imental details, atomic coordinates and thermal parameters, and selected distances and angles (7 pages); listing of observed and calculated structure factors for **3** (31 pages). Ordering information is given on any current masthead page.

Reversible Generation of Trimethylenemethanes by Mild Thermolysis of Dialkoxymethylenecyclopropanes

Eiichi Nakamura,*,†,‡ Shigeru Yamago,† Satoshi Ejiri,†
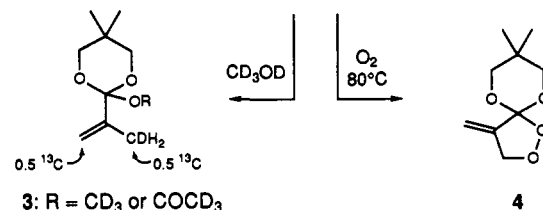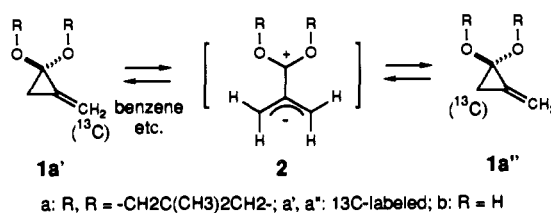Andrea E. Dorigo,§ and Keiji Morokuma*,§

*Department of Chemistry, Tokyo Institute of Technology
Meguro, Tokyo 152, Japan
Institute for Molecular Science
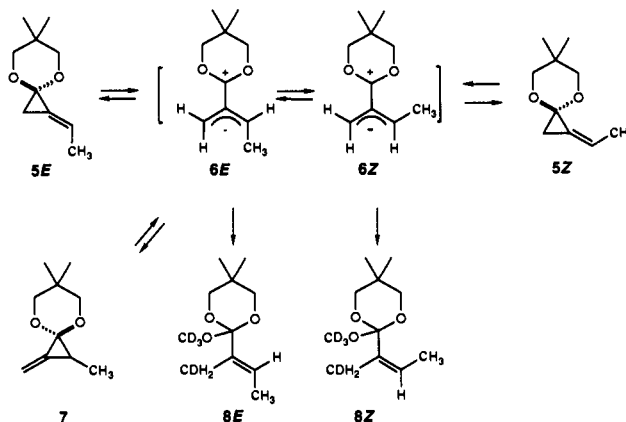Myodaiji, Okazaki 444, Japan*

Trimethylenemethane (TMM) is a uniquely important diradical species that has long attracted the interest of chemists.[1] Thermolysis of methylenecyclopropanes (MCPs) should provide a simple entry to the TMMs, and indeed we find many such allusions in the literature.[2] However, to date no direct evidence for the formation of a discrete TMM has been obtained,[3] except for the thermolysis of a strained [2.1.0] bicyclic skeleton.[4] We now report the first direct experimental evidence that *reactive TMM species can be generated thermally and reversibly from simple monocyclic MCPs.* We also describe ab initio theoretical studies on a model species.

The specific MCP under study is the dialkoxy MCP **1a**, which has apparent thermal stability (100 °C, 24 h, toluene), yet undergoes thermal [3 + 2] cycloadditions.[5] Initial information on the dynamic properties of **1a** was gained by the observation of the facile thermal rearrangement of **1a′** [6] (the *exo*-methylene carbon is ^{13}C labeled) to **1a″**, which now bears the ^{13}C label on the ring carbon (Scheme I). The isomerization proceeded rapidly at 40-70 °C, producing a 1:1 mixture of **1a′** and **1a″**.[7] The first-order rate constant (k) of the reaction (60 °C, C_6D_6: 0.30 M solution throughout the studies) was 9.6×10^{-5} s^{-1}, and the activation energy (E_a) was 25.5 kcal/mol (50-70 °C), a value

† Tokyo Institute of Technology.
‡ Adjunct professor of the Institute for Molecular Science.
§ Institute for Molecular Science.

(1) (a) Theory: Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967 and references therein. (b) Physical organic chemistry: Weiss, F. *Q. Rev., Chem. Soc.* **1970**, *24*, 1970. Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799. See also ref 10b. (c) Synthesis: Little, R. D. *Chem. Rev.* **1986**, *86*, 875. Welzel, P. *Nachr. Chem., Tech. Lab.* **1983**, *31*, 638. (d) Organometallics: Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279. Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 357.

(2) (a) Reviews: Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980, p 311. Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981. (b) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904 and references therein.

(3) (a) Diradical transition state hypothesis: Buchwalter, S. L. *Tetrahedron* **1984**, *24*, 5112. (b) A concerted transition state located with ab initio SCF/6-31G* and MP2/6-31G* calculations (Skancke, A.; Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5315) collapses upon geometry optimization to TMM at a CASSCF level employed in this work.

(4) (a) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 684. (b) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2233. (c) For an excellent account of the problems in the MCP rearrangements, see: Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2228.

(5) (a) Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1989**, *111*, 7285. (b) Yamago, S.; Nakamura, E. *J. Org. Chem.* **1990**, *55*, 5553.

(6) See the supplementary material.

(7) The precision of NMR measurements precludes investigation of the isotope effects.

Scheme I

a: R, R = -CH2C(CH3)2CH2-; a′, a″: 13C-labeled; b: R = H

3: R = CD₃ or COCD₃   **4**

Scheme II

much lower than that for the unsubstituted MCP.[8] The E_a of the rearrangement in CD₃CN was 22.2 kcal/mol ($k = 6.0 \times 10^{-4}$ s^{-1}, 60 °C). The rate (60 °C) increased by a factor of 191 as the solvent was changed from C_6D_{12} (5.7×10^{-6} s^{-1}) to DMSO-d_6 (1.1×10^{-3} s^{-1}), suggesting a relatively polar transition state. The rate of the rearrangement of **1a′** changed little in the presence of 1,4-dinitrobenzene (1 equiv, a radical trap) or under 1 atm of oxygen. However, bubbling oxygen into a heated toluene solution of **1a** (80 °C, 24 h) effect slow conversion of **1a** to an unstable peroxide **4** (40%).[9] In no cases did we observe CIDNP signals during the NMR analyses.[10]

Direct evidence for the TMM **2a** was obtained by solvolysis of **1a′** in deuterated acidic solvents. Thus, the reaction of **1a′** in CD₃COOD or CD₃OD at 40-60 °C gave an ortho ester **3** in quantitative yield, *wherein a deuterium was specifically found on the allylic methyl group with complete scrambling of the ^{13}C label whereas the label in 1a′ remained intact throughout the reaction*, indicating that the "memory" of the labeling in **1a′** was lost at a D⁺ quenching stage.[11] No products due to D· abstraction from the CD₃ group of the solvent were observed. Hydrolysis of **1a′** in DCl/D₂O also proceeded quantitatively with complete ^{13}C scrambling. The pseudo-first-order rate constant of the methanolysis of **1a** at 60 °C was 1.1×10^{-3} s^{-1} with $E_a = 24.9$ kcal/mol

(8) (a) Ullmann, E. F. *J. Am. Chem. Soc.* **1960**, *82*, 505. Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720. Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 4450. (b) LeFevre, G. N.; Crawford, R. J. *J. Org. Chem.* **1986**, *51*, 747 and references therein. (c) For the rearrangement of monoalkoxy MCPs: Baldwin, J. E.; Ghatlia, N. D.; Lundbäck, M. O. *Acta Chem. Scand.* **1987**, *B41*, 698. Kirmse, W.; Murawski, H.-R. *J. Chem. Soc., Chem. Commun.* **1977**, 122.

(9) Cf.: Wilson, R. M.; Geiser, F. *J. Am. Chem. Soc.* **1978**, *100*, 2226.

(10) For CIDNP in TMM chemistry, see: Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276.

(11) The [3 + 2] cycloaddition[5a] to dimethyl fumarate (solvent) and the label scrambling proceeded at a comparable rate.
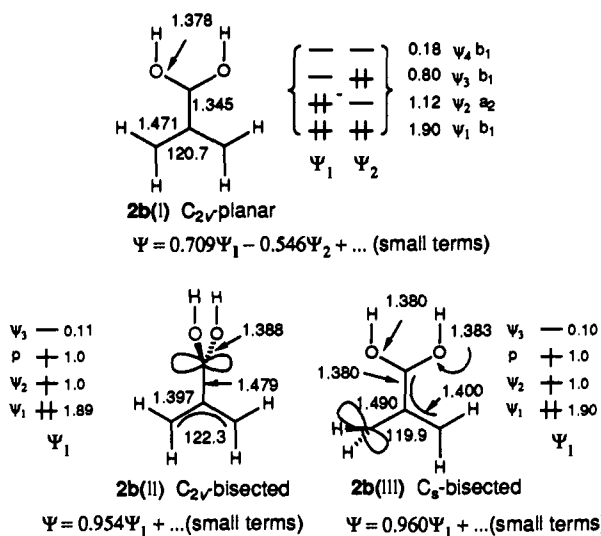
J. Am. Chem. Soc. 1991, 113, 3184–3186

Figure 1. Optimized geometries (Å; deg) and natural orbital occupancies of 2b(i)–(iii).

(40–60 °C). These solvolysis experiments are consistent with the formation of a *symmetrical* zwitterionic intermediate **2a**, wherein the two methylene groups are nucleophilic and chemically equivalent. The close similarity of the E_a of the rearrangement and the methanolysis suggests that both reactions proceed through the same reaction pathway involving the dialkoxy TMM **2a**.[12]

We also generated the methyl-substituted TMMs **6** from MCPs **5**[4b] and studied their stereochemical behavior through methanol trapping and thermal isomerization (Scheme II). Thus, the reaction of **5E**[5b] and **5Z**[5b] in CD_3OD at 70 °C quantitatively and stereospecifically gave the (*E*)-tiglate (**8E**) and (*Z*)-tiglate ortho esters (**8Z**), respectively.[6] Evidently, the stereospecific ring opening gave TMMs, **6E** and **6Z**, as discrete intermediates. While the methanolysis allowed trapping of each TMM stereoisomer, thermolysis experiments indicated that these isomers undergo stereochemical isomerization. Thus, heating of both **5E** and **5Z** at 100 °C in toluene resulted in clean interconversion of these isomers. This experiment also generated a third isomer, **7**,[5] as the result of an alternative ring closure (Scheme II), and **7** in turn gave **5E** and **5Z** upon heating. The equilibrium ratio (100 °C) of **5E**, **5Z**, and **7** (starting from pure isomer) was 62:30:8.[13]

Ab initio four electron/four orbital CASSCF (three π orbitals of the allylic system and the p orbital of the remaining carbon: 6-31G basis set) calculations were carried out on the singlet state of **2b**[14] to determine the geometry and nature of the intermediate (Figure 1). It has been found that all three possible low-energy conformers, the C_{2v}-planar **2b(i)**, the C_{2v}-bisected **2b(ii)**, and the C_s-bisected **2b(iii)**, have nearly the same energy. The C_s-bisected conformer **2b(iii)** was found to be most stable, and **2b(ii)** and **2b(i)** were found to be only 4.23 and 4.44 kcal/mol higher in energy, respectively.[15] All these conformers should be equally available for the intermolecular reactions, since the energy barriers separating the three rotational isomers must be small.[1a] Although **2b(ii)** and **2b(iii)** are pure diradicals by symmetry, **2b(i)** has some zwitterionic character (Figure 1) and is best described in terms

of the resonance structures **2b(i)**ₗ and **2b(i)**ₗₗ. It is reasonable to suggest that the contribution of these two resonance forms should be influenced upon going from the gas to the polar liquid phase and that the reactivity of **2a** toward polar reactants (e.g., methanol) is governed by the zwitterionic character of **2b(i)**. In this case, the allylic moiety of **2a** can be viewed as a four π electron system (**2b(i)**ₗ) suitable for undergoing stereospecific [3 + 2] cycloaddition to electron-deficient olefins.[5a]

Supplementary Material Available: Preparation of MCPs and the experimental details of their rearrangement and methanolysis (14 pages). Ordering information is given on any current masthead page.

The First Homoleptic Alkoxide Dimers of Rhenium(V) and Tungsten(V). Stereochemical Consequences of Metal–Metal Bonding in Edge-Shared Bioctahedra

Jeffrey C. Bryan,[1a] David R. Wheeler,[1a] David L. Clark,[1b]
John C. Huffman,[1c] and Alfred P. Sattelberger*,[1d]

*Inorganic and Structural Chemistry Group (INC-4) and
Nuclear and Radiochemistry Group (INC-11)
Los Alamos National Laboratory
Los Alamos, New Mexico 87545
Molecular Structure Center, Indiana University
Bloomington, Indiana 47405*

Received November 26, 1990

Edge-shared bioctahedral transition-metal complexes of general formula M_2L_{10} have long been recognized as one of the four most frequently occurring structural types for dinuclear compounds that contain metal–metal bonds.[2] Such complexes can, in principle, exhibit metal–metal single, double, and triple bonds by overlap of metal d orbitals. While the concept of a triple bond for edge-shared bioctahedra is enigmatic,[3–5] single and double bonds of valence electronic configuration σ^2 and $\sigma^2\pi^2$ are well-known for d^1 and d^2 early transition metals.[3] An exception to this observation can be found in high-oxidation-state d^1 and d^2 metal halides, M_2Cl_{10} (M = Mo, W, Re), which are paramagnetic with M–M distances on the order of 3.7 Å.[6–8] It has been suggested that replacement of bridging chloride ligands with bridging-oxygen donors may reduce the positive charge on the metal atoms and facilitate d–d overlap in d^1 and d^2 dimers.[9] Here we describe the synthesis and molecular and electronic structures of two new high-oxidation-state edge-shared bioctahedral complexes, $W_2(OMe)_{10}$ and $Re_2(OMe)_{10}$, which fulfill this expectation.

The addition of 1 equiv of lithium powder to a THF solution of *cis*-$WF_2(OMe)_4$ (prepared from WF_6 and neat Me_3SiOMe[10]) produces a mixture of red tungsten(V) products characterized as $W_2F_x(OMe)_{10-x}$ where x = 1–3 based on ^1H and ^{19}F NMR. This mixture reacts with excess sodium methoxide in THF to form blue $W_2(OMe)_{10}$ (**1**)[11] as the only soluble tungsten product (70% yield,

(12) An unlikely alternative (experimentally distinguishable, however, ref 4a) is that the methanolysis involves a bimolecular addition of a methoxide anion to **1a** to give a symmetrical allylic anion. We thank a referee for reminding us of this possibility.
(13) Interconversion between **5E** and **7** takes place rapidly at 80 °C, while conversion to and from **5Z** requires a week at 100 °C.
(14) (a) For the chemistry and molecular orbitals of dimethoxy TMM incorporated in a five-membered ring, see: Carpenter, B. K.; Little, R. D.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5723. Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725. Siemionko, R.; Shaw, A.; O'Connell, G.; Little, R. D.; Carpenter, B. K.; Shen, L.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3529. (b) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.
(15) Presumably, all of these are not local minima, but no confirmation has been made.

(1) (a) INC-4, Mail Stop C345. (b) INC-11, Mail Stop G739. (c) Indiana University. (d) INC-DO, Mail Stop J515.
(2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; Chapter 23.
(3) Cotton, F. A. *Polyhedron* **1987**, *6*, 667.
(4) Cotton, F. A.; Diebold, M. P.; O'Connor, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438.
(5) Chakravarty, A. R.; Cotton, F. A.; Diebold, M. P.; Lewis, D. B.; Roth, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 971.
(6) Sands, D. E.; Zalkin, A. *Acta Crystallogr.* **1959**, *12*, 723.
(7) Cotton, F. A.; Rice, C. E. *Acta Crystallogr., Sect. B* **1978**, *34*, 2833.
(8) Mucker, K.; Smith, G. S.; Johnson, Q. *Acta Crystallogr., Sect. B* **1968**, *24*, 874.
(9) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Ilsley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.
(10) Handy, L. B.; Sharp, K. G.; Brinkman, F. E. *Inorg. Chem.* **1972**, *11*, 523.

0002-7863/91/1513-3184$02.50/0 © 1991 American Chemical Society