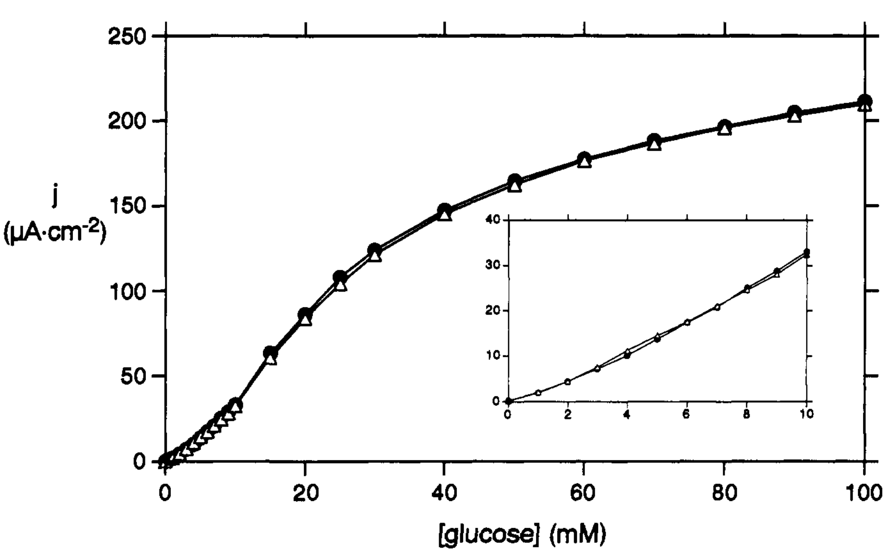

Figure 2. Calibration curve for glucose using the bilayer electrode of Figure 1 in the presence of 1.0 mM hydrogen peroxide: (a) (Δ) without interferants present and (b) (●) in the simultaneous presence of 0.1 mM ascorbate, 0.1 mM *p*-acetamidophenol, and 0.5 mM urate. The insert shows the calibration in the physiological concentration range of glucose.

a sensing layer. The glucose oxidase (GOD) was electrically "wired" to the electrode with a redox epoxy gel matrix.[7] This electrode is based on a 130 kilodalton poly(vinylpyridine) complex of osmium bis(bipyridyl) chloride with GOD cross-linked with a 400 dalton polyethyleneglycol diglycidyl ether. This glucose electrode of high current density and fast response is sensitive to electrooxidizable interferants. This sensitivity is eliminated by coating the glucose sensing layer with a layer of immobilized HRP. While the interferants are eliminated, the response to glucose is unaffected (Figure 1). The current, increasing monotonically with glucose concentration, does not change when the concentration of the interferants is increased. An electrode potential of +0.5 V (SCE) was maintained throughout these measurements to prevent potentially interfering HRP-catalyzed electroreduction of H_2O_2. Figure 2 shows calibration curves under elimination conditions for glucose and for glucose in the presence of the interferants at their physiological levels. It is seen that the glucose response is not affected by the addition of interferants even though in the absence of hydrogen peroxide the current density for the combined interferants is 10^2 $\mu A{\cdot}cm^{-2}$.

Hydrogen peroxide, essential for eliminating the interferants, cannot be externally added in in vivo assays but can be produced in situ by oxidases; thus, lactate oxidase (LOD) generates hydrogen peroxide in the presence of lactate and oxygen (eq 2). Using an electrode containing LOD (250 $U{\cdot}cm^{-2}$) coimmobilized with HRP and physiological levels of lactate (0.5 mM) we oxidatively stripped the interferants and accurately measured glucose levels without adding hydrogen peroxide. The results we obtained were similar to those shown in Figure 2. A control experiment performed to examine the effect of addition of lactate (1.5 mM) on the electrocatalytic oxidation current for 5 mM glucose showed that the change in the current was less than 2%. Since electrooxidation of glucose at the wired GOD does not involve O_2, the removal of oxygen by lactate (eq 2) has only a marginal effect on the glucose assay. The current does not change with lactate concentration, because LOD is not "wired" to the electrode being physically separated from the redox epoxy. The one purpose of LOD in this structure is to produce in situ hydrogen peroxide for the HRP-catalyzed elimination of interferants. The LOD-catalyzed generation of H_2O_2 is O_2 dependent, and no peroxide is formed in the total absence of oxygen. In the physiological range oxygen concentrations provide, however, the excess hydrogen peroxide needed, and thus fluctuations in oxygen concentration do not affect the elimination of interferants.

$$2CH_3CH(OH)COO^- + O_2 \xrightarrow{LOD} 2CH_3COCOO^- + H_2O_2 \qquad (2)$$

In summary, peroxidase-based layers effectively eliminate interferants in the presence of hydrogen peroxide without affecting the glucose quantitation, allowing selective measurement of its concentration.

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The Ring Opening and Unusual Coupling of 3,3-Dimethylthietane Ligands in a Dirhenium Carbonyl Complex

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Recent reports have described the first examples of ring-opening reactions of thietane ligands by metal cluster complexes.[1–6] A range of processes have been observed: thermal,[1,2,6] photochemical,[3] and nucleophile promoted,[4,5] which suggests that a variety of mechanisms may be operative. We have recently reported the first example of a facile, metal-promoted, head-to-tail ring-opening oligomerization of 3,3-dimethylthietane, DMT, through a process that is initiated by a bridging coordination of the first molecule to a triosmium cluster.[4] We have now discovered a novel photoassisted ring opening and coupling of two DMT ligands in a dirhenium complex that culminates with the formation of a disulfide link between two metallacycles.

The reaction of $Re_2(CO)_8[\mu\text{-}C(H)CBu^n](\mu\text{-}H)$[7] with DMT in refluxing CH_2Cl_2 yielded the complex 1,2-$Re_2(CO)_8$-$(\overline{SCH_2CMe_2CH_2})_2$ (**1**) in 71% yield.[8] Compound **1** was char-

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(1) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 2651.
(2) Yamamoto, J. H.; Yap, G. P. A.; Jensen, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 5060.
(3) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 1718.
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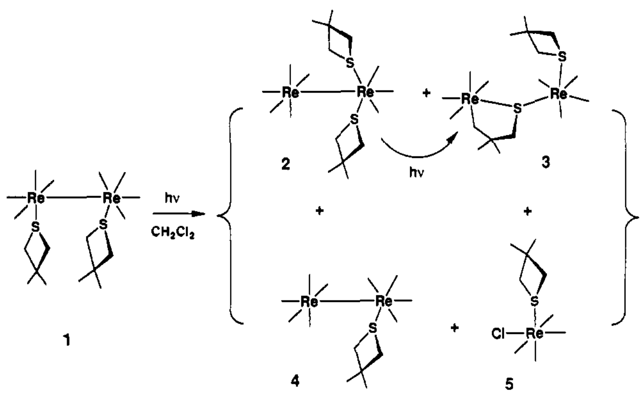
Scheme I



acterized crystallographically and was found to contain the expected 1,2-disubstituted $Re_2(CO)_{10}$ structure with the sulfur-coordinated DMT ligands in equatorial coordination sites.[9,10] Four new compounds were formed when compound **1** was exposed to fluorescent room light over a period of 4 days.[11] These compounds have been identified as 1,1-$Re_2(CO)_8(\overline{SCH_2CMe_2CH_2})_2$ (**2**), 8%; $Re_2(CO)_8(\overline{SCH_2CMe_2CH_2})(\mu\text{-}SCH_2CMe_2CH_2)$ (**3**), 16%; $Re_2(CO)_9(\overline{SCH_2CMe_2CH_2})$ (**4**), 6%; and *cis*-$ReCl(CO)_4(\overline{SCH_2CMe_2CH_2})$ (**5**), 19%. All four compounds were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.[9,11,12] Compound **2** is an isomer of **1** formed by the interchange of one DMT ligand and one carbonyl ligand between the metal atoms; see Scheme I.

Compound **3** is an isomer of both **1** and **2**, but has one of its DMT rings opened to form a 3,3-dimethylthiametallacyclopentane ring. The sulfur atom bridges the two metal atoms, while the carbon atom is coordinated solely to Re(1), Re(1)–C(3) = 2.27 (1) Å. The metal–metal bond was cleaved, Re(1)⋯Re(2) = 4.425 (1) Å, and the untransformed DMT ligand is coordinated to Re(2) in a site cis to the bridging sulfur atom. Compound **4** is a monosubstituted DMT derivative of $Re_2(CO)_{10}$. Compound **5** is a monosubstituted DMT derivative of $Re(CO)_5Cl$. The chloro ligand was evidently abstracted from the solvent. $Re_2(CO)_{10}$ is also known to abstract halogen from halogenated solvents when exposed to UV–vis radiation.[13] Compound **3** can be obtained from **2**, but the yield is not high (~10%). When the transformation of compound **2** was followed by ^1H NMR spectroscopy, large amounts of free DMT were observed to form (which may account for the low yield) together with some **4** (7%) and **5** (15%).

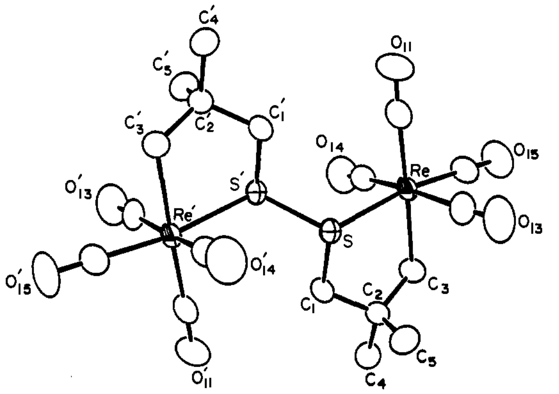
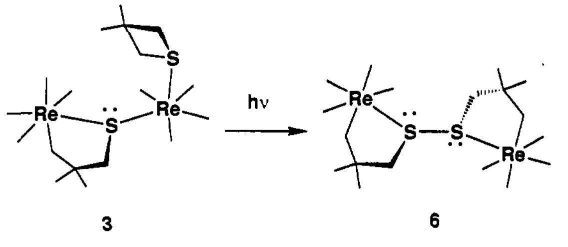


Figure 1. ORTEP diagram of $[\overline{Re(CO)_4(SCH_2CMe_2CH_2)}]_2$ (**6**). Selected interatomic distances (Å) and angles (deg) are Re–S = 2.450 (2), S–S′ = 2.121 (3), Re–C(3) = 2.267 (6), S–C(1) = 1.830 (6), and Re–S–S′ = 111.6 (1).

A most unusual photoreaction was observed when compound **3** was exposed to radiation from a closely placed fluorescent lamp. Another isomer, $[\overline{Re(CO)_4(SCH_2CMe_2CH_2)}]_2$ (**6**), was obtained, in 18% yield, after 6 h in CH_2Cl_2 solvent, eq 1.[14] The molecular structure of **6** was established crystallographically and is shown in Figure 1.[15] This molecule contains two $\overline{Re(CO)_4(SCH_2CMe_2CH_2)}$ metallacycles joined by a disulfide link, S–S′ = 2.121 (3) Å, and has a crystallographically imposed center of symmetry midway between the sulfur atoms. The rhenium–sulfur and rhenium–carbon distances are similar to those in **3**, Re–S = 2.540 (2) Å and Re–C(3) = 2.267 (6) Å. Each sulfur atom donates a lone pair of electrons to the metal in its ring system, and the metal atoms then achieve 18-electron configurations. However, the sulfur atoms also contain an uncoordinated pair of electrons, which induces a pronounced pyramidal geometry.



(1)

The mechanisms of the ring openings and formation of the

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(8) The reaction of 333 mg (0.49 mmol) of $Re_2(CO)_8[\mu\text{-}C(H)CBu^n](\mu\text{-}H)$ with 115 μL (1.19 mmol) of DMT in refluxing CH_2Cl_2 for 2 h yielded the complex 1,2-$Re_2(CO)_8(\overline{SCH_2CMe_2CH_2})_2$ (**1**) in 71% yield. Yellow **1** was isolated by chromatography on a silica gel column with a hexane/CH_2Cl_2 solvent mixture: IR [ν(CO), cm^{-1}, in hexane] 2070 (w), 2031 (s), 2018 (sh), 1972 (vs), 1944 (w), 1918 (s); ^1H NMR (δ in CD_2Cl_2) 3.42 (s, 8 H), 1.33 (s, 12 H). Anal. Calcd for **1**: C, 26.99; H, 2.52. Found: C, 27.02; H, 2.30.

(9) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was carried out by using the TEXSAN structure solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

(10) Crystal data for **1**: space group *C*2/*c*, *a* = 13.660 (3) Å, *b* = 9.501 (3) Å, *c* = 19.109 (4) Å, β = 100.72 (2)°, *Z* = 4, 1413 reflections, *R* = 0.021.

(11) **1** (153.5 mg) was exposed to fluorescent room light for 4 days at 25 °C in CH_2Cl_2 solvent. The products were isolated by TLC on silica gel using hexane/benzene, 4/1, solvent. In order of elution: 4.4 mg of **4** (6%); 81.4 mg of unreacted **1**; 6.0 mg of **2**, 8%; 11.6 mg of **3**, 16%; 13.6 mg of **5**, 19%. Yields are based on the amount of **1** consumed. IR [ν(CO), cm^{-1}, in hexane] for **2**: 2082 (m), 1999 (s), 1969 (vs), 1923 (w), 1918 (w), 1902 (w), 1892 (s). For **3**: 2108 (m), 2071 (m), 2018 (s), 2007 (s), 1974 (s), 1960 (vs), 1916 (m). For **4**: 2104 (w), 2043 (s), 2016 (w), 1997 (vs), 1990 (vs), 1978 (w), 1969 (m), 1956 (w), 1934 (m). For **5**: 2112 (w), 2011 (s), 1952 (m). ^1H NMR (δ in CD_2Cl_2) for **2**: 3.46 (s, 8 H), 1.36 (s, 12 H). For **3**: 3.53 (br, 4 H), 2.65 (s, 2 H), 1.41 (br s, 6 H), 1.28 (s, 2 H), 1.14 (s, 6 H). For **4**: 3.47 (s, 4 H), 1.36 (s, 6 H). For **5**: at 25 °C, 4.00 (br, 2 H), 3.00 (br, 2 H), 1.15 (br, 6 H); at −48 °C in toluene-d_8, 3.55 (d, 2 H, $^2J_{H-H}$ = 9.5 Hz), 1.50 (d, 2 H, $^2J_{H-H}$ = 9.5 Hz), 0.75 (s, 3 H), 0.58 (s, 3 H). The mass spectrum of **5** shows the parent ion, *m*/*e* = 728, with an isotope pattern for one Re and one Cl, and it shows fragment ions corresponding to the loss of one, three, and four CO ligands. No significant transformation of **1** was observed by ^1H NMR spectroscopy when a solution was maintained in the dark at 25 °C for 6 days.

(12) Crystal data for **2**: space group $P\bar{1}$, *a* = 13.030 (3) Å, *b* = 18.180 (5) Å, *c* = 11.442 (2) Å, α = 107.78 (2)°, β = 90.24 (2)°, γ = 75.63 (2)°, *Z* = 4, 4608 reflections, *R* = 0.037. For **3**: space group $P2_1/n$, *a* = 9.578 (1) Å, *b* = 16.514 (4) Å, *c* = 15.699 (2) Å, β = 102.36 (2)°, *Z* = 4, 2372 reflections, *R* = 0.028. For **4**: space group $P2_1/c$, *a* = 9.360 (2) Å, *b* = 11.976 (5) Å, *c* = 17.688 (5) Å, β = 99.10 (2)°, *Z* = 4, 1514 reflections, *R* = 0.030. For **5**: space group $P2_1/c$, *a* = 13.060 (2) Å, *b* = 5.870 (2) Å, *c* = 17.305 (2) Å, β = 98.72 (1)°, *Z* = 4, 1130 reflections, *R* = 0.021.

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(14) At 25 °C, 9.6 mg of **3** was dissolved in CD_2Cl_2 and placed in an NMR tube 2 in. in front of a 15-W fluorescent light. After 6 h, the products were separated by TLC on silica gel (hexane/CH_2Cl_2, 9/1, solvent) to yield 1.0 mg of $Re_2(CO)_8(SCH_2CMe_2CH_2)_2$ (**6**), 18%; 3.6 mg of unreacted **3**; and 1.8 mg of **5**, 31% (yields based on the amount of **3** consumed). A similar yield of **6** was obtained using fluorescent ceiling light over a period of 10 days. For **6**: IR [ν(CO), cm^{-1}, in hexane] 2082 (m), 1989 (vs), 1950 (s); ^1H NMR (δ in CD_2Cl_2) 3.33 (s br, 4 H), 1.52 (s br, 4 H), 1.22 (s br, 12 H). The broad singlets are indicative of dynamical averaging of the inequivalent methyl groups and methylene protons. There was no evidence for the formation of **6** by ^1H NMR spectroscopy when a solution of **3** was maintained in the dark at 25 °C for 6 days.

(15) For **6**: space group $P\bar{1}$, *a* = 8.938 (2) Å, *b* = 9.594 (3) Å, *c* = 7.549 (2) Å, α = 100.10 (2)°, β = 93.44 (2)°, γ = 66.60 (2)°, *Z* = 1, 1400 reflections, *R* = 0.019.

disulfide link are not known at this time, but radical intermediates are suspected for the following reasons. (1) The formation of compound **5** by halogen abstraction from the solvent is a process characteristic of reactions involving radicals.[13] (2) Oxidation of organometallic complexes containing thiolato ligands has been observed to yield complexes containing dialkyl disulfide and diaryl disulfides, presumably via radical intermediates.[16] The novel photoassisted ring opening and coupling that we have described here provides further evidence of the rich reaction chemistry of thietane molecules in polynuclear metal complexes. The ring opening of sulfur-containing heterocycles is believed to be a key step in their desulfurization.[17]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: ORTEP diagrams of the molecular structures of compounds **1–5** and tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for compounds **1–6** (54 pages); tables of observed and calculated structure factors for **1–6** (87 pages). Ordering information is given on any current masthead page.

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Experimental and Theoretical Investigation of the Inversion of Configuration during Thermal Nitrogen Loss from 2,3-Diazabicyclo[2.2.1]hept-2-ene-*exo*,*exo*-5,6-d_2

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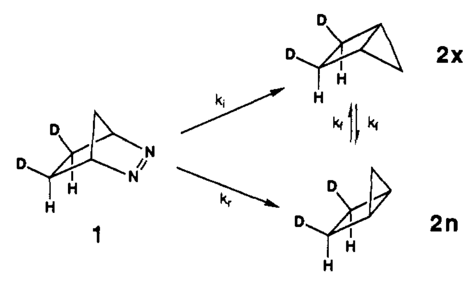
The puzzling preference for stereochemical inversion during thermal formation of bicyclo[2.1.0]pentane-*2,3*-d_2 from 2,3-diazabicyclo[2.2.1]hept-2-ene-*exo,exo-5,6*-d_2 (**1**), discovered by Roth and Martin nearly 25 years ago, is still not clearly understood.[1] Recently evidence for the involvement of a diazenyl biradical has been reported.[2] This communication suggests a theoretical model for the reaction and reports experiments designed to test it.



$$[2x] = 0.5 + [(k_i - k_r)/D]\exp[-2k_f t] + [2(k_f - k_i)/D]\exp[-(k_i + k_r)t]$$

$$[2n] = 0.5 - [(k_i - k_r)/D]\exp[-2k_f t] + [2(k_f - k_r)/D]\exp[-(k_i + k_r)t]$$

$$D = 2(k_i + k_r - 2k_f)$$

T °C	k_i/k_r
129.8	4.53±2.40
140.0	5.04±2.10
150.1	5.11±1.96
160.0	5.01±2.47
170.0	4.38±1.23
180.5	5.46±3.44

$\Delta\Delta H^{\ddagger}$ = 0.60±0.86 kcal/mol
F = 0.852
F_o = 0.800

Figure 1. Temperature dependence of the ratio of intrinsic rate constants for inversion and retention of configuration during nitrogen extrusion from the title compound. See ref 4 for an explanation of $\Delta\Delta H^*$, F, and F_o.

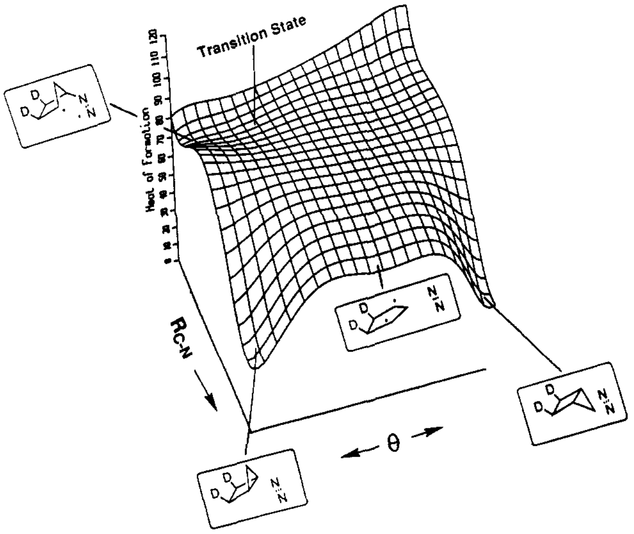


Figure 2. Semiempirical enthalpy surface for the title reaction. R_{C-N} is the length of the C–N bond in the diazenyl biradical. θ is the angle between planes defined by the three- and four-membered rings of bicyclo[2.1.0]pentane. Heats of formation are in kcal/mol.

The lack of a measurable equilibrium isotope effect on the epimerization of bicyclo[2.1.0]pentane-*cis-2,3*-d_2[3] permits evaluation of the intrinsic rate constants for inversion and retention of configuration during nitrogen extrusion (k_i and k_r, respectively) from the analytical integrated rate equations (see Figure 1 for gas-phase results). The experimental uncertainties (95% confidence interval, including covariances) become relatively large when propagated into k_i/k_r; nevertheless, application of an F test reveals no significant temperature dependence in the ratio.[4] This result renders improbable any mechanistic explanation relying on two different transition states for formation of **2x** and **2n**, since the two hypothetical transition states would then have to have coincidentally equal heats of formation (despite presumably significantly different geometries).

The mechanism we prefer involves branching to the two products and to the cyclopentane-1,3-diyl biradical *after* a single transition state for nitrogen loss from the diazenyl biradical (Figure 2).

When classical trajectory calculations were run on a model surface for this mechanism,[5] k_i/k_r was calculated to be 2.30 at 130 °C and 2.22 at 180 °C. The agreement with experiment is

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(4) F is the ratio of variance of the data for a temperature-independent model, in which k_i/k_r was set equal to a constant, to that for a temperature-dependent model in which the rate constant ratio was assumed to be described by the formula

$$k_i/k_r = \exp(-\Delta\Delta H^*/RT)\exp(\Delta\Delta S^*/R)$$

(See, for example, ref 7.) F should be >1 if k_i/k_r is temperature dependent and <1 if it is temperature independent. The lower limit of F in the latter case is given by $F_o = (N - 2)/(N - 1)$, where N is the number of temperatures studied.

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