3), 3.33, 2.94 (s, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 272.2 (s, $=CPh$), 202.9, 200.9 (s, S_2CNEt_2), 136.3-126.0 (C_6H_5), 94.4 (d, $^1J_{CH} = 173$ Hz, $=CPhCPhCPhCPh$), 62.0 (t, $^1J_{CH} = 156$ Hz, CH_2), 45.2-39.2 (q, overlapping, CH_3); IR (CH_2Cl_2) ν_{CN} 1550 cm^{-1} . Anal. Calcd for $MoS_4N_2C_2H_2BF_4$: Mo, 15.27; N, 4.46; C, 42.04; H, 4.02. Found: Mo 15.51; N, 4.99; C, 41.02; H, 4.36.

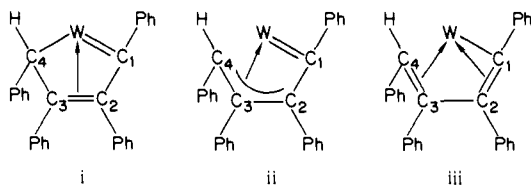
(4) $W(O)(C_4Ph_4H)(S_2CNEt_2)$ (**a** isomer): 1H NMR ($CDCl_3$) δ 7.42-6.58 (m, 20, C_6H_5), 4.05 (s, 1, $^2J_{WH} = 21$ Hz, $CHPh$), 3.94-3.52 (m, 4, CH_2), 1.25 (t, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 266.5 (s, $=CPh$), 204.5 (S_2CNEt_2), 144.2-123.2 (C_6H_5 and one $=CPhCPhCPhCPh$), 119.1 (s, one of $=CPhCPhCPhCPh$), 68.0 (d, $^1J_{CH} = 136$, $^1J_{WC} = 53$ Hz, $CHPh$), 46.1, 45.3 (t, $^1J_{CH} = 135$ Hz, CH_2), 12.7, 12.5 (q, $^1J_{CH} = 127$ Hz, CH_3); IR (KBr) ν_{CN} 1510, ν_{WO} 957 cm^{-1} ; $W(O)(C_4Ph_4H)(S_2CNEt_2)$ (**b** isomer): 1H NMR ($CDCl_3$) δ 7.45-6.70 (m, 20, C_6H_5), 5.77 (s, 1, $^1J_{WH} = 9$ Hz, $CHPh$), 3.89-3.32 (m, 4, CH_2), 1.33, 1.15 (t, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 271.8 (s, $=CPh$), 207.1 (s, S_2CNEt_2), 145.4-123.5 (C_6H_5 and $=CPhCPhCPhCPh$), 76.8 (d, $^1J_{CH} = 144$ Hz, $CHPh$), 45.8, 45.4 (t, $^1J_{CH} = 135$ Hz, CH_2), 12.5, 12.2 (q, $^1J_{CH} = 128$ Hz, CH_3); IR (KBr) ν_{CN} 1525, ν_{WO} 955 cm^{-1} .

(5) (a) Green, M. L. H.; Nagy, P. L. *Adv. Organomet. Chem.* **1964**, *2*, 325. (b) Pettit, R.; Emerson, G. F. *Adv. Organomet. Chem.* **1964**, *1*, 1. (c) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; Oxford University Press: Mill Valley, CA, 1980.

Table I. Selected Bond Distances and Angles for W(O)(C₄Ph₄H)(S₂CNET₂)

atoms	distance, Å	atoms	angle, deg
W-C1	1.96 (1)	S1-W-C1	138.1 (4)
W-C2	2.52 (1)	S2-W-C4	140.0 (3)
W-C3	2.61 (1)	C2-W-O	141.1 (4)
W-C4	2.25 (1)	C3-W-O	143.6 (4)
W-O	1.66 (1)	C1-W-O	107.7 (5)
W-S1	2.532 (3)	W-C1-C2	94.3 (8)
W-S2	2.417 (3)	C1-C2-C3	116 (1)
C1-C2	1.44 (1)	C2-C3-C4	115 (1)
C2-C3	1.43 (1)	C3-C4-W	86 (1)
C3-C4	1.49 (1)		
C1-C4	2.69 (2)		

The geometry of isomer **a** was determined by single-crystal X-ray diffraction (see Figure 1).⁶ Selected distances and angles are listed in Table I. The structure of W(O)(C₄Ph₄H)(S₂CNET₂) is roughly octahedral with C₂ and C₃ of the metallacycle bound at most only weakly to the metal approximately trans to the oxo ligand (O-W-C2, 141°; O-W-C3, 144°). An alternate description of the coordination geometry as a square pyramid with C₁, C₄, S₁, and S₂ in the basal plane and the tungsten atom displaced toward the oxo ligand in the apical position neglects any bonding of C₂ and C₃ to the metal. A crude structural analogy is provided by high oxidation state early transition metal π -butadiene complexes. In contrast to the nearly equivalent four M-C distances of iron⁷ and molybdenum⁸ η^4 -diene examples, the 2,3-dimethylbutadiene ligand of (π -C₅H₅)₂Zr(η^4 -C₆H₁₀)⁹ has the two internal carbons 0.3 Å further from the metal than the two terminal carbons. The C₄-based ligand in W(O)(C₄Ph₄H)(S₂CNET₂) shows a related asymmetry as it appears to have a metal-carbon double bond to C₁ (1.96 Å cf. 1.94 Å for W=CHCMe₃¹⁰), a single bond to C₄ (2.25 Å cf. 2.26 Å for W-CH₂CMe₃¹⁰) and only weak donation from the C₂ and C₃ to the metal (2.52 and 2.61 Å, respectively). Several resonance structures can be drawn to represent the W(η^4 -C₄Ph₄H) fragment. These resonance forms illustrate the similarity of the C(Ph)H terminus to π -allyl and π -butadiene terminal carbons as reflected in the NMR data. In representation iii the W-C₁-C₂ moiety is reminiscent of η^2 -vinyl ligands which have been characterized recently.¹¹



The η^4 -C₄Ph₄H ligand has been prepared previously by hydride attack on a cationic π -cyclobutadiene ruthenium derivative.¹² The

(6) The crystal selected was monoclinic of space group *P*2₁/*c* with unit cell dimensions of *a* = 16.302 (5) Å, *b* = 9.450 (3) Å, *c* = 20.242 (7) Å, and β = 108.89 (3°), with *Z* = 4. Data were collected at ambient temperature on an Enraf-Nonius CAD4 diffractometer using monochromated Mo K α radiation. Of the 6406 reflections monitored, 2487 independent reflections with *I* > 3 σ (*I*) were used in the structure solution and refinement, which converged to *R* = 7.3% and *R*_w = 6.6% with hydrogens in calculated positions, phenyl carbons refined isotropically, and all other heavy atoms refined anisotropically. An empirical absorption correction was applied based on psi scans with χ near 90°.

(7) (a) Mills, O. S.; Robinson, G. *Acta Crystallogr.* **1963**, *16*, 758. (b) Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522. (c) Herbstein, F. H.; Reinson, M. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3304.

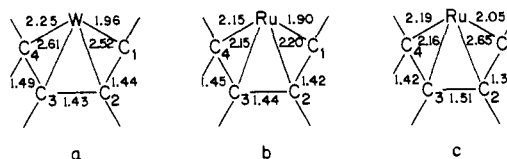
(8) Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 195.

(9) Erker, G.; Wicher, J.; Engle, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6346.

(10) (a) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454. (b) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.

(11) (a) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (b) Davidson, J. L.; Vasapollo, G.; Manojlovic-Muir, L. J.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025. (c) Carlton, L.; Davidson, J. L.; Miller, J. C.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1984**, 11.

structure of (π -C₅H₅)Ru(η^4 -C₄Ph₄H) has all four ligand carbons in one plane as does the tungsten oxo complex reported here. The high trans influence of the oxo ligand and steric congestion around the metal due to the bulky phenyl substituents probably cause the M-C₁-C₂ angle to open from 82° in the ruthenium case to 95° here with the W-C₂ and W-C₃ distances elongated accordingly. Comparison of the metallacycle ring distances in W(O)(C₄Ph₄H)(S₂CNET₂) (a), (π -C₅H₅)Ru(C₄Ph₄H) (b),¹² and



(π -C₅H₅)Ru(PPh₃)(C₄(CF₃)₄H) (c),¹³ where only three rather than five electrons are required from the C₄R₄H ligand, underscores the carbenoid character of C₁ for a and b. The formation of a tungsten oxo carbene derivative from a low oxidation state tungsten alkyne complex with acid and aqueous reagents is noteworthy.

Acknowledgment. This work was generously supported by the National Science Foundation (CHE8310121).

Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters, complete bond distances, calculated hydrogen positions, and *F*_{obsd} and *F*_{calcd} (24 pages). Ordering information is given on any current masthead page.

(12) Crocker, M.; Green, M.; Orpen, A. G.; Neumann, H. P.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1351.

(13) (a) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106. (b) Blackmore, T.; Bruce, M. I.; Stone, F. G. A.; Davis, R. E.; Garza, A. *J. Chem. Soc., Chem. Commun.* **1971**, 852.

Synthesis and Characterization of a New Fe/Mo/S Cluster Containing the [Fe₆Mo₂S₆]³⁺ Core. A Precursor to a Possible Structural Analogue for the Fe/Mo Site of Nitrogenase

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Received April 15, 1985

Structural and spectroscopic studies on the Fe/Mo center in the Fe/Mo protein of nitrogenase¹ and the nitrogenase cofactor² have revealed the presence of a most interesting Fe/Mo/S aggregate.

Analyses of the Mo³ and Fe⁴ x-ray absorption fine structures in the Fe/Mo protein of nitrogenase and (for the Mo only) in the nitrogenase cofactor have established (a) the close proximity (~2.7 Å) of the Mo atom or two or three Fe atoms, (b) coordination of three of four S atoms to the Mo atom (at 2.35 Å) and of two or three S atoms to the Fe atom (at 2.25 Å), and (c) the probable

(1) (a) Orme-Johnson, W. H.; Davis, L. C. In "Iron Sulfur Proteins"; Lovenberg, W., Ed.; Academic Press: New York, 1976; Vol. III, Chapter 2. (b) Burgess, B. J. In "Advances in Nitrogen Fixation Research"; Veeger, C., Newton, W. E., Eds.; Nijhoff-Junk-Pudoc: Wageningen, 1983.

(2) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249.

(3) (a) Cramer, S. P.; Gillum, W. D.; Hodgson, K. O.; Mortenson, L. E.; Stiefel, E. I.; Chisnell, J. R.; Brill, W. J.; Shah, V. K. *J. Am. Chem. Soc.* **1978**, *100*, 4630. (b) Cramer, S. P.; Hodgson, K. O.; Gillum, W. O.; Mortenson, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 3398. (c) Newton, W. E.; Burgess, B. J.; Cummings, S. C.; Lough, S.; McDonald, J. W.; Rubinson, J. F.; Conradson, S. D.; Hodgson, K. O. In "Advances in Nitrogen Fixation Research"; Veeger, C., Newton, W. E., Eds.; Nijhoff-Junk-Pudoc: Wageningen, 1983; p 160.

(4) Antonio, M. R.; Teo, B. K.; Orme-Johnson, W. H.; Nelson, M. J.; Groh, S. E.; Lindahl, P. A.; Kaulzarich, S. M.; Averill, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4703.