Professor Richard Holm and the Stanford Chemistry Department for their hospitality during a portion of the 1977-1978 academic year.

Supplementary Material Available: Final atomic positional parameters as well as a listing of observed and calculated structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

References and Notes

(1) C. LeVanda, D. O. Cowan, C. Leitch, and K. Bechgaard, *J. Am. Chem. Soc.*, **96,** 6788 (1974); C. LeVanda, D. O. Cowan, and K. Bechgaard, *ibid.*, **97,** 1980 (1975); D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, **6,** 1 (1973); D. O. Cowan and C. LeVanda, *J. Am. Chem. Soc.*, **94,** 9271 (1972).

(2) (a) P. Shu, K. Bechgaard, and D. O. Cowan, *J. Org. Chem.*, **41,** 1849 (1976). (b) H. Rosenberg and F. L. Hedberg, *Abstr. Int. Symp. Organomet. Chem., 3rd, 1967*, 108 (1967); E. W. Post, R. G. Cooks, and J. C. Kotz, *Inorg. Chem.*, **9**, 1670 (1970).

(3) A. N. Nesmeyanov, V. A. Sazoniva, and V. A. Blinova, *Dokl. Akad. Nauk SSSR*, **198,** 848 (1971); A. N. Nesmeyanov, V. A. Sazonova, V. A. Blinova, and S. G. Dychenko, *ibid.*, **200,** 1365 (1971).

(4) G. M. Brown, T. J. Meyer, D. O. Cowan, C. LeVanda, F. Kaufman, P. V. Roling, and M. D. Rausch, *Inorg. Chem.*, **14,** 506 (1975).

(5) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9,** 373 (1956); R. K. Bohn and A. Haaland, *J. Organomet. Chem.*, **5,** 470 (1966).

(6) S. S. Crawford, C. B. Knobler, and H. D. Kaesz, *Inorg. Chem.*, **16**, 3201 (1977); G. J. Palenik, *Inorg. Chem.*, **9,** 2424 (1970).

(7) R. C. Pettersen, Ph.D. Thesis, University of California, Berkeley, Calif., 1966; T. Bernstein and F. H. Herbstein, *Acta Crystallogr., Sect. B*, **24,** 1640 (1968); J. W. Bats, J. J. deBoer, and D. Bright, *Inorg. Chim. Acta*, **5,** 605 (1971); A. G. Landers, M. W. Lynch, S. B. Raaberg, A. L. Rheingold, J. E. Lewis, N. J. Mammano, and A. Zalkin, *J. Chem. Soc., Chem. Commun.*, 931 (1976); N. J. Mammano, A. Zalkin, A. Landers, and A. L. Rheingold, *Inorg. Chem.*, **16,** 297 (1977).

(8) The Johns Hopkins University.

(9) Wright-Patterson Air Force Base.

Dwaine O. Cowan,*[8] Paul Shu,[8] Frederick L. Hedberg*[9]
Miriam Rossi,[8] Thomas J. Kistenmacher*[8]

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218, and
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio 45433

Received July 3, 1978

Hydrogenation of Small Molecules by Transition Metal Cluster Hydrides. Reaction of $H_2Os_3(CO)_{10}$ with Carbon Disulfide

Sir:

The hydrogenation of small molecules by transition metal cluster hydrides is presently an area of intense study.[1] In connection with our studies on the hydrogenation abilities of $H_2Os_3(CO)_{10}$,[1d] we have investigated its reaction with carbon disulfide. Here we report that we have found an unusual dicluster reaction in which two triosmium clusters cooperatively attack and reduce a single molecule of carbon disulfide.

Over a period of 34 hr a solution of $H_2Os_3(CO)_{10}$ in refluxing CS_2 solvent slowly changes color from purple to yellow. This is accompanied by the formation of a brown precipitate. From the solution we have isolated[2] (21% yield) a yellow compound which we have analyzed as $H_2CS_2[HOs_3(CO)_{10}]_2$ on the basis of IR,[3] ^1H NMR, and X-ray crystallographic analyses.[4] The molecular structure is shown in Figure 1. Two regular $HOs_3(CO)_{10}$ groupings are bridged by an $S\text{-}CH_2\text{-}S$ ligand.[5,6] Each sulfur atom bridges two osmium atoms in separate cluster units. The $S(\mu\text{-}H)Os_3(CO)_{10}$ units are structurally similar to those observed in related monocluster systems.[7] Although the hydrogen atoms were not observed crystallographically, the presence of two hydrogen atoms on the carbon atom of the $S\text{-}CH_2\text{-}S$ bridge is indicated by the following considerations. The ^1H NMR spectrum shows only two resonances which are at δ 2.92 and -17.46 ppm with relative intensities of ~1:1. We assign the latter to a combination of equivalent bridging hydride ligands (one from each cluster) and the former to a methylene group. An alternative formulation as a dithioformate is considered most unlikely since the proton shifts in these ligands lie in the very characteristic region δ 10.0-15.0 ppm.[8] Structural considerations also support the formulation as a *gem*-dithiamethylene group. The C-S distances of 1.82 (2) and 1.86 (2) Å are similar to the distances 1.81-1.82 Å found in both monothia-[9] and *gem*-dithiaalkanes[10] and the 1.89 (4) Å found for the compound $(\mu\text{-}H)(\mu\text{-}SC_2H_5)Os_3(CO)_{10}$.[7b] In contrast the C-S distances in dithioformate ligands are considerably shorter and lie in the range 1.64-1.68 Å.[11,12]

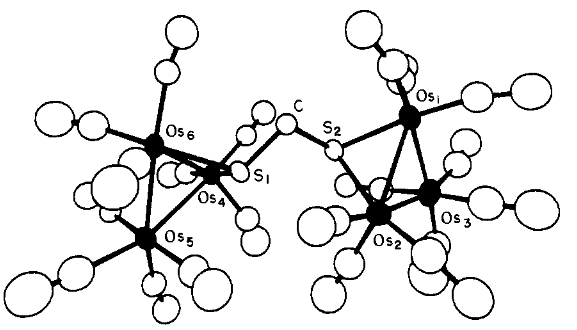


Figure 1. ORTEP diagram of $(H_2CS_2)[(H)Os_3(CO)_{10}]_2$ showing 50% probability ellipsoids.

The ligand behavior of carbon disulfide has been demonstrated in numerous metal complexes.[14] Carbon disulfide reacts with mononuclear metal hydrides to produce complexes containing chelating dithioformate ligands.[8,11,15] Our reaction shows that the cluster reduction proceeds one step farther to a $CH_2S_2{}^{2-}$ unit which might be viewed as a precursor of dithioacetal. The reason for this is presently unclear, but may center on the tendency of sulfur atoms to favor bridging positions across two metal atoms. The greater reducing effects produced by the bridging environment may promote reduction reactions beyond the dithioformate stage. Efforts to produce still further reduction of the CH_2S_2 unit are currently in progress.

Acknowledgment. Support of this research under Contract No. ER-78-S-02-4900 from the Office of Basic Energy Sciences, U.S. Department of Energy, is gratefully acknowledged. We thank Engelhard Industries for a gift of osmium tetroxide.

Supplementary Material: Fractional atomic coordinates (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) (a) E. L. Muetterties, *Science*, **196,** 839 (1977), and references therein; (b) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85,** 451 (1976); (c) M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, **99,** 6763 (1977); (d) R. D. Adams and N. M. Golembeski, *ibid.*, **100,** 4622 (1978); (e) E. Band, W. R. Pretzer, M. G. Thomas, and E. L. Muetterties, *ibid.*, **99,** 7380 (1977).

(2) The compound was isolated by column chromatography over $Al_2O_3 \cdot 6\%$ H_2O with benzene solvent.

(3) 2105 (w), 2075 (s), 2065 (w, sh), 2025 (s), 2015 (m), 2000 (w, sh), 1990 (w) in CCl_4 solvent.

(4) Crystal data: $a = 10.067$ (9), $b = 13.240$ (7), $c = 13.794$ (5) Å; $\alpha = 84.59$ (3) $\beta = 75.45$ (4), $\gamma = 88.23$ (6)°; space group $P\bar{1}$; $Z = 2$. Diffraction data were collected on an Enraf–Nonius CAD-4 automatic diffractometer; 3780 reflections ($F^2 \geq 3.0\sigma(F^2)$) were used in the structure solution and refinement. The structure was solved by the heavy-atom method. All programs used were those of the Enraf–Nonius structure determination program library. Current values of the residuals are $R = 0.051$ and $R_w = 0.061$.

(5) Selected bond distances (ångstroms): Os(1)–Os(2) = 2.867 (1), Os(1)–Os(3) = 2.872 (1), Os(2)–Os(3) = 2.854 (1), Os(4)–Os(5) = 2.875 (1), Os(4)–Os(6) = 2.871 (1), Os(5)–Os(6) = 2.875 (1), Os(1)–S(2) = 2.403 (4), Os(2)–S(2) = 2.414 (4), Os(4)–S(1) = 2.411 (4), Os(6)–S(1) = 2.419 (4), C–S(1) = 1.86(2), C-S(2) = 1.82(2).

(6) Selected bond angles (degrees): Os(3)–Os(1)–Os(2) = 59.65 (2), Os(1)–Os(2)–Os(3) = 60.27 (3), Os(1)–Os(3)–Os(2) = 60.08 (2), Os(5)–Os(4)–Os(6) = 60.04 (2), Os(4)–Os(5)–Os(6) = 59.92 (2), Os(4)–Os(6)–Os(5) = 60.04 (2), Os(1)–S(2)–Os(2) = 73.0 (1), Os(4)–S(1)–Os(6) = 73.0 (1), Os(1)–S(2)–C = 110.2 (5), Os(2)–S(2)–S(2)–C = 110.0 (5), Os(4)–S(1)–C = 112.4 (5), Os(6)–S(1)–C = 114.4 (5), S(1)–C–S(2) = 105.3 (8).

(7) (a) B. F. G. Johnson, J. Lewis, D. Pippard, and P. R. Raithby, *J. Chem. Soc.*,

0002-7863/79/1501-1306$01.00/0

Chem. Commun., 551 (1978); (b) V. F. Allen, R. Mason, and P. B. Hitchcock, *J. Organomet. Chem.*, **140**, 297 (1977).
(8) S. D. Robinson and A. Sahajpal, *J. Organomet. Chem.*, **99**, C65 (1975).
(9) L. E. Sutton, *Chem. Soc., Spec. Publ.*, **No. 18**, S 22s (1965).
(10) (a) G. W. Frank and P. J. Degen, *Acta Crystallogr., Sect. B*, **29**, 1815 (1973); (b) G. Vallee, V. Busetti, M. Mammi, and G. Carazzolo, *Ibid.*, **25**, 1432 (1969); (c) G. Vallee, V. Busetti, M. Mammi, and G. Carazzolo, *ibid.*, **25**, 1631 (1969); (d) J. E. Fleming, and H. Lynton, *Can. J. Chem.*, **45**, 353 (1967).
(11) (a) A. E. Kalinin, A. I. Gusev, and Y. T. Struchkov, *J. Struct. Chem.*, **14**, 804 (1973); (b) V. G. Albano, P. L. Bellon, and G. Ciani, *J. Organomet. Chem.*, **31**, 75 (1971).
(12) The remarkable compound $Mn(CO)_3[(C_6H_5)_2PCH_2P(C_6H_5)_2C(H)S_2]$[13] has one phosphorus atom of the DPM chelate bonded to the carbon atom of the $C(H)S_2$ group. The resulting tetravalent carbon atom has a structural arrangement, C–S = 1.83 Å and S–C–S = 105°, very similar to that of the H_2CS_2 ligand in our complex.[5,6]
(13) F. W. Einstein, E. Enwall, N. Flitcroft, and J. M. Leach, *J. Inorg. Chem.*, **34**, 885 (1972).
(14) I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, **66**, 161 (1974).
(15) (a) R. O. Harris, N. K. Hota, L. Sadavoy, and J. M. C. Yuen, *J. Organomet. Chem.*, **54**, 259 (1973); (b) F. G. Moers, R. W. M. Ten Hoedt, and J. P. Langhout, *Ibid.*, **65**, 93 (1974).

Richard D. Adams,* Nancy M. Golembeski
Department of Chemistry, Yale University
New Haven, Connecticut 06520

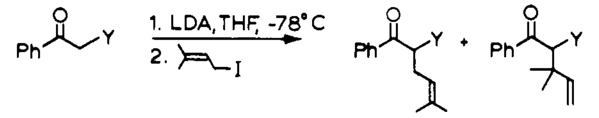
Received October 30, 1978

Selenium Stabilized Carbanions.[1] Ylide Formation during Alkylation of Selenium and Sulfur Substituted Enolates

Sir:

We report here unambiguous evidence that seleno- and thio-substituted ketone enolates can undergo significant or even predominant alkylation at the heteroatom. The key observations are shown in Scheme I. Treatment of the enolate of α-(phenylseleno)acetophenone[2] with prenyl iodide or bromide led to the unexpected material **3a** (formally corresponding to an S_N2' attack on the allyl halide), in addition to the normal alkylation product **2a**. Varying the reaction conditions gave different amounts of the two products, **3a** being formed in all cases. It was convenient to analyze the deselenated or desulfenylated products **2b** and **3b** obtained by treatment with benzene- or methanethiol and triethylamine in ethanol.[3]

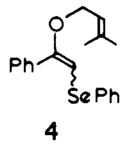
Scheme I



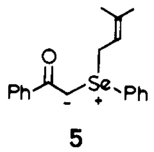
1a Y = SePh
b Y = H
c Y = SPh

1a, THF, 0°C	47:53 (60%)
1a, THF, HMPA, -78° to 25°	61:39 (66%)
1c, THF, 0°C	69:31 (67%)
1b, THF, 0°C	>99:<1 (43%)

Two reasonable pathways for the formation of **3a** can be envisaged: (1) O-alkylation to give **4**, followed by [3,3] sigmatropic rearrangement, or (2) alkylation at selenium to give the ylide **5** followed by [2,3] sigmatropic rearrangement. Direct S_N2' displacement is not considered likely with prenyl halides, nor is any observed during alkylation of acetophenone enolate (Scheme I).



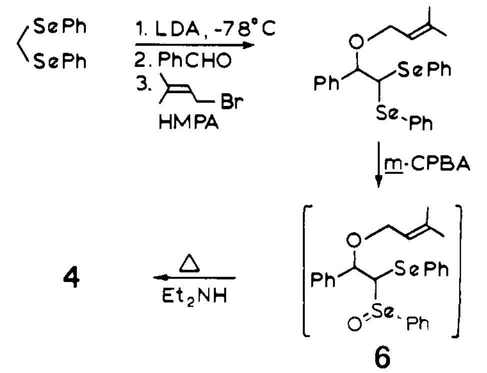
4



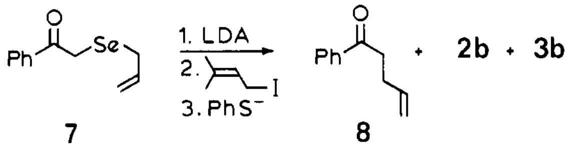
5

Authentic **4** was prepared by the method outlined in Scheme II. It is essential to perform the syn elimination of the selenoxide **6** in the presence of diethylamine to trap PhSeOH which otherwise reacts with the enol ether.[4] Compound **4** rearranges to **3a** slowly at 85 °C ($k_1 = 3.6 \times 10^{-5}\ s^{-1}$ in THF-d_8); it can therefore be ruled out as a precursor of **3a** during the alkylation of **1a** since **3a** is formed when the reaction is carried out below room temperature.

Scheme II

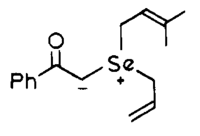


Support for the ylide mechanism was provided by the product mixture from alkylation of α-allylselenoacetophenone (**7**).[5] The *C*-allyl product (**8**) must be formed by [2,3] sigmatropic rearrangement of an intermediate (**9**) capable of allyl migration.[6] When the selenium is highly hindered (as in the mesitylene system **10**), 63% of **2** and only trace amounts (~1%) of abnormal product (**3**) are formed on alkylation with prenyl iodide. An ylide intermediate analogous to **9** was also generated by a different route. Treatment of diprenyl selenide with phenacyl trifluoromethanesulfonate[7] gave an intermediate selenonium salt which was observed spectroscopically. Deprotonation with DBU led to rapid conversion to **3** (Y = Se-prenyl). The ylide was not detected by NMR observation at 25 °C. After deselenation with PhSH/NEt$_3$/EtOH a 61% yield of **3b** was isolated. The absence of **2b** strongly suggests that Stevens rearrangement does not compete with [2,3] sigmatropic rearrangement of the intermediate ylide.

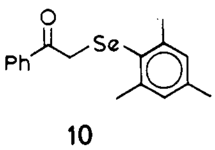


7 **8**

35:58:6 (69%)



9



10

Reaction at the heteroatom is not limited to seleno-substituted enolates, nor to unusual alkylating agents such as prenyl iodide. α-(Phenylthio)acetophenone (**1c**) gives 31% abnormal product **3c** with prenyl iodide. Alkylation of the enolate from **7** with methyl iodide (0 °C, THF) gives, after deselenation, a 41:59 ratio of **8** and propiophenone.

Alkylation at sulfur has been suggested to account for unusual reactivity in reactions involving cycloalkylation of a lithium reagent derived from a methylthiocarboxylic acid[8] and methylation of a methylthiovinylcopper derivative.[9] Our results would indicate that anomalous alkylations are more common than had been previously suspected. Moreover, it is likely that low yields sometimes reported for alkylation of thio substituted enolates are a consequence of the formation of stable ylides. These are lost as water-soluble sulfonium salts upon protonation and workup.[10]

Our survey of a number of thio- and seleno-substituted lithium reagents has revealed few other cases of anomalous