We now report the synthesis and X-ray crystal structure of 11-bromo-*endo*-9-chloro-7-ethoxybicyclo[5.3.1]undec-1(11)-ene (**1**), which has the eight-membered-ring double bond in the particularly unfavorable position toward the smallest, i.e., one-carbon, bridge.

Compound **1** was unexpectedly obtained in quantitative yield from the propellane **2** on attempted crystallization from boiling ethanol; **2**, a somewhat unstable compound, was prepared in 16% yield by dibromocarbene addition ($CHBr_3$/KO-*t*-Bu in pentane[8]) to 9-chlorobicyclo[5.3.0]dec-1(7)-ene (**3**)[9] (Scheme I). The formation of **1** can be rationalized by invoking electrocyclic ionization and ring opening of **2** to furnish the intermediate cation **4**, which is intercepted by the solvent. This type of solvolysis has ample precedent in the work or Warner et al. involving the isomeric bicyclo[4.4.1]undecane system where, incidentally, the primary solvolysis products analogous to **1** contain a *trans*-cycloheptane ring and therefore were not stable enough to be isolated.[1a]

Several crystallizations of **1**[10] from ethanol yielded colorless crystals suitable for X-ray crystal structure determination[11] (Figure 1).

Analysis of the X-ray data shows one of the most distorted C=C double bonds experimentally observed so far. This is most clearly seen on inspection of Figure 2. Note, e.g., the large torsion between C2 and C7 ($180 - \theta_1 = 46.4\ (6)°$). In comparison with other highly strained olefins,[3,4,7] it is remarkable that the strain in **1** is revealed not so much by pyramidalization of the olefinic carbon atoms ($\chi_m = 0.5(\chi_1 + \chi_2) = 17.1\ (7)°$) as by an unusually high degree of torsion ($\tau = 29.3°$). This must at least in part be a consequence of the geometrical restrictions imposed by the bicyclo[5.3.1]undecene skeleton. Per degree of deformation, torsion requires more energy than pyramidalization,[7b,c] and therefore geometrically less restricted alkenes respond preferentially by pyramidalization; however, placing the double bond in the shortest bridge of **1** obviously enforces torsion which can be alleviated by pyramidalization only to a minor extent. Interestingly, semiempirical calculations such as MNDO[12] overemphasize this effect by predicting even higher torsion ($\tau = 36.9°$) at the expense of pyramidalization ($\chi_m = 9.6°$). An additional factor may be the bromine substituent at position 11 interacting with C4-H(exo) of the pentamethylene bridge.

Intuitively, one would expect that torsion should weaken the double bond due to decrease of the π-overlap; the calculations seem to support this ($d = 1.36$ Å). Surprisingly, like in other strained olefins,[3,4,7] this is actually not the case in **1**, which has a rather short double bond (d(C1=C11) = 1.319 (8) Å!).

Contrary to other strained anti-Bredt compounds,[1] **1** is not reactive toward oxygen and moisture. Further chemical and physical properties of **1** are presently being investigated.

Acknowledgment. This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid (G.W.W., A.L.S.) from the Netherlands Organization for Scientific Research (NWO).

Registry No. 1, 143841-68-3; **2**, 143841-69-4; **3**, 102836-25-9.

Supplementary Material Available: Tables of crystal data and details of the structure determination, all atomic coordinates and thermal parameters, bond lengths, and bond angles and a thermal motion ellipsoid plot (9 pages); listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

---

(7) For the crystal structure of a nonbridged *trans*-cyclooctene derivative, see: (a) Ermer, O. *Angew. Chem.* **1974**, *86*, 672. (b) Ermer, O. *Aspecte von Kraftfeldrechnungen*; Bauer: München, 1981. (c) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.

(8) Skattebøl, L. *J. Org. Chem.* **1964**, *29*, 2951.

(9) Jenneskens, L. W.; Turkenburg, L. A. M.; de Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 184.

(10) **1**: mp 130 °C; ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.02 (m, 1 H), 1.28 (t, $^3J_{HH} = 7$ Hz, 3 H, Me), 1.6–2.0 (m, 5 H), 2.0–2.3 (m, 4 H), 2.5–2.9 (m, 3 H), 3.18 (m, 1 H), 3.37 (dq, $^3J_{HH} = 7$ Hz, $^2J_{HH} = 8$ Hz, 1 H, OCH_2), 3.49 (dq, $^3J_{HH} = 7$ Hz, $^2J_{HH} = 8$ Hz, 1 H, OCH_2), 4.11 (m, 1 H, CHCl); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 15.5 (q, $J_{CH} = 126$ Hz, Me), 25.6 (t, $J_{CH} = 124$ Hz), 25.9 (t, $J_{CH} = 124$ Hz), 36.6 (t, $J_{CH} = 127$ Hz), 38.1 (t, $J_{CH} = 134$ Hz), 43.3 (t, $J_{CH} = 135$ Hz), 43.8 (t, $J_{CH} = 132$ Hz), 48.6 (t, $J_{CH} = 129$ Hz), 53.4 (d, $J_{CH} = 152$ Hz, CHCl), 59.4 (t, $J_{CH} = 140$ Hz, OCH_2), 83.2 (s), 128.9 (s), 143.7 (s); HRMS ($C_{13}H_{20}O^{81}Br^{35}Cl$) calcd 308.0364, found 308.031.

(11) Crystal data for **1**: $C_{13}H_{20}BrClO$, plate-shaped crystal, monoclinic, space group $P2_1/a$, $V = 1340.15\ (15)$ Å^3, $Z = 4$, μ(Mo Kα) = 32.2 cm^{-1}, 3076 independent reflections ($1.3° < \theta < 27.5°$, $T = 298$ K, Zr-filtered Mo Kα radiation). Data were corrected for Lp, observed linear decay, absorption, and extinction. The structure was solved by automated direct methods (SHELXS86). Refinement on F by full-matrix least-squares techniques (SHELX76); $R = 0.0497$, $wR = 0.0246$, $w^{-1} = \sigma^2(F)$, $S = 1.47$ for 1339 reflections with $I > 2.5\sigma(I)$. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included on calculated positions (C–H = 0.98 Å) in riding mode. No residual density outside −0.47 and 0.61 e Å^{-3}.

(12) MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

Negative Ion Photoelectron Spectroscopy of $CH_2{=}SiH$ and $CH_3{-}Si$

Ashfaq A. Bengali and Doreen G. Leopold*[,1]

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received July 21, 1992

Simple organosilicon radicals are of interest as intermediates in the gas-phase reactions occurring during chemical vapor deposition of silicon carbide,[2] as astrochemically important species,[3] and as benchmarks for theoretical models of silicon–carbon multiple bonding.[4] The electron affinities of several silicon hydrides[5,6] and Si_n clusters[7,8] have been measured by negative ion photoelectron spectroscopy, and values for a number of R_3Si radicals have been obtained by electron photodetachment spectroscopy.[9] We report here the 488-nm photoelectron spectra of the isomeric organosilicon anions $CH_3{-}Si^-$ and $CH_2{=}SiH^-$. These data yield electron affinities for $CH_3{-}Si$ (0.852 ± 0.010 eV) and $CH_2{=}SiH$ (2.010 ± 0.010 eV), as well as vibrational frequencies for both molecules. The measured electron affinities are used to estimate Si–H gas-phase acidities of 372 ± 3 kcal/mol for $CH_3{-}SiH$ and 364 ± 5 kcal/mol for $CH_2{=}SiH_2$. These results provide the first spectroscopic data for $CH_3{-}Si$, $CH_2{=}SiH$, and their negative ions and illustrate of the ability of this experimental technique to identify isomeric structures.

The experimental apparatus employed in these studies has recently been described in detail.[10] Negative ions were prepared at 0.5 Torr in a flowing afterglow ion source by seeding a small amount (1–10 std cm^3/min) of tetramethylsilane-H_{12} or -D_{12} into a fast flow of helium (~8 std l/min) just downstream of a 2.45-GHz microwave cavity. Similarly, a $[Si,C,H_3]^-$ anion was prepared from methylsilane in a previous flowing afterglow study of this system.[11] In the present study, anions sampled from the plasma were mass selected, and the 43 (protonated) or 46 amu

---

(1) NSF Presidential Young Investigator, 1988–1993.

(2) Stinespring, C. D.; Wormhoudt, J. C. *J. Cryst. Growth* **1988**, *87*, 481. Allendorf, M. D.; Kee, R. J. *J. Electrochem. Soc.* **1991**, *138*, 841.

(3) Herbst, E.; Millar, T. J.; Wlodek, S.; Bohme, D. K. *Astron. Astrophys.* **1989**, *222*, 205.

(4) Schaefer, H. F., III *Acc. Chem. Res.* **1982**, *15*, 283. Baldridge, K. K.; Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. Boatz, J. A.; Koseki, S.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1987**, *38*, 211. Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 57.

(5) Kasdan, A.; Herbst, E.; Lineberger, W. C. *J. Chem. Phys.* **1975**, *62*, 541.

(6) Nimlos, M. R.; Ellison, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 6522.

(7) Nimlos, M. R.; Harding, L. B.; Ellison, G. B. *J. Chem. Phys.* **1987**, *87*, 5116.

(8) Kitsopoulos, T. N.; Chick, C. J.; Weaver, A.; Neumark, D. M. *J. Chem. Phys.* **1990**, *93*, 6108. Kitsopoulos, T. N.; Chick, C. J.; Zhao, Y.; Neumark, D. M. *J. Chem. Phys.* **1991**, *95*, 1441.

(9) Wetzel, D. M.; Salomon, K. E.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 3835.

(10) Bengali, A. A.; Casey, S. M.; Cheng, C.-L.; Dick, J. P.; Fenn, P. T.; Villalta, P. W.; Leopold, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 5257.

(11) Damrauer, R.; DePuy, C. H.; Barlow, S. E.; Gronert, S. *J. Am. Chem. Soc.* **1988**, *110*, 2006.

0002-7863/92/1514-9192$03.00/0

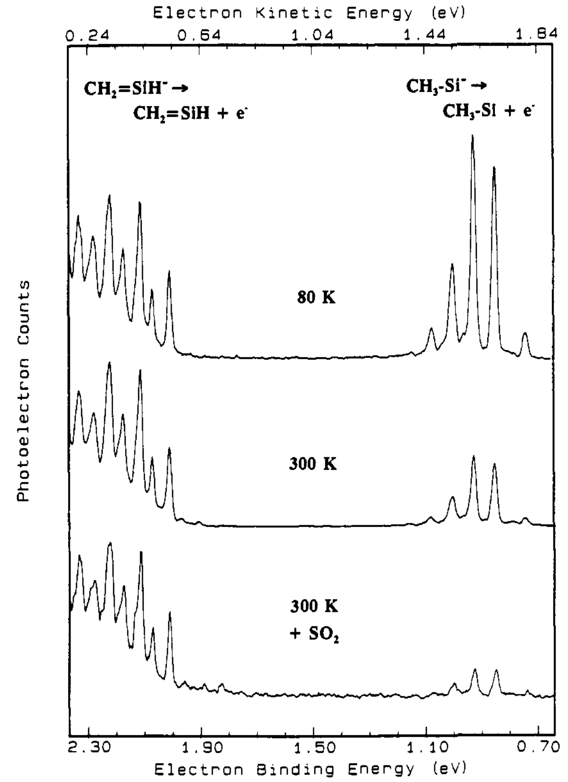


Figure 1. Negative ion photoelectron spectra (488 nm, 2.540 eV) obtained with the flow tube at 80 K (top), at 300 K (middle), and at 300 K after the addition of a small amount of the electron-transfer reagent SO_2 (bottom). The spectra are scaled to show the low eBE bands with the same intensity for ease of comparison. The dramatically different relative intensities of the two band systems under these different ion source conditions demonstrate that they arise from different isomers of the ion. (The weak peak at ~0.74 eV eBE is due to $^{29}SiCH_2^-$.)

(deuterated) ~30-pA ion beam was intersected by an argon ion laser beam. The resulting photoelectrons were energy analyzed at a resolution of 5 meV (40 cm^{-1}).

The 488-nm photoelectron spectrum of the 43 amu ion beam, shown in Figure 1, contains two vibrationally resolved bands. When the temperature of the flow tube is increased from 80 to 300 K, the relative intensity of the band at low electron binding energy (eBE) decreases by a factor of 3. When a small amount of the electron-transfer reagent SO_2 (whose electron affinity is 1.107 ± 0.008 eV)[12] is added to the 300 K flow tube, the relative intensity of the low eBE band decreases by an additional factor of 2. These results show conclusively that these two bands are associated with two different isomers of the anion. Electron photodetachment from these isomeric anions then prepares the corresponding two isomers of the neutral molecule.

The position of the origin of the low eBE band gives an electron affinity of 0.852 ± 0.010 eV for the corresponding isomer. This band shows a single vibrational progression in a mode with a frequency of 610 ± 15 cm^{-1} in the neutral molecule. Since this frequency does not shift significantly on perdeuteration, we assign it as the Si–C stretching vibration. This low frequency is indicative of a single Si–C bond,[13] which limits the possible isomers to CH_3–Si or SiH_3–C. Since the latter is expected[14] to have a substantially higher electron affinity than the value measured here, we assign this band to the CH_3–Si isomer. This is also the more likely species to be produced from $(CH_3)_4Si$; in addition, calculations by Schmidt and Gordon[15] predict CH_3–Si^- to be 59 kcal/mol more stable than SiH_3–C^-.

The spectrum of CD_3–Si^- (not shown) displays a second active mode with a neutral molecule frequency of 470 ± 20 cm^{-1}, which is evidently not resolved from the Si–C stretch in the CH_3–Si^- spectrum. This mode is assigned as the CD_3 rock which is of A′ symmetry in the predicted[14] Jahn–Teller distorted C_s neutral molecule. Its activity in the spectrum indicates that this is the coordinate along which the molecule distorts from C_{3v} symmetry upon electron detachment from the anion, which is predicted[14,15] to have a non-Jahn–Teller distorted triplet $(e)^2$ ground state.

In the high eBE band, the origin peak position gives an electron affinity of 2.010 ± 0.010 eV for the second isomer. This isomer is assigned as CH_2=SiH^- in view of the calculated relative stability of this anion. Schmidt and Gordon predict CH_3–Si^-, SiH_2=CH^-, and SiH_3–C^- to be 10, 35, and 69 kcal/mol higher in energy, respectively.[15] The assignment of the high eBE band to CH_2=SiH^- is supported by the good agreement described below between the observed vibrational frequencies and our calculated values for the corresponding neutral molecule. Since this structure cannot be formed by simple fragmentation of the $(CH_3)_4Si$ precursor, it evidently forms by a more complicated reaction. A slower reaction rate accounts for the reduced yield of CH_2=SiH^- relative to CH_3–Si^- when the flow tube is cooled.

The CH_2=SiH^- band shows two active vibrational modes, with neutral molecule frequencies of 830 ± 15 and 490 ± 15 cm^{-1}. Both frequencies shift substantially on perdeuteration, to 650 ± 15 and 370 ± 15 cm^{-1}, precluding assignment to the Si=C stretch. Our ab initio GAMESS[16] calculations of the neutral molecule, which assumed the previously published[17,18] planar geometry, predict (after application of the usual[19] 10% scaling factor) two modes at 810 and 524 cm^{-1} which shift to 628 and 376 cm^{-1} on perdeuteration, in good agreement with the observed values. These are in-plane modes that involve both HSiC bending and CH_2 rocking motions.

The Si–H gas-phase acidities of methylsilylene (CH_3–SiH) and silaethylene (CH_2=SiH_2) can be estimated from the electron affinities (EA) measured here using the following relation:[20]

$$\Delta H_{\mathrm{ACID},298}(\mathrm{RSi{-}H}) = D_{298}(\mathrm{RSi{-}H}) - \mathrm{EA}(\mathrm{RSi}) + \mathrm{IP}(\mathrm{H})$$

The Si–H bond dissociation energies of CH_3–SiH and CH_2=SiH_2 have not been measured experimentally, but have been calculated by Allendorf and Melius[17] to be 78 ± 3 and 97 ± 5 kcal/mol, respectively. Use of these D_{298} values and the 313.6 kcal/mol ionization potential[21] of H gives Si–H acidities of 372 ± 3 kcal/mol for CH_3–SiH and 364 ± 5 kcal/mol[22] for CH_2=SiH_2. Thus, CH_3–SiH is less acidic than SiH_2 (ΔH_{ACID} = 360 ± 4 kcal/mol)[21] due to the expected[9,23,24] electron-donating effect of the methyl group, which destabilizes the anion and reduces the electron affinity of the corresponding radical (EA[HSi] = 29.4 ± 0.2 kcal/mol,[5] EA[CH_3–Si] = 19.6 ± 0.2 kcal/mol). In addition, silaethylene is more acidic than ethylene (ΔH_{ACID} = 409.4

---

(12) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574.

(13) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 993–1102. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975.

(14) Kalcher, J.; Sax, A. F. *Chem. Phys. Lett.* **1988**, *150*, 99.

(15) Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 5244.

(16) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(17) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1992**, *96*, 428. The uncertainties given above were obtained by adding in quadrature those given in ref. 17 for the corresponding $\Delta H_{f,298}$ values.

(18) Supplementary tables to ref 17.

(19) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1981**, *15*, 269. Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *73*, 2310.

(20) This expression neglects a small heat capacity correction (normally less than 1 kcal/mol) for converting the EA to 298 K (see ref 25).

(21) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.

(22) A value of 363.4 kcal/mol for the gas-phase acidity of CH_2=SiH_2 has been predicted by ab initio molecular orbital calculations: Hopkinson, A. C.; Lien, M. H. *J. Organomet. Chem.* **1981**, *206*, 287. However, this excellent agreement may be somewhat fortuitous, as the same calculation predicted the gas-phase acidity of ethylene to be 431.5 kcal/mol, 22 kcal/mol higher than the measured value (ref 25).

(23) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637.

(24) Weeks, G. H.; Adcock, W.; Klingensmith, K. A.; Waluk, J. W.; West, R.; Vasak, M.; Downing, J.; Michl, J. *Pure Appl. Chem.* **1986**, *58*, 39.

kcal/mol)[25] by ~45 kcal/mol, as is silane (372.2 kcal/mol)[21] than methane (416.8 kcal/mol).[21] This trend reflects the greater ability of the silicon radical to stabilize the negative charge, as is indicated by the 31 kcal/mol higher electron affinities of $CH_2{=}SiH$ (46.4 ± 0.2 kcal/mol) than $CH_2{=}CH$ (15.4 ± 0.6 kcal/mol)[25] and of SiH_3 (32.4 ± 0.3 kcal/mol)[6,9] than CH_3 (1.8 ± 0.7 kcal/mol).[26]

Acknowledgment. We thank Mr. Gregg Dahlke, Dr. Steven Kass, and Mr. Sean Casey for their help with this study. Graduate fellowship support for A.A.B. from the Allied Signal Corporation is also gratefully acknowledged. This research was supported by the NSF under PYI Grant CHE-8858373 and by matching grants from the Amoco, Cray, Ford, GE, and IBM Corporations and from the Electric Power Research Institute.

---

(25) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(26) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

A Single Model Displaying All the Important Centers and Processes Involved in Catalysis by Molybdoenzymes Containing $[Mo^{VI}O_2]^{2+}$ Active Sites

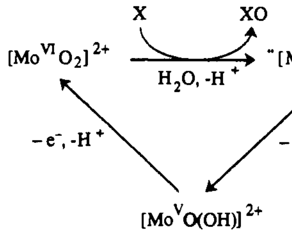
Zhiguang Xiao,[†] Charles G. Young,*[,‡] John H. Enemark,*[,§] and Anthony G. Wedd[†,‡]

Department of Chemistry, La Trobe University
Bundoora, Victoria 3083, Australia
School of Chemistry, University of Melbourne
Parkville, Victoria 3052, Australia
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

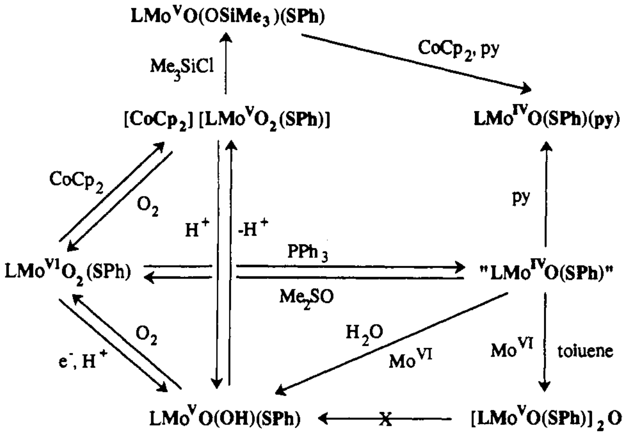
Received June 17, 1992

The molybdopterin enzymes catalyze a variety of two-electron redox reactions involving net exchange of an oxygen atom between substrate and water.[1-4] EPR studies[3] support the regeneration of the active site by two one-electron processes, the first of which produces transient Mo^V states. Many of these enzymes feature $[Mo^{VI}O_2]^{2+}$ resting centers, and Scheme I presents a minimal catalytic cycle, based upon current physical and chemical evidence, for an enzyme such as sulfite oxidase.[1-4] In this and similar systems, transfer of the oxygen atom from Mo to substrate and its replacement from water appear to occur in the Mo^{VI} to Mo^{IV} transformation.[4-6]

Scheme I



Scheme II



No single model system which incorporates all of the species and processes shown in Scheme I has been described. Oxygen-atom-transfer reactions which interconvert $[Mo^{VI}O_2]^{2+}$ and $[Mo^{IV}O]^{2+}$ centers are well-established.[4,7,8] In contrast, the regeneration of a $[Mo^{VI}O_2]^{2+}$ center by two *one-electron* processes initiated on a $[Mo^{IV}O(X)]^{n+}$ ($X = OH^-$ or H_2O from water) center has not been demonstrated. Progress in ligand design has been able to inhibit the condensation of mononuclear Mo^V ($4d^1$) species[7-12] and has allowed characterization of the enzymatically relevant $[Mo^VO_2]^+$ and $[Mo^VO(OH)]^{2+}$ centers in solution.[11,12] However, a combination of redox potentials and reaction rates which allows observation of the full cycle has not been found to date. This communication reports that a model based upon $LMo^{VI}O_2(SPh)$ [L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion] has that necessary combination: observed reactions are outlined in Scheme II. The facially tridentate pyrazolylborate ligand inhibits dinucleation and restricts chemistry to the remaining facial sites; an accurate model of the crucial oxo-ligand based chemistry taking place at the enzyme active site is thereby facilitated. In addition, a $[Mo^VO_2]^+$ center has been isolated in substance for the first time.

Brown $LMo^{VI}O_2(SPh)$ is produced conveniently from the reaction of $LMoO_2Br$, HSPh, and NEt_3 in dichloromethane.[13] In DMF or MeCN, oxygen atom abstraction by PPh_3[8] leads to an intermediate which behaves as if it were coordinatively-unsaturated $LMo^{IV}O(SPh)$ or weakly solvated $LMo^{IV}O(SPh)(solvent)$. It can be trapped as $LMo^{IV}O(SPh)(py)$ in pyridine (85% yield) or, oxidatively, as mononuclear $LMo^VOCl(SPh)$ in CH_2Cl_2 (52% yield) or as binuclear $[LMo^VO(SPh)]_2O$ in dry toluene (13% yield). Unreacted $LMo^{VI}O_2(SPh)$ is the source of oxidizing equivalents in the latter case:

$$\text{“}LMo^{IV}O(SPh)\text{”} + LMo^{VI}O_2(SPh) \rightarrow [LMo^VO(SPh)]_2O$$

Addition of Me_2SO to the Mo^{IV} complexes above regenerates $LMoO_2(SPh)$ in greater than 90% isolable yield.

[†] La Trobe University.
[‡] University of Melbourne.
[§] University of Arizona.

(1) Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59.

(2) Spiro, T. G., Ed. *Molybdenum Enzymes*; Wiley: New York, 1985.

(3) Bray, R. C. *Q. Rev. Biophys.* **1988**, *21*, 299.

(4) Holm, R. H. *Coord. Chem. Rev.* **1990**, *110*, 183.

(5) Hille, R.; Sprecher, H. *J. Biol. Chem.* **1987**, *262*, 10914.

(6) McWhirter, R. B.; Hille, R. *J. Biol. Chem.* **1991**, *266*, 23724.

(7) Holm, R. H.; Berg, J. M. *Acc. Chem. Res.* **1986**, *19*, 363.

(8) Roberts, S. A.; Young, C. G.; Kipke, C. A.; Cleland, W. E., Jr.; Yamanouchi, K.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1990**, *29*, 3650.

(9) (a) Chang, C.-S. J.; Enemark, J. H. *Inorg. Chem.* **1991**, *30*, 683 and references therein. (b) Cleland, W. E., Jr.; Barnhardt, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017.

(10) Spence, J. T.; Minelli, M.; Kroneck, P. *J. Am. Chem. Soc.* **1980**, *102*, 4538.

(11) Dowerah, D.; Spence, J. T.; Singh, R.; Wedd, A. G.; Wilson, G. L.; Farchione, F.; Enemark, J. H.; Kristofzski, J.; Bruck, M. *J. Am. Chem. Soc.* **1987**, *109*, 5655.

(12) Wilson, G. L.; Greenwood, R. J.; Pilbrow, J. R.; Spence, J. T.; Wedd, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 6903.

(13) A solution of $LMoO_2Br$ (0.5 g, 1.0 mmol) in dry, deoxygenated dichloromethane (30 mL) was treated with a solution of HSPh (0.22 mL, 2.0 mmol) and NEt_3 (0.55 mL) in toluene (2 mL), and the mixture was stirred for 2 h. After reducing the volume of solvent, the mixture was column chromatographed (silica/dichloromethane), and the first brown band was collected and evaporated to dryness. The residue was recrystallized from dichloromethane/methanol to give $LMoO_2(SPh)$ (yield 0.48 g, 91%) with spectroscopic properties identical to those previously reported.[8]

0002-7863/92/1514-9194$03.00/0