6160 *J. Am. Chem. Soc.* **1983**, *105*, 6160–6162

to that of the corresponding hydrocarbon, any (E)-**4** formed would isomerize to (Z)-**4**, even at 10 K. We thus suggest that the IR spectrum of **4** corresponds to the Z isomer. Further work to distinguish the spectra and properties of **4** and **5** is in progress.[16,17]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Camille and Henry Dreyfus Foundation for support of this work. The infrared spectrometer was purchased in part with funds from the National Science Foundation (Grant CHE-8117318). G.A.G. thanks Du Pont for a summer research assistantship. We also thank Professor C. P. Casey for the use of an analytical gas chromatograph.

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(15) For ab initio calculations on methanimine's inversional barrier and pertinent references see: Lang, T. J.; Wolber, G. J.; Bach, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 3275. The barrier for **4** may be higher, however, since only limited linearization at N can occur.

(16) As this work was completed we learned that Prof. J. Michl and co-workers have obtained similar results in the photolysis of 1-azidoadamantane to generate matrix-isolated 4-azahomoadamant-3-ene. The infrared spectrum of 4-azahomoadamant-3-ene exhibits a C=N stretch at 1602 cm^{-1}, ca. 15 cm^{-1} higher in energy than the corresponding stretch in **4**. This difference in stretching frequencies is gratifyingly consistent with the calculated differences in olefinic strain values calculated for the corresponding hydrocarbons;[14] OS = 20 kcal/mol for 3-homoadamantene, and OS = 29 kcal/mol for (Z)-bicyclo[3.2.1]oct-1-ene. Interestingly, azahomoadamantene is destroyed photochemically under matrix-isolation conditions, in contrast to **4** and **5**, which are photostable. The reason for this difference in excited-state behavior is not known. The above results have recently appeared: Michl, J.; Radziszewski, G. J.; Downing, J. W.; Wiberg, K. B.; Walker, F. H.; Miller, R. D.; Kovacic, P.; Jawdosiuk, M.; Bonacic-Koutecky, V. *Pure Appl. Chem.* **1983**, *55*, 315. We thank Prof. Michl for communicating these results to us prior to publication.

(17) A referee has questioned whether **4** might not be the corresponding nitrene. The nitrene, however, would not be expected to show a major absorption at 1585 cm^{-1} but would rather appear similar to the IR of 1-norbornylamine. Moreover, the addition product of methanol with **4** is not consistent with the chemistry expected for a nitrene.[2,3]

Sequential Electron-Transfer–Desilylation Pathways for *C*-Vinylazomethine Ylide Formation in the Photochemistry of (1-(Triethylsilyl)allyl)iminium Salts

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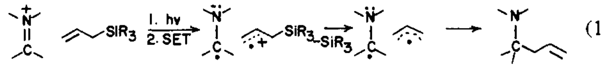
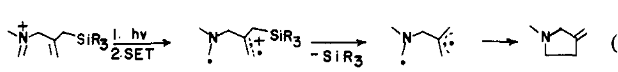
Received May 23, 1983

Studies in our laboratory over the past several years have concentrated on two interconnected aspects of iminium cation photochemistry concerned with the development of mechanistic principles for electron-transfer-initiated photoreactions and explorations for new and synthetically useful photochemical transformations.[1] Several observations made in our recent study of allylsilane–iminium salt systems have demonstrated the mechanistic features of photoaddition reactions initiated by electron transfer and driven by desilylation of allylsilane-derived cation radicals (eq 1).[2] Further investigations have shown that this process serves as the basis for a synthetically useful method for photocyclization (eq 2).[3]



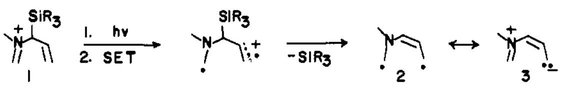
(1)

Our continuing interests in transformtions that follow sequential electron-transfer–desilylation pathways are kindled by thoughts about the development of useful procedures for forming interesting reactive intermediates.



(2)

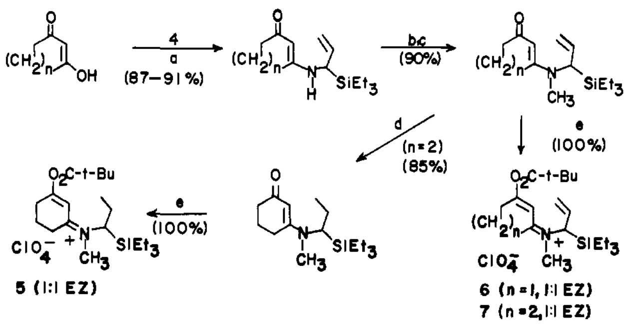
With this aim in mind, we envisaged that the operation of pathways of this type in the excited-state chemistry of (1-(trialkylsilyl)allyl)iminium salts **1** would serve to generate species that can be formulated as diradicals **2** or, if produced in the ground-state singlet manifold, as C-vinylazomethine ylides **3** (eq 3).



(3)

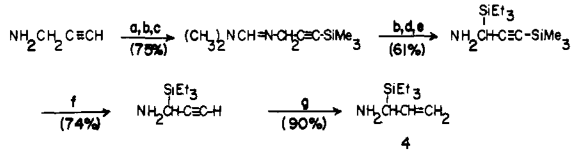
Transformations based upon this design would represent fundamentally important methods for the prepartion of conjugated ylides like **3** and would serve to further verify the generality of electron-transfer–desilylation pathways in excited-state chemistry. The hypothesis embodied in eq 3 has been successfully tested through studies with the β-enaminone-derived ((triethylsilyl)allyl)iminium perchlorates **6** and **7** and the saturated analogue **5**.

Scheme I



(a) C_6H_6, ref; (b) *n*-BuLi, THF, −78 °C; (c) CH_3I, 25 °C, 1 h; (d
(d) H_2, Pd/C, EtOAc, 30 psi; (e) *t*-BuCOCl, $AgClO_4$, CH_3CN.

Scheme II



(a) $(CH_3)_2NCH(OCH_3)_2$, ref, 3 h; (b) *n*-BuLi, −78 °C TMSCl, 25 °C, 1 h; (d) TESCl, 25 °C, 1 h; (e) N_2H_4, *t*-BuOH, 25 °C, 15 h; (f) LiOEt, 25 °C, 10 h; (g) H_2, Pd/$CaCO_3$, Pb pois, THF, 1 atm.

Synthetic routes for preparation of the required allyliminium perchlorates are outlined in Scheme I.[4] The key starting material, and one that will find general use in the preparation of a variety of compounds in this class,[5] is the 1-(triethylsilyl)allylamine **4**. A short, efficient procedure for preparation of **4**, patterned after one employed by Barth and Kolb[6] for unsaturated amino acid synthesis, has been developed starting with propargylamine (Scheme II).[7] It should be noted that selection of the triethylsilyl rather than trimethylsilyl substituents in the iminium salts is dictated by the instability of substances containing the latter grouping under desilylation conditions used for terminal acetylene liberation (Scheme II).

Irradiations of acetonitrile solutions of the allyliminium perchlorates **6** and **7** with light of $\lambda > 280$ nm followed by treatment of the photolysates with aqueous $NaHCO_3$ and silica gel chro-

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(1) For a recent summary of these chemical studies see: Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130.

(2) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617.

(3) Tiner-Harding, T.; Ullrich, J. W.; Chiu, F. T.; Chen, S. F.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 3360.

(4) All new compounds have satisfactory spectroscopic properties and elemental compositions.

(5) Iminium salt preparation can occur by addition of electrophiles to nitrogen of imines derived by reaction of amine **4** with carbonyl compounds.

(6) Kolb, M.; Barth, J. *Tetrahedron Lett.* **1979**, 2999; *Angew. Chem.* **1980**, *19*, 725.

(7) Characteristic spectroscopic properties of the allyliminium perchlorates are as follows. **7**: UV (CH_3CN) λ_{max} 285 nm (ϵ 15 500); ^1H NMR ($CDCl_3$) δ 6.78, 6.70 (OC=CH), 4.53, 4.43 (NC*H*TES), 3.58, 3.49 (NCH_3). **6**: UV (CH_3CN) λ_{max} 279 nm (ϵ 20 200); ^1H NMR ($CDCl_3$) δ 6.82, 6.81 (OC=C-H), 4.49, 4.38 (NC*H*TES), 3.51, 3.45 (NCH_3).

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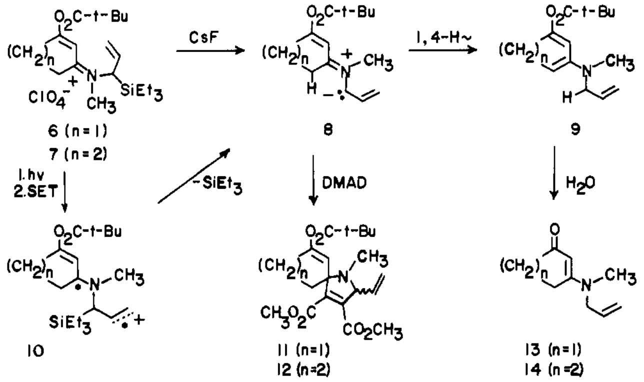
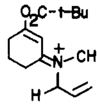
Scheme III



matography leads to efficient (ca. 70%) formation of the *N*-allyl-β-enaminones **13** and **14**, characterized by comparisons of their spectroscopic properties with those of the known six-membered ring compound.[8] Importantly, these β-enaminones are also generated in high yields when the salts are subjected to fluoride ion induced desilylation reaction conditions ((a) CsF, CH_3CN; (b) H_2O) which mimic those used in the elegant method of Vedejs[9] to produce nonconjugated azomethine ylides. On the basis of these observations, we speculate that the enaminones **13** and **14** arise in both the ground- and excited-state processes by secondary intramolecular reactions of initially formed *C*-vinylazomethine ylides **8** involving 1,4-sigmatropic shifts of hydrogen from the ring γ-carbons (Scheme III). The resultant (acyloxy)cycloalkadienes **9** should be readily converted to **13** and **14** under the hydrolytic conditions used in the workup of reaction mixtures.

Definitive proof for the existence of vinylazomethine ylides **8** and dienes **9** as intermediates in the ground- and excited-state transformations has come from UV spectroscopic monitoring of the reaction progresses and from ylide trapping reactions. An intermediate with UV absorption (λ_{max} 295 nm),[10] expected for the cyclohexadiene **9** (n = 2), has been detected in both the photochemical and fluoride ion reactions of **7**. More importantly, irradiation (λ >280 nm) of the iminium perchlorates **6** and **7** in CH_3CN containing 1.3×10^{-1} M dimethyl acetylenedicarboxylate (DMAD) leads to smooth formation (74–75%) of 1:1 mixtures of the epimeric spirocyclic amines **11** and **12** (Scheme III).[11] These products of π4 + π2 dipolarophilic trapping of ylides **8** are also generated when **13** and **14** are treated with CsF in CH_3CN solutions of 1.3×10^{-1} M DMAD. In both processes, intermolecular ylide cycloadditions occur to the total exclusion of intramolecular sigmatropic hydrogen shifts.[12]

Additional information has been gained about the nature of the photochemical reaction pathway for ylide **8** formation and for conversion of **8** to the β-enaminone **14**. An alternate mechanism for conversion of **8** to **14**, for example, could involve proton transfer from the medium to generate a desilylated allyliminium salt **15**, which then undergo hydrolytic conversion to **14**. The operation of this intermolecular pathway appears unlikely since a fully (>95%) protonated β-enaminone is formed when the perchlorate salt **7** is treated with CsF in CD_3CN containing excess D_2O. Thus, the allowed, suprafacial-1,4-sigmatropic hydrogen shift mechanism via diene **9** is in accord with the requirement that the hydrogen delivered to the allylic C-1 position derives from intramolecular sources.



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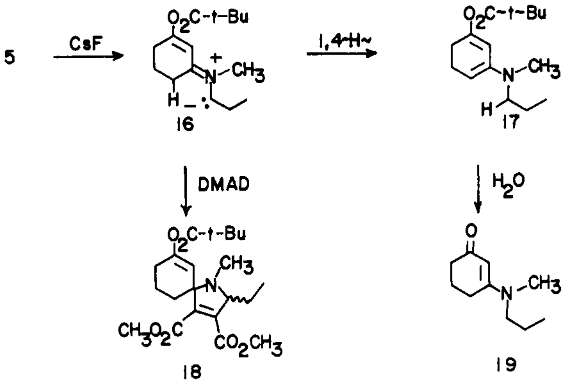
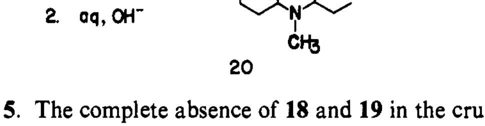
The pathway proposed in Scheme III for *C*-vinylazomethine ylide **8** formation in the excited-state manifold is based upon the expectation that photostimulated electron transfer from the allylsilane to iminium cation groupings in **6** and **7** will be thermodynamically favorable ($\Delta G_{et} < 0$)[13] and, thus, will result in rapid formation of the cation diradicals **10**.[2,3] Nucleophile (CH_3CN or ClO_4^-) induced desilylation should then ensue to produce a ground-state species having ylide rather than diradical character.[14] However, since direct proof for the intermediacy of cation diradicals **10** is missing, it is necessary to consider other reasonable pathways for ylide formation. The possibility exists, for example, that excitation of the iminium cation moiety in these salts brings about population of π–π* singlet states with increased positive charge density on nitrogen, and, thus, it is activated for heterolytic cleavage of the Si–C bond. In order to gain information about this possibility, we have investigated the photochemistry of the iminium salt **5**, which lacks a π-donor grouping in the nitrogen appendage. Prior to this, we observed that indeed the β-enaminone **19** (70%) and spirocyclic amines **18** (76%) are produced by reaction of **5** with CsF (CH_3CN) in the presence and absence of DMAD, respectively. This demonstrates that the ylide **16** is chemically similar to its unsaturated analogues **8**. However, irradiation of **5** in CH_3CN with and without DMAD present followed in each case by aqueous base treatment leads to exclusive production of the triethylsilyl-containing β-enaminone **20**. This substance arises by simple base hydrolysis of unreacted iminium salt **5**. The complete absence of **18** and **19** in the crude photolysates serves as supportive evidence to rule out the intervention of direct heterolytic cleavage pathways for ylide formation and, thus, as indirect evidence in support of the sequential electron-transfer–desilylation mechanism shown in Scheme III.





The observations summarized above exemplify the mechanistic intricacies and potential synthetic applications of iminium salt, electron-transfer photochemistry. Continuing efforts in this area

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[8] Tamura, Y.; Ishibashi, H.; Hirai, M.; Kita, Y.; Ikeda, M. *J. Org. Chem.* **1975**, *40*, 2702.

[9] Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6452; **1980**, *102*, 7993.

[10] The UV maximum at 295 nm, developing during the course of these reactions, shifts to 283 nm upon addition of $HClO_4$ to withdrawn aliquots. This is expected since protonation of the diene should regenerate an iminium salt with properties similar to **7**.

[11] Characteristic spectroscopic data for these substances are as follows. **12** ^{1}H NMR ($CDCl_3$) δ 5.5–5.8 (CH=C), 5.2–5.4 (C=CH_2 and OC=CH), 4.2, 4.4 (NCH), 3.70–3.85 (OCH_3), 2.35 (NCH_3); IR ($CHCl_3$) 1720, 1730, 1650 cm^{-1}. **11**: ^{1}H NMR ($CDCl_3$) δ 5.5–5.8 (CH=C), 5.2–5.5 (C=CH_2, OC=CH), 5.1 (NCH), 3.7–3.8 (OCH_3), 2.25, 2.26 (NCH_3); IR ($CHCl_3$) 1750, 1730, 1675 cm^{-1}.

[12] It is interesting to note that 6-π-electron disrotatory electrocyclizations of ylides **8** are predicted to be allowed and yet do not occur in these systems to a detectable extent. It is highly unlikely that these electrocyclization converting vinylazomethine ylides to Δ^2-pyrrolines would be reversible.

[13] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[14] The excess energy in the cation diradicals **10** gained in the electron-transfer processes ($\Delta G_{et} \sim -20$ kcal/mol) should be rapidly dissipated to the environment prior to desilylation. Thus, reaction of the singlet excited iminium salts should produce singlet ground states which in this case are best represented by zwitterionic rather than diradical structures.

should uncover further information about the fundamental importance of these processes.

Acknowledgment. Support for this research was from grants from the National Institutes of Health (GM-27251) and the National Science Foundation (CHE-09813). Preliminary efforts conducted by Lario V. Yerino are acknowledged.

Reactions of M-M Triple Bonds with C-N Triple Bonds: Adduct Formation (M = Mo) and Metathesis (M = W) As Seen in the Reactions between Dimethylcyanamide and Hexaalkoxides of Dimolybdenum and Ditungsten

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Metal-metal multiple bonds[1] provide the basis for extensive reactivity, which includes redox reactions, cluster syntheses, activation of small unsaturated molecules, and cleavage reactions, yielding new or alternate syntheses of mononuclear compounds.[2] The reactions between $W_2(OR)_6(M{\equiv}M)$ compounds and alkyl or aryl nitriles $R'C{\equiv}N$, which give nitrides, $(RO)_3W{\equiv}N$, and carbynes, $(RO)_3W{\equiv}CR'$, are striking examples of the latter.[3] We report here some observations on the reactions between $M_2(OR)_6(M{\equiv}M)$ compounds (M = Mo, W) and dimethylcyanamide, $Me_2NC{\equiv}N$, which we believe provide insight into the reaction pathway leading to the metathesis of $W{\equiv}W$ and $C{\equiv}N$ bonds.

Hexane solutions of $W_2(O\text{-}t\text{-}Bu)_6$[4] and Me_2NCN (1 equiv) react[5] at room temperature to give a white precipitate of the linear polymer $[(t\text{-}BuO)_3W{\equiv}N]_x$[6] and the hydrocarbon-soluble compound $(t\text{-}BuO)_3W{\equiv}CNMe_2$. The reaction is complete within minutes. The carbyne compound is obtained in analytically pure, crystalline form by (i) filtering off the hexane-insoluble nitride, (ii) stripping the solvent from the filtrate, and (iii) sublimation at 25 °C, 10^{-4} torr. The molecular structure deduced from a single-crystal X-ray study[7] revealed the weakly associated dimer shown in Figure 1. Through the agency of a pair of OR bridges, two TBP tungsten atoms are united along a common axial–equatorial edge. The molecule has virtual C_{2h} symmetry and a crystallographically imposed mirror plane containing the central $[NC{\equiv}W\text{-}\mu\text{-}O]_2$ unit.

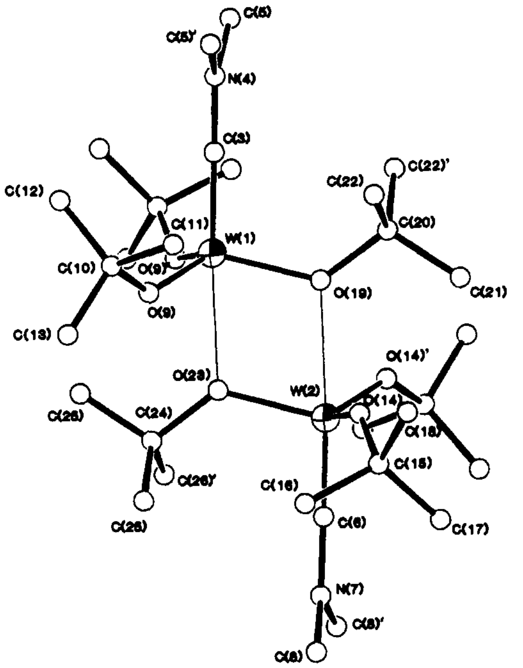

Figure 1. Ball and stick view of the $[(t\text{-}BuO)_3W{\equiv}CNMe_2]_2$ molecule emphasizing the trigonal-bipyramidal coordination at each tungsten atom. Pertinent distances (Å) and angles (deg) are W(1)–O(9) = 1.89 (1), W(1)–O(19) = 1.95 (1), W(1)–O(23) = 2.42 (1), W(1)–C(3) = 1.77 (2), W(2)–O(14) = 1.88 (1), W(2)–O(19) = 2.43 (1), W(2)–O(23) = 1.94 (1), W(2)–C(6) = 1.75 (2), N(4)–C(3) = 1.34 (2), N(7)–C(6) = 1.39 (2); ∠W(1)–C(3)–N(4) = ∠W(2)–C(6)–N(7) = 179 (2), ∠O(23)–W(1)–C(3) = ∠O(19)–W(2)–C(6) = 177 (1).

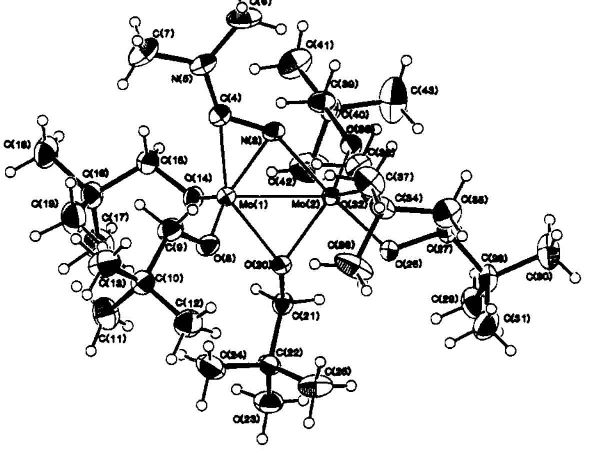

Figure 2. ORTEP view of the $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$ molecule. Pertinent distances (Å) and angles (deg) are Mo–Mo = 2.449 (1), Mo–O (terminal OR) = 1.92 (2) (averaged), Mo(1)–O(20) = 2.146 (2), Mo(1)–N(3) = 1.908 (3), Mo(1)–C(4) = 2.014 (4), Mo(2)–O(20) = 1.999 (2), Mo(2)–N(3) = 2.134 (2), N(3)–C(4) = 1.333 (4), C(4)–N(5) = 1.324 (4); ∠Mo(1)–C(4)–N(5) = 167.0 (3), ∠(3)–C(4)–N(5) = 127.1 (3), ∠C–N(5)–C = 120 (1) (averaged).

Addition of dimethylcyanamide (1 equiv) to $Mo_2(OR)_6$[8] compounds under directly analogous conditions gives 1:1 adducts $Mo_2(OR)_6(\mu\text{-}NCNMe_2)$, where R = *t*-Bu,[9] *i*-Pr[9], and $CH_2\text{-}t\text{-}Bu$. Crystals suitable for an X-ray study were obtained for the neopentoxide from hexane and thereafter revealed[7] the fascinating molecular structure shown in Figure 2. Superficially, the central $Mo_2(\mu\text{-}NCNMe_2)$ unit appears similar to that in $Cp_2Mo_2(CO)_4(\mu\text{-}NCNMe_2)$,[10] as indeed was suggested[9] for the compounds $Mo_2(OR)_6(\mu\text{-}NCNMe_2)$, where R = *t*-Bu and *i*-Pr, on the basis of IR and NMR spectroscopic data. However, in the structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$, we see (relative to $Cp_2Mo_2(CO)_4(NCNMe_2)$) (i) a much longer $Me_2NC\text{-}N$ distance, 1.333 (4) Å (cf. 1.236 (9) Å), comparable to that in pyridine and

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[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[2] Chisholm, M. H. *ACS Symp. Ser.* **1981**, *No. 155*.

[3] Schrock, R. R.; Listerman, M. L. Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

[4] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

[5] All reactions and manipulations were carried out using dry and oxygen-free solvents and atmospheres.

[6] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.*, in press.

[7] Crystal data for $(t\text{-}BuO)_3W{\equiv}CNMe_2$: orthorhombic, space group *Pnma* with $a = 23.246$ (9), $b = 17.031$ (5), $c = 9.719$ (2) Å; $D_{calcd} = 1.586$ gm cm^{-3} for $Z = 8$; temperature, −104 °C. Phase transition (reversible) at ca. −120 °C, yielding triclinic cell of approximately the same dimensions; $R = 0.045$ and $R_w = 0.043$ for 2336 observed data to $2\Theta = 45°$ (Mo*Kα*). Crystal data for $Mo_2(OCH_2\text{-}t\text{-}Bu)_6(\mu\text{-}NCNMe_2)$: triclinic, space group $P\bar{1}$ with $a = 19.738$ (6), $b = 11.390$ (2), $c = 10.112$ (2) Å, $\alpha = 85.42$ (1), $\beta = 104.69$ (1), $\gamma = 104.20$ (1)°; $D_{calcd} = 1.232$ gm cm^{-3} for $Z = 2$; temperature, −120 °C; $R = 0.031$ and $R_w = 0.032$ for 4771 observed data to $2\Theta = 45°$ (Mo K*α*). A second phase, also triclinic, occurs below −140 °C, yielding an identical structure with the exception of a different conformer for one of the terminal $OCH_2\text{-}t\text{-}Bu$ groups.

[8] Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

[9] Chisholm, M. H.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 2321.

[10] Chisholm, M. H.; Cotton, F. A.; Extine, M. Ws.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 807.

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