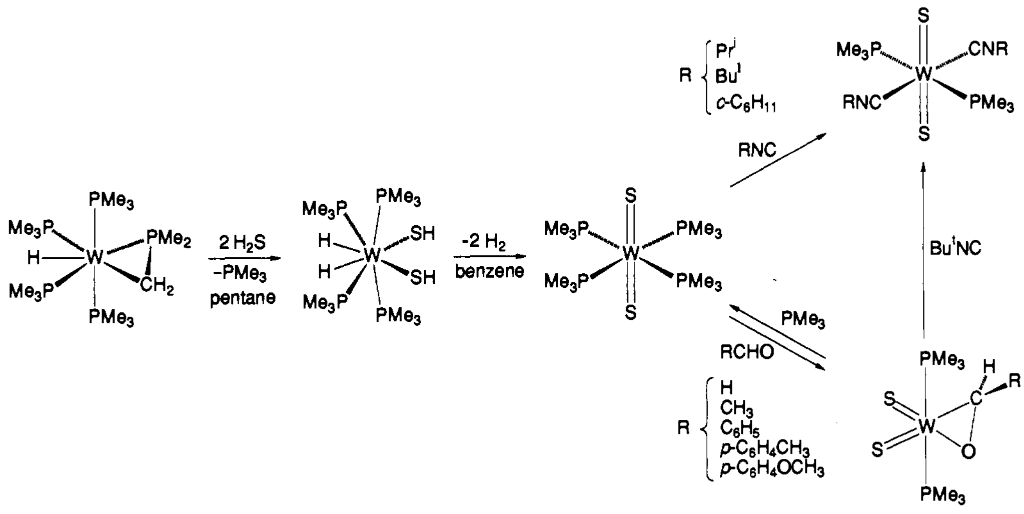
Scheme I



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.

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(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

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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,

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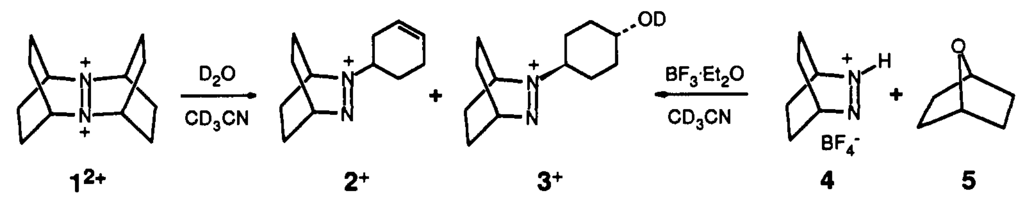
(1) For a review, see: Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

(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.

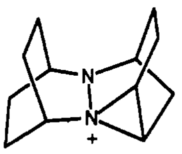
(3) (a) Nelson, S. F. *Acc. Chem. Res.* **1981**, *14*, 131. (b) Nelson, S. F. In *Molecular Structures and Energetics*; Liebman, J. F.; Greenberg, A. Ed.; VCH: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, p 1.

Scheme I

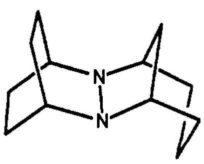


however, typically results in submillisecond lifetimes, as shown by cyclic voltammetry (CV). Loss of a proton from carbon α to nitrogen is presumably the fastest decomposition reaction for compounds with secondary C_α groups. Incorporation of these substituents into bicyclic systems results in great kinetic stabilization when all C_α–H bonds are held near the nodal plane of the N-centered p orbitals.[4] The second CV oxidation waves of such bis(bicycloalkyl)hydrazines are typically completely chemically reversible at slow scan rates, demonstrating dication lifetimes of at least seconds. The only tetraalkyldiazenium dication which has yet proven isolable is that from 2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradecane, **1**,[4b] and crystal structures are available for **1**, $\mathbf{1}^{\bullet+}$, and $\mathbf{1}^{2+}$.[5] This work concerns the unusual reactivity conferred upon $\mathbf{1}^{2+}$ by its doubly positive N-centered π bond.

A solution of $\mathbf{1}^{2+}(PF_6^-)_2$ in 9:1 CD_3CN/D_2O reacts at room temperature over several days to give an approximately 3:1 mixture of trialkyldiazenium cations[6] $\mathbf{2}^+$ and $\mathbf{3}^+$, which were characterized by ^1H an ^{13}C NMR.[7] The structure of $\mathbf{3}^+$ was verified by independent synthesis through alkylation of protonated diazene **4** with 7-oxanorbornane (**5**) and $BF_3 \cdot Et_2O$. Both products could arise from trapping of the carbocation generated by C_α–N cleavage in the polar reaction medium. Reactions run at lower temperature in the presence of base, however, and indicate that $\mathbf{2}^+$ may be formed by decomposition of a thermally unstable intermediate. Reaction of $\mathbf{1}^{2+}$ at 0 °C with K_2CO_3/D_2O solution is complete in 2 h and produces mixtures of $\mathbf{2}^+$ with an unstable intermediate, shown below to be $\mathbf{6}^+$. Mixtures of $\mathbf{2}^+$ and $\mathbf{6}^+$ are also produced at 0 °C by treatment of CD_3CN solutions of $\mathbf{1}^{2+}$ with suspensions of $Me_4N^+Cl^-$ or Na^+OAc^- within 1–4 h. Consumption of $\mathbf{1}^{2+}$ is more rapid with pyridine as the base, and $\mathbf{6}^+$ is formed with only traces of $\mathbf{2}^+$ being produced in 4 h at −25 °C. The ^{13}C and ^1H NMR spectra[8] and chemical reactions of $\mathbf{6}^+$ show it to be the N-alkyl-N-dialkylaminoaziridinium cation illustrated,[9] which is the product of proton loss from C_β of $\mathbf{1}^{2+}$. The intermediate $\mathbf{6}^+$ cleaves exclusively to $\mathbf{2}^+$ with a half-life of 4.1 h at 0 °C, corresponding to a $\Delta G^\ddagger$ of 21 kcal/mol. Conversion of $\mathbf{6}^+$ to $\mathbf{2}^+$ is a retrocheletropic addition of an α-aminonitrenium cation to a double bond, a 4e process which ought to require unsymmetrical twisting at the transition state for orbital symmetry reasons.[10] Such twisting is difficult to accommodate in the tetracyclic structure, presumably contributing to a high enough activation energy for the cleavage to allow $\mathbf{6}^+$ to build up.



$\mathbf{6}^+$



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The C_β–H hydrogens are greatly acidified by the diazenium dication functionality. *It is notable that chloride deprotonates* $\mathbf{1}^{2+}$ *to* $\mathbf{6}^+$, *indicating that* $\mathbf{1}^{2+}$ *is a CH acid which is effectively stronger than HCl.* The reaction could in principle proceed by single electron transfer to produce $\mathbf{1}^{\bullet+}$ and $Cl^\bullet$, followed by hydrogen atom abstraction. The hydrogen atom abstraction would, however, have to be very rapid to compete with other $Cl^\bullet$ reactions. When the weaker base but stronger reductant $Me_4N^+Br^-$ was employed, bromine color and production of $\mathbf{1}^{\bullet+}$ were observed. Use of Na^+PhS^-, a considerably stronger base and reductant than Cl^-, gave diphenyl disulfide and neutral **1**. From these results the SET/hydrogen atom abstraction pathway seems unlikely to us for either Cl^- or pyridine as base.

Chemical evidence for the structure of $\mathbf{6}^+$ is provided by its reduction products. Reaction of $\mathbf{6}^+$ (from $\mathbf{1}^{2+}$ and pyridine) at −25 °C with either solid $NaBH_4$ (for 15 h) or Me_4NBH_4 (for 5 h) produced an approximately 1:1 mixture of **1** and an isomeric $C_{12}H_{20}N_2$ hydrazine identified as **7** from its spectral properties.[11] Hydrazines **1** and **7** each result from reductive cleavage of an $HC–N^+$ bond of $\mathbf{6}^+$. The overall oxidation, deprotonation, reduction route from **1** to **7** is both an interesting 1,2-carbon shift and a synthetic method to obtain "sesquibicyclic" hydrazines that are not available by Diels–Alder addition. Although 6,7-diazabicyclo[3.2.1]oct-6-ene has been prepared in low yield from the tosylhydrazone of 5-hexenal,[12] it is not an easily available compound, in contrast to bicyclic diazenes prepared by Diels–Alder addition of azodicarboxylate derivatives to cyclic dienes. The reaction of $\mathbf{6}^+$ with other nucleophiles and extension of this chemistry to sesquibicyclic hydrazines of other ring sizes are being pursued.

Acknowledgment. We thank the National Institutes of Health for financial support of this work under GM 25949.

Supplementary Material Available: Summary of ^1H NMR assignments for $\mathbf{6}^+$ and **7** and H,H COSY spectra (3 pages). Ordering information is given on any current masthead page.

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(4) (a) Nelson, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702. (b) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 3366. (c) Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *Tetrahedron* **1986**, *42*, 1769. (d) Nelsen, S. F.; Frigo, T. B.; Kim, Y. *J. Am. Chem. Soc.* **1989**, *111*, 5387.

(5) Nelsen, S. F.; Blackstock, S. C.; Haller, K. J. *Tetrahedron* **1986**, *42*, 6101.

(6) (a) Nelson, S. F.; Landis II, R. T. *J. Am. Chem. Soc.* **1973**, *95*, 2719. (b) Nelsen, S. F.; Landis II, R. T. *J. Am. Chem. Soc.* **1974**, *96*, 1788. (c) Snyder, J. P.; Heyman, A. R.; Gundestrup, M. *J. Org. Chem.* **1978**, *43*, 2224. (d) For the X-ray of an *N*-aryl example, see: Engel, P. S.; Hoque, A. K. M. M.; Scholz, J. N.; Shine, H. J.; Whitmire, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 7880.

(7) $\mathbf{2}^+$: ^{13}C NMR (CD_3CN, 90 MHz) δ 126.5, 121.8, 74.7, 68.0, 67.6, 28.1, 25.4, 24.6, 22.7, 22.2; ^1H NMR (CD_3CN, 500 MHz) δ 5.77–5.82 (m, 2 H), 5.68–5.71 (m, 1 H), 5.43 (t, J = 4.0 Hz), 5.06 (tdd, J = 10.5, 5.2, 3.1 Hz, 1 H), 2.69–2.72 (m, 1 H), 2.49–2.55 (m, 1 H), 2.14–2.36 (m, 6 H), 2.05–2.08 (m, 2 H), 1.61–1.66 (m, 2 H), 1.53–1.58 (m, 2 H). $\mathbf{3}^+$: ^{13}C NMR (CD_3CN, 90 MHz) δ 76.9, 67.9, 67.6, 67.5, 31.6, 27.6, 25.5, 22.3; ^1H NMR (CD_3CN, 200 MHz) δ 5.80 (br, 1 H), 5.63 (br, 1 H), 4.71 (tt, J = 10.8, 4.8 Hz, 1 H), 3.57 (tt, J = 10.6, 5.2 Hz, 1 H), 2.4–1.2 (complex, ~16 H). The couplings show that $\mathbf{3}^+$ has trans substituents on its cyclohexane ring.

(8) $\mathbf{6}^+$: ^{13}C NMR (CD_3CN, 125 MHz) δ CH, 61.1, 58.5, 53.6, 50.5, 49.7; CH_2, 30.7, 27.7, 26.6, 23.7, 23.3, 21.9, 16.3; ^1H NMR (CD_3CN, 500 MHz) δ 3.95 (dd, J = 7.5, 5.0 Hz), 3.74 (t, J = 5.3, 5.3 Hz), 3.45, 3.44, 3.23, 2.50, 2.30, 2.26, ~2.18 (3 H), 2.10, 2.00, 1.82 (2 H), 1.74 (2 H), 1.65 (dddd, J = 11.8, 10.6, 7.8, 1.2 Hz, 1 H), 1.45 (dddd, J = 12.6, 11.3, 6.6, 1.2 Hz, 1 H). See supplementary material for partial assignments.

(9) The only other *N*-aminoaziridinium species which have been detected are not closely related structurally, being zwitterionic adducts of triazolinediones to alkenes: (a) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548. (b) Squillacote, M.; Mooney, M.; De Felippis, J. *J. Am. Chem. Soc.* **1990**, *112*, 5364.

(10) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergstr.: Germany, and Academic Press: New York, 1970; p 152. (b) Atkinson and co-workers have shown that reactions formulated for years as proceeding through neutral *N*-nitrenes (for discussion of transition-state geometry, see: Atkinson, R. S.; Grimshire, M. J. *J. Chem. Soc., Perkin Trans. I* **1987**, 1135) involve *N*-acetoxyamino intermediates: Atkinson, R. S.; Kelly, B. *J. Chem. Soc., Chem. Commun.* **1987**, 1362. Atkinson, R. S.; Grimshire, M. J.; Kelly, B. J. *Tetrahedron* **1975**, *45*, 2875.

(11) **7**: empirical formula $C_{12}H_{20}N_2$ established by HRMS; ^{13}C NMR ($CDCl_3$, 90 MHz) δ 67.2, 51.4, 37.6, 33.8, 28.1, 27.3, 21.1; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.40 (~t, 2 H), 2.77 (m, 2 H), 2.17 (m, 3 H), 1.91 (m, 2 H), 1.82 (~nonet, 1 H), 1.65 (m, 4 H), 1.48 (~dt, 1 H), 1.41 (m, 3 H), 1.29 (~td, 2 H). See supplementary material for partial assignments.

(12) Wilson, R. M.; Rekers, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 4005.