In our previous report[3] an earlier proposed enzyme mechanism of nucleophilic catalysis[13] was shown to lead to an intermediate capable of bicycle-pedal motion and consequently to a one-step double-cis-trans isomerization. Similarly, attack of a nucleophile at C13 of I,[14] could, by bicycle-pedal-motion, reversibly yield the 13-cis,15-syn isomer after loss of the nucleophile. An alternate mechanism involving the movement of a counteranion from the region of the protonated imine to the vicinity of C13 of I also seems reasonable. This could induce transitory localization of the positive charge of I at C13 thereby reducing the C13-C14 and C15-C16 bond orders and allow concerted rotation about these bonds.[15] Aspartate 212 might fulfill either catalytic role, i.e., as a nucleophile or to provide electrostatic stabilization[16] during charge localization at C13. Apparent support for this idea comes from pH-rate data of dark isomerization.[17] Within the pH range 6.5-10.0 there is a (broad, shallow) bell-shape curve which has been verified in our laboratory and which could be accommodated by the interaction of a carboxylate ion with a protonated Schiff base. Further studies are required to establish the mechanism.

**Acknowledgment.** This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

**Registry No.** *all-trans*-Retinal, 116-31-4; 13-*cis*-retinal, 472-86-6.

(13) Seltzer, S.; Lin, M. *J. Am. Chem. Soc.* **1979**, *101*, 3091-3097.
(14) For previous examples of nucleophilic catalysis of retinal cis-trans isomerization, see: (a) Reference 5b. (b) Sack, R.; Seltzer, S. *Vision Res.* **1978**, *18*, 423-426. (c) Lukton, D.; Rando, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4525-4531.
(15) Recent studies of model systems have implicated external charges in catalyzed cis-trans isomerization: Sheves, M.; Baasov, T. *J. Am. Chem. Soc.* **1984**, *106*, 6840-6841.
(16) See, e.g., for the relative importance of electrostatic catalysis in lipophilic environments: Fersht, A. "Enzyme Structure and Mechanism"; W. H. Freeman: San Francisco, 1977; pp 48-49.
(17) Ohno, K.; Takeuchi, Y.; Yoshida, M. *Biochim. Biophys. Acta* **1977**, *462*, 575-582.

## Insertion of Elemental Sulfur into Tungsten-Carbon Bonds[1]

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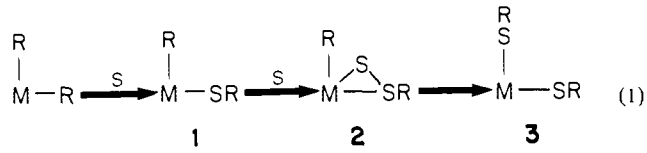
Insertion reactions of metal-carbon $\sigma$ bonds are an integral and important part of transition-metal organometallic chemistry.[2] However, few such insertions involving elemental sulfur as the intervening species have been described.[3] We now wish to report the sequential transformations shown in eq 1



(1)

(where M = $(\eta^5\text{-}C_5H_5)W(NO)$ and R = $CH_2SiMe_3$) which constitute the first documented examples of this type of reactivity.

The new complexes **1-3** may be synthesized in high yields (i.e. >80% isolated) by employing the experimental conditions summarized in Scheme I. Hence, treatment of $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$[4] in toluene with a stoichiometric amount of elemental sulfur results in the formation of the thiolato complex **1**, which is ultimately obtained as a red-violet solid by crystallization from hexanes. Further treatment of **1** with an equimolar amount of sulfur in THF affords the alkylperthio complex **2**, which is isolable as an orange-red, crystalline solid from hexanes. When **2** is maintained in toluene at 35 °C for 12 h, it converts to the red dithiolate complex **3**, which may also be purified by crystallization from hexanes. Each of the complexes **1-3** may also be synthesized directly from $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$ as shown in Scheme I.

The complexes **1-3** are diamagnetic solids which are freely soluble in common organic solvents to give moderately air-sensitive solutions. Their spectroscopic properties[5] are consistent with their possessing monomeric "piano-stool" molecular structures, a fact that has been confirmed by single-crystal X-ray crystallographic analyses of **1** and **2**.[6] In particular, their solid-state molecular geometries indicate that the organosulfur ligands are attached to the tungsten centers by essentially single W-S bonds (~2.4 Å).[6] Hence, **1** is best viewed as being a 16-electron complex, whereas **2** can be formulated as an 18-electron species in which the $\eta^2\text{-}S_2R$ ligand functions as a formal 3-electron donor.

Given these facts, the sequential conversions summarized in eq 1 may then be viewed as occurring in the manner depicted in Scheme II. The original $(\eta^5\text{-}C_5H_5)W(NO)R_2$ reactant, a demonstrated 16-electron Lewis acid,[4] first coordinates $S_8$. This coordination renders the coordinated S atom prone to intramolecular nucleophilic attack by one of the alkyl groups,[7] a process that is accompanied by the concomitant expulsion of the residual sulfur fragment which equilibrates with the $S_8$ reagent in solution.[8] The resulting 16-electron complex **1** may coordinate a further molecule of $S_8$. Once bound, the coordinated S atom undergoes intramolecular attack by the SR ligand (a stronger nucleophile than the R group) to afford **2**. Upon warming, **2** converts to **3** (possibly also a 16-electron complex) by transfer of a sulfur atom, but on the basis of the present evidence no inferences concerning the mechanism of this step may be drawn. Nevertheless, since each of the transformations presented in eq 1 can be effected independently, it is clear that the activation barrier increases for each sequential step.

Mechanisms similar to that presented in Scheme II may well be operative for the analogous insertion reactions involving elemental oxygen[9] and selenium[10] for which intermediate species have neither been isolated nor detected spectroscopically. Consistent

(1) Organometallic Nitrosyl Chemistry. 26. For part 25, see: Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* **1985**, *4*, 1263.
(2) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.
(3) (a) Giannotti, C.; Fontaine, C.; Septe, B.; Doue, D. *J. Organomet. Chem.* **1972**, *39*, C74. (b) Giannotti, C.; Merle, G. *Ibid.* **1976**, *113*, 45.
(4) Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.
(5) Supplementary material.
(6) Evans, S. V.; Legzdins, P.; Rettig, S. J.; Sánchez, L.; Trotter, J., unpublished observations.
(7) The migration of organic ligands to coordinated sulfur atoms has been previously reported: Giolando, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 6455 and references therein.
(8) Meyer, B. *Chem. Rev.* **1976**, *76*, 367.

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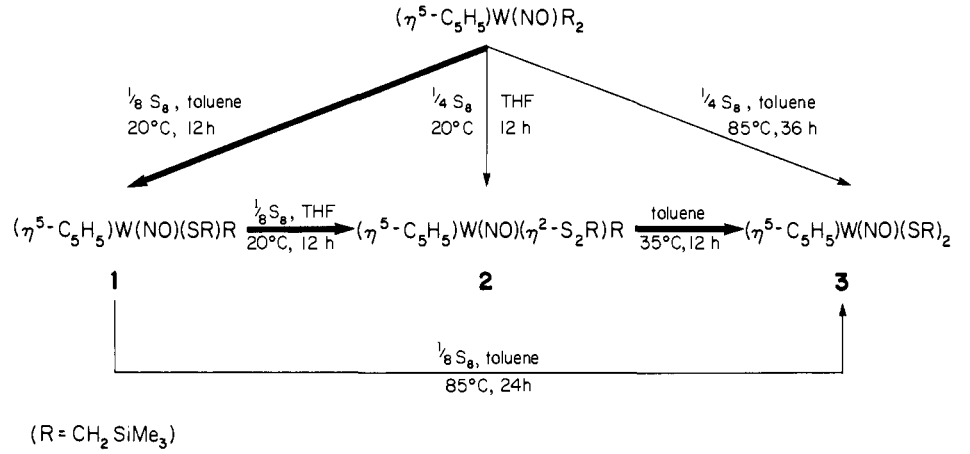
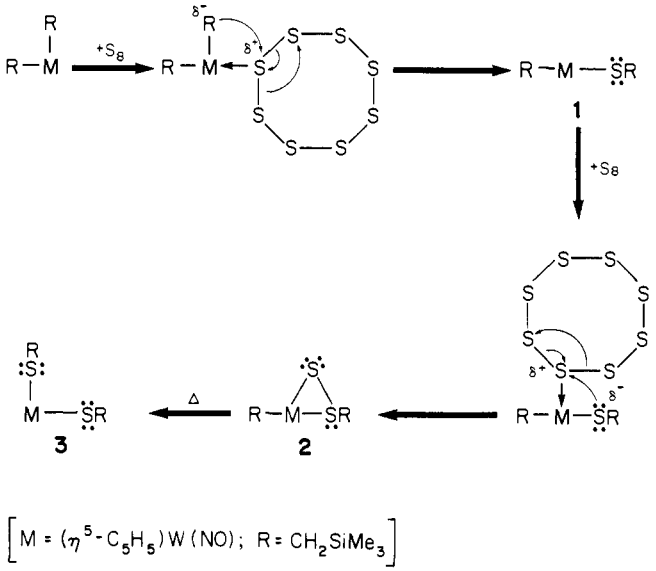
**Scheme I**




**Scheme II**




with this view is the fact that the dialkyl reactants which undergo the net conversion

(2)

(M = transition metal, R = alkyl, E = O[9] or Se[10]) are also 16-electron complexes. However, it is possible that in the case of $O_2$ the alkylperoxo complex similar to **2** in Scheme II is formed in a concerted rather than in a stepwise fashion.[11] In any event, the mechanistic proposals presented for the sulfur complexes in Scheme II suggest other experiments to substantiate their validity. Such experiments are presently in progress.

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L., and L.S. acknowledges the Spanish Ministry of Education for the award of a postdoctoral fellowship. We also thank Jeffrey T. Martin for technical assistance and a referee for insightful comments.

**Supplementary Material Available:** Elemental analysis and spectroscopic (IR, $^1H$ and $^{13}C\{^1H\}$ NMR, mass spectral) data for **1-3** (1 page). Ordering information is given on any current masthead page.

(9) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1985**, *107*, 701 and references therein.

(10) Gautheron, B.; Tainturier, G.; Meunier, P. *J. Organomet. Chem.* **1981**, *209*, C49 and references therein.

(11) The solid-state structure of a vanadium complex containing an $\eta^2$-$O_2$(*t*-Bu) ligand has been determined: Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 467.

## Synthesis and Thermal Rearrangement of Homopentafulvalenes

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Thermal rearrangements of cyclopropanes belong to the most thoroughly investigated fields of organic chemistry due to their low activation energies.[1] In the course of our work on the preparations of cyclopenta[*a*]pentalenes,[2] we have synthesized dispiro[4.0.4.1]undeca-1,3,7,9-tetraene (homopentafulvalene) (**2**) and its di-*tert*-butyl derivatives and found them to undergo stereoselective cyclopropane ring opening reactions already at room temperature.

The unsubstituted homopentafulvalene (**2**)[3] is easily prepared in 24% yield by oxidation of the dianion **1**[4] with copper(II) chloride in tetrahydrofuran at −70 °C. When a $10^{-3}$ M solution of **2** in pentane is refluxed for 10 h, rearrangement to *trans*-3a,3b-dihydro-7*H*-cyclopenta[*a*]pentalene (**3**)[3] occurs. Due to its great

(1) (a) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 27-39. (b) Berson, J. A. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 324-387.

(2) Hafner, K.; Thiele, G. F. *Tetrahedron Lett.* **1984**, *25*, 1445-1448.

(3) Physical data of compounds **2**, **3**, **5**, and **6**. **2**: mp 47 °C; UV (*n*-hexane) $\lambda_{max}$ (log $\epsilon$) 234 nm (4.07); $^1H$ NMR ($CDCl_3$) $\delta$ 2.64 (s, 2 H, $CH_2$), 6.32, 6.42 (AA'BB', 8 H, $J_{1,2}$ = 5.3, $J_{1,3}$ = 1.4, $J_{1,4}$ = $J_{2,3}$ = 2.1 Hz). Anal. ($C_{11}H_{10}$) C, H. **3**: oil; UV (*n*-hexane) $\lambda_{max}$ 260 nm; $^1H$ NMR ($CDCl_3$) $\delta$ 2.57 (s, 2 H, $CH_2$), 3.31 (br s, 2 H, $H_{3a,3b}$), 6.18 (m, 2 H, $H_{1,6}$), 6.45 (m, 2 H, $H_{3,4}$), 6.57 (dd, 2 H, $H_{2,5}$, $J_{1,2}$ = 1.8, $J_{2,3}$ = 5.2 Hz). Anal. ($C_{11}H_{10}$) C, H. **5**: oil; UV (*n*-hexane) $\lambda_{max}$ 236 nm; $^1H$ NMR (benzene-$d_6$), **5a**, $\delta$ 1.09 (s, 18 H, *t*-Bu), 2.26 (s, 2 H, $CH_2$), 5.86 (dd, 2 H, $H_{1,7}$), 6.25 (dd, 2 H, $H_{4,10}$), 6.45 (dd, 2 H, $H_{3,9}$) ($J_{1,3}$ = 1.7, $J_{1,4}$ = 2.1, $J_{3,4}$ = 5.4 Hz), **5b**, $\delta$ 1.09 (s, 18 H, *t*-Bu), 2.21, 2.26 (AB, 2 H, $CH_2$, $J$ = 4.0 Hz), 5.90 (dd, 2 H, $H_{1,7}$), 6.23 (dd, 2 H, $H_{4,10}$), 6.45 (dd, 2 H, $H_{3,9}$) ($J_{1,3}$ = 1.7, $J_{1,4}$ = 2.1, $J_{3,4}$ = 5.4 Hz). **6a**: mp 101 °C; UV (*n*-hexane) $\lambda_{max}$ (log $\epsilon$) 239 (3.53) 260 nm (3.56); $^1H$ NMR (benzene-$d_6$) $\delta$ 1.19 (s, 18 H, *t*-Bu), 2.69 (s, 2 H, $H_7$), 3.23 (s, 2 H, $H_{3a,3b}$), 6.09 (s, 2 H, $H_{3,4}$), 6.19 (s, 2 H, $H_{1,6}$). Anal. ($C_{19}H_{26}$) C, H. **6b**: $^1H$ NMR (benzene-$d_6$) $\delta$ 1.19 (s, 9 H, *t*-$Bu_2$), 1.24 (s, 9 H, *t*-$Bu_4$), 2.72, 2.82 (AB, 2 H, $H_7$, $J$ = 11 Hz), 3.20 (s, 2 H, $H_{3a,3b}$), 6.00 (m, 1 H, $H_5$), 6.17 (m, 2 H, $H_{1,6}$), 6.26 (s, 1 H, $H_3$).

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