In conclusion, a novel, Lewis acid assisted Michael reaction was realized by the combined use of a bulky nucleophile [enolate–aluminum porphyrin (**2**)] and sterically crowded Lewis acids (**3a–c**, **4a**), where the reaction was dramatically rapid and clean owing to the steric suppression of the undesired attack of the nucleophile to the Lewis acidic center.

---

(9) ^{1}H NMR at 25 °C [CD_2Cl_2, CH_2Cl_2 (δ 5.30) as internal standard] for MMA: δ 6.00 and 5.49 ($=CH_2$), 3.66 (OCH_3), 1.86 (CH_3). For MMA/**3b** (1/1): δ 6.41 and 5.81 ($=CH_2$), 3.92 (OCH_3), 1.98 (CH_3).

The Syntheses, Structures, and Reactivity of Monomeric Tungsten(IV) and Tungsten(VI) Bis(sulfido) Complexes: Facile Elimination of H_2 from H_2S

Daniel Rabinovich and Gerard Parkin*

Department of Chemistry, Columbia University
New York, New York 10027

Received March 4, 1991

Complexes containing metal–ligand multiple bonds,[1,2] e.g., $L_nM{=}E$ (E = O, S; NR, PR; CR_2, SiR_2) and $L_nM{\equiv}E$ (E = N, P; CR), are of considerable interest both in terms of their bonding and reactivity. Furthermore, research in this area has been prompted as a consequence of the roles that such groups may play in important processes such as oxidation, hydrodesulfurization, hydrodenitrification, and nitrogen fixation. Although the most common class of metal–ligand multiple bond encountered is the metal–oxo, surprisingly few studies have been reported on the closely related terminal metal–sulfido systems. In part this is a result of the lack of suitable synthetic methods for terminal sulfido complexes and also the tendency for sulfido ligands to bridge two or more metal centers.[3] Here we report the syntheses, structures, and reactivity of some tungsten bis(sulfido) complexes that are stabilized by trimethylphosphine coligands.

The purple bis(sulfido) complex *trans*-$W(PMe_3)_4(S)_2$ is readily obtained by the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$[4] with H_2S in benzene at room temperature (Scheme I).[5,6] Although sulfido and imido ligands are isoelectronic, it is interesting to contrast the formation of the six-coordinate 18-electron bis(sulfido) complex *trans*-$W(PMe_3)_4(S)_2$ with that of the related bis(imido) system reported by Schrock, for which the four-coordinate tetrahedral derivative $W(PMe_2Ph)_2(NAr)_2$ (Ar = 2,6-$C_6H_3Pr^i_2$) was isolated.[7]

The facile elimination of hydrogen from H_2S giving $W(PMe_3)_4(S)_2$ is of considerable interest in view of the proposal that hydrogenation of organic substrates during hydrodesulfurization may involve hydrogen transfer from a -SH group.[8] Thus, we have demonstrated that the elimination of dihydrogen from H_2S proceeds via the initial formation of the proposed hydrido–hydrosulfido intermediate $W(PMe_3)_4(H)_2(SH)_2$, which may be isolated if the reaction is carried out in pentane. Although complete characterization of $W(PMe_3)_4(H)_2(SH)_2$ is precluded by its instability in solution (vide infra), evidence for its formulation is provided by the observation of both ν_{W-H} and ν_{S-H} at 1860 and 2545 cm^{-1}, respectively, in the solid-state (KBr pellet) IR spectrum.[9] Solutions of yellow $W(PMe_3)_4(H)_2(SH)_2$ immediately eliminate hydrogen at room temperature giving purple $W(PMe_3)_4(S)_2$. The stoichiometry of this reaction has been confirmed by carrying out the reaction in the presence of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$, a hydrogen trap (eq 1).[10] In this regard,

$$W(PMe_3)_4(H)_2(SH)_2 + 2W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4) \rightarrow W(PMe_3)_4(S)_2 + 2W(PMe_3)_4H_3(OC_6H_5) \quad (1)$$

the reactions of other transition-metal complexes with H_2S have been the subject of previous investigations. Whereas the formation of a bridging sulfido complex accompanied by elimination of H_2 has been observed,[11] the facile elimination of H_2 and formation of a terminal sulfido complex at a single metal center has not previously been reported to our knowledge.[12]

Dissociation of the trimethylphosphine ligands from $W(PMe_3)_4(S)_2$ is facile, as evidenced by the rapid formation of the red-brown isocyanide derivatives *trans,trans,trans*-$W(PMe_3)_2(CNR)_2(S)_2$ [R = Pr^i, Bu^t, c-C_6H_{11}].[6] The complexes $W(PMe_3)_4(S)_2$ and $W(PMe_3)_2(CNR)_2(S)_2$ represent rare examples of 18-electron complexes containing terminal sulfido ligands, and, as such, the electronic nature of the tungsten center inhibits lone-pair donation so that the bond order in these complexes is aptly described as two (i.e., $W{=}S$ versus $W^{-}{\equiv}S^{+}$).[13] Support for this formalism is provided by the observation of particularly low $\nu_{W=S}$ stretching frequencies in the range 385–393 cm^{-1}.[14] Furthermore, the molecular structure of the derivative $W(PMe_3)_2(CNBu^t)_2(S)_2$ has been determined,[15] and the W=S bond

---

(1) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(2) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186–193, and references therein.

(3) (a) Do, Y.; Holm, R. H. *Inorg. Chim. Acta* **1985**, *104*, 33–40. (b) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322–329. (c) Rice, D. A. *Coord. Chem. Rev.* **1978**, *227*, 199–227.

(4) (a) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025–2035. (b) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227–2236.

(5) A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (1.0 g, 1.8 mmol) in pentane (ca. 30 mL) was treated with H_2S (1 atm) resulting in the rapid formation of yellow microcrystalline $W(PMe_3)_4(H)_2(SH)_2$, which was isolated by filtration at −78 °C. The isolated $W(PMe_3)_4(H)_2(SH)_2$ was redissolved in benzene to give a red-purple solution, accompanied by the evolution of H_2. The solution was filtered, and the solvent was removed in vacuo to give purple $W(PMe_3)_4(S)_2$ (0.63 g, 63%). NMR data for $W(PMe_3)_4(S)_2$ (in C_6D_6): ^{1}H δ 1.67, virtual triplet, J_{P-H} = 2.7 Hz; $^{13}C\{^1H\}$ δ 25.1, multiplet, J_{P-C} = 13 Hz; $^{31}P\{^1H\}$ (relative to H_3PO_4) δ −44.3, s, J_{W-P} = 268 Hz; IR data (KBr pellet): $\nu_{W=S}$ = 390 cm^{-1}. Anal. Calcd for $C_{12}H_{36}S_2W$: C, 26.1; H, 6.6. Found: C, 26.1; H, 6.4.

(6) All new compounds have been characterized analytically and spectroscopically (see supplementary material).

(7) Williams, D. S.; Schofield, M. H.; Anhaus, J. T.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6728–6729.

(8) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387–400.

(9) IR assignments have been confirmed by deuterium labeling: ν_{W-D} = 1337 cm^{-1} (ν_H/ν_D = 1.39) and ν_{S-D} = 1850 cm^{-1} (ν_H/ν_D = 1.38). Further support for the formulation of the intermediate as $W(PMe_3)_4(H)_2(SH)_2$ is provided by the observation that oxidative addition of other reagents HX (X = H, SiH_3, Cl) to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ gives similar products $W(PMe_3)_4(H)_2(X)_2$: ref 4 and Rabinovich, D.; Parkin, G., unpublished results.

(10) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632–9633.

(11) (a) Dubois, M. R. *Chem. Rev.* **1989**, *89*, 1–9. (b) Besenyei, G.; Lee, C.-L.; Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622–3628. (c) Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175–1176.

(12) Although there are several reports of the formation of dihydrogen sulfide and hydrosulfido derivatives, these complexes have not been reported to eliminate dihydrogen. See, for example: (a) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426–6428. (b) Amarasekera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989**, *28*, 3875–3883. (c) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1967**, *98*, 689–702. (d) Osakada, K.; Yamamoto, T.; Yamomoto, A. *Inorg. Chim. Acta* **1984**, *90*, L5–L6. (e) Morelli, D.; Segre, A.; Ugo, R.; La Monica, G.; Cenini, S.; Conti, F.; Bonati, F. *Chem. Commun.* **1967**, 524–526. Ugo, R.; La Monica, G.; Cenini, S.; Segre, A.; Conti, F. *J. Chem. Soc. (A)* **1971**, 522–528. (f) Mueting, A. M.; Boyle, P.; Pignolet, L. H. *Inorg. Chem.* **1984**, *23*, 44–48. (g) Han, R.; Looney, A.; Parkin, G. *J. Am. Chem. Soc.* **1989**, *111*, 7276–7278. (h) Köpf, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 953. (i) Schmidt, M.; Hoffmann, G. G.; Höller, R. *Inorg. Chim. Acta* **1979**, *32*, L19–L20. (j) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. (A)* **1967**, 1455–1458. (k) Cecconi, F.; Innocenti, P.; Midollini, S.; Moneti, S.; Vacca, A.; Ramirez, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1129–1134.

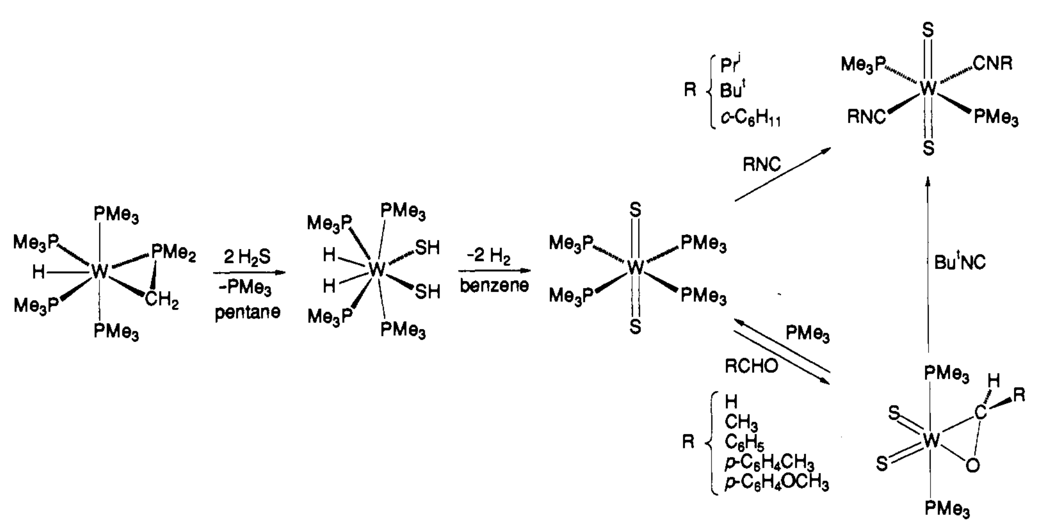
(13) The 18-electron sulfido complexes $W(PMe_3)_4(S)_2$ and $W(PMe_3)_2(CNBu^t)_2(S)_2$ can be seen to be closely related to oxo complexes of the type $[OsL_4(O)_2]^{2+}$ (see ref 1).

(14) $\nu_{W=S}$ stretching frequencies and W=S bond lengths are typically in the ranges 450–570 cm^{-1} and 2.06–2.18 Å, respectively. (a) Chisholm, M. H.; Huffman, J. C.; Pasterczyk, J. W. *Polyhedron* **1987**, *6*, 1551–1557, and references therein. (b) Müller, A. *Polyhedron* **1986**, *5*, 323–340, and references therein.

(15) Crystal data for $W(PMe_3)_2(CNBu^t)_2(S)_2$: monoclinic, $P2_1/n$ (no. 14), a = 11.003 (2) Å, b = 10.513 (3) Å, c = 11.947 (3) Å, β = 109.87 (2)°, V = 1299.6 (6) Å^3, Z = 2, ρ_{calcd} = 1.57 g cm^{-3}, μ (Mo Kα) = 49.9 cm^{-1}, λ (Mo Kα) = 0.71073 Å (graphite monochromator); 2978 unique reflections with 3° < 2θ < 55° were collected of which 2032 reflections with $F > 6\sigma(F)$ were used in refinement; R = 0.0302, R_w = 0.0389, GOF = 2.108.

0002-7863/91/1513-5904$02.50/0

Scheme I



length [2.248 (2) Å] is longer[16] than those observed in a variety of other tungsten sulfido complexes.[14] Indeed, $W(PMe_3)_2(CNBu^t)_2(S)_2$ appears to be the first structurally characterized complex containing a "pure" W═S double bond.[17]

$W(PMe_3)_4(S)_2$ also reacts rapidly with aldehydes to give the red-purple η^2-aldehyde complexes $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHR)$ (R = H, CH_3, C_6H_5, $p\text{-}C_6H_4CH_3$, $p\text{-}C_6H_4OCH_3$).[6] Although η^2-aldehyde complexes are now well-known,[18] the overall transformation involving the substitution of *two* PMe_3 ligands for *one* aldehyde moiety is unusual. It is more commonly observed that an aldehyde molecule displaces only one PR_3 ligand, as illustrated by the reactions of $W(PMe_2Ph)_4Cl_2$[19] and $W(PMe_2Ph)_2(NAr)_2$.[7]

The molecular structure of the η^2-benzaldehyde complex $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)$ has been determined by X-ray diffraction.[20] The six-coordinate environment may be viewed as being related to a distorted trigonal bipyramid with axial PMe_3 ligands, if the η^2-aldehyde ligand is considered to occupy a single equatorial coordination site. The observation of both (i) a C–O bond length of 1.376 (9) Å[21] and (ii) a degree of nonplanarity within the PhCHO moiety suggests that the complex is best described as a W^{VI} metallaoxirane complex, rather than a W^{IV} aldehyde adduct. However, despite this metallaoxirane formalism, the aldehyde ligands are labile, and treatment with excess PMe_3 or Bu^tNC results in the formation of $W(PMe_3)_4(S)_2$ and $W(PMe_3)_2(CNBu^t)_2(S)_2$, respectively.

In conclusion, these studies have demonstrated that elimination of H_2 from H_2S may be readily effected by the electron-rich complex $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, to give the terminal (bis)-sulfido complex $W(PMe_3)_4(S)_2$, which is a useful precursor to other derivatives, namely $W(PMe_3)_2(CNR)_2(S)_2$ and $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHR)$. The structures of these complexes are markedly dependent upon the electronic nature of the tungsten center. In particular, whereas the 18-electron d^2 complexes $W(PMe_3)_2L_2(S)_2$ [L = PMe_3, CNR] exhibit a trans disposition of the sulfido ligands, the formally 16-electron d^0 derivatives $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHR)$ exhibit a *cisoid* arrangement in order to maximize lone pair donation from sulfur to tungsten.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. G.P. is the recipient of an A. P. Sloan Research Fellowship (1991–1993) and a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996).

Supplementary Material Available: Tables of analytical and spectroscopic data for all new compounds, crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters and ORTEP drawings for $W(PMe_3)_2(CNBu^t)_2(S)_2$ and $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)$ (18 pages); tables of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

---

[16] We hesitate to attach too much significance to this observed bond length in view of the small data base available for 18-electron terminal sulfido complexes. See: Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 1437–1438.

[17] A related molybdenum complex $Mo(dppe)_2(O)(S)\cdot SO_2\cdot H_2SO_4\cdot PhCH_3\cdot EtOH$ has recently been structurally characterized [d(Mo═S) = 2.415 (7) Å, d(Mo═O) = 1.77 (1) Å]. Lorenz, I.-P.; Walter, G.; Hiller, W. *Chem. Ber.* **1990**, *123*, 979–982.

[18] (a) Huang, Y.-H.; Gladysz, J. A. *J. Chem. Ed.* **1988**, *65*, 298–303. (b) Garner, C. M.; Quirós Méndez, N.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146–5160. (c) Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1473–1474.

[19] Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298–2308.

[20] Crystal data for $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)$: monoclinic, $P2_1/c$ (no. 14), a = 12.561 (3) Å, b = 8.684 (1) Å, c = 18.182 (3) Å, β = 108.57 (2)°, V = 1879.9 (6) Å^3, Z = 4, ρ_{calcd} = 1.75 g cm^{-3}, μ (Mo Kα) = 68.7 cm^{-1}, λ (Mo Kα) = 0.71073 Å (graphite monochromator); 3686 unique reflections with $3° < 2\theta < 52°$ were collected of which 2820 reflections with $F > 6\sigma(F)$ were used in refinement; R = 0.0348, R_w = 0.0479, GOF = 1.322.

[21] Typical single (C–O) and double (C═O) bond lengths are 1.41 and 1.20 Å, respectively. March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 19.

Facile β-Deprotonation of a Tetraalkyldiazenium Dication

Stephen F. Nelsen* and Yichun Wang

S. M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received February 6, 1991
Revised Manuscript Received May 28, 1991

Removal of an electron from a nitrogen lone pair greatly weakens the C–H bonds α to N. Alkylamine radical cations are therefore typically unstable in nonacidic solution; exceptions require either π delocalization[1] or substituents which enforce geometries having low overlap between the π(N) orbital and σ-(C_α–H) bonds.[2] An adjacent N lone pair is sufficient to stabilize the radical cation toward C_α–H cleavage, as most tetraalkylhydrazine radical cations are long-lived in solution.[3] Removal of a second electron to give the tetraalkyldiazenium dication,

---

[1] For a review, see: Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

[2] (a) Nelsen, S. F.; Kessel, C. R. *J. Chem. Soc., Chem. Commun.* **1977**, 490. (b) Nelsen, S. F.; Cunkle, G. T. *J. Org. Chem.* **1985**, *50*, 3701. (c) Long-lived examples of NN 3e σ-bonded hexaalkylhydrazine radical cations all have low N(SOMO), C_α–H overlap enforced by their structures, see: Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321. Alder, R. W. *Tetrahedron* **1990**, *46*, 683. Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 971.

[3] (a) Nelson, S. F. *Acc. Chem. Res.* **1981**, *14*, 131. (b) Nelson, S. F. In *Molecular Structures and Energetics*; Liebman, J. F.; Greenberg, A. Ed.; VCH: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, p 1.

0002-7863/91/1513-5905$02.50/0