Acknowledgment. This research was generously supported by a grant from the National Cancer Institute (Grant CA 26830). We thank Professor Ch. Tamm for providing an authentic sample of natural verrucarol.

Supplementary Material Available: Spectroscopic data (^1H NMR, IR, mass), physical constants, and combustion analytical or high-resolution mass spectral data are reported for all synthetic intermediates (7 pages). Ordering information is given on any current masthead page.

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(15) Natural verrucarol crystallized from hexane–benzene had mp 160–161 °C (lit. mp 158–159 °C (ether–CH_2Cl_2); see: Cole, R. J.; Cox, R. H. "Handbook of Toxic Fungal Metabolites"; Academic Press: New York, 1981; p 157).

(16) This synthesis is comparable in length (21 steps from (methylcyclopentadienyl)trimethylsilane)) to that reported by Schlessinger (20 steps from 2-methylcyclopentane-1,3-dione). The synthesis recently reported by Trost[17] also proceeds in 20 steps from 2-methylcyclopentane-1,3-dione.

(17) A synthesis of racemic verrucarol was published by Trost after our paper was submitted for publication (Trost, B. M.; McDougal, P. G. *J. Am. Chem. Soc.* **1982**, *104*, 6110). This group reports a melting point of 165.5–167 °C (ether–$CHCl_3$) for the synthetic trichothecene.

Incorporating Metal–Metal Multiple Bonds into Heterometallic Chains: Bis(tris(trimethylstannyl)tin)tetrakis(dimethylamido)dimolybdenum and -ditungsten and Related Compounds

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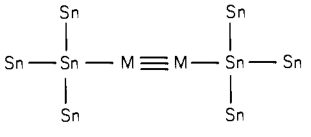
There is now a fairly extensive body of chemistry surrounding compounds containing metal-to-metal multiple bonds.[1] To our knowledge, however, compounds containing the connectivity $M'{-}M{\equiv}M{-}M'$ or $M'{-}M\overset{4}{-}M{-}M'$, wherein a central metal–metal triple or quadruple bond supports metal–metal bonds to different metal atoms, have not been reported. Compounds of this type could play a significant role in the development of polynuclear/cluster chemistry. We here report our preparation and characterization of compounds of formula 1,2-$M_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ which contain the metal atom connectivity shown in I.



$$\mathrm{Sn_3Sn{-}M{\equiv}M{-}SnSn_3}$$

I, M = Mo and W

Previous work has shown that $M_2Cl_2(NMe_2)_4$[2] compounds (M = Mo, W) are labile toward metathetic reactions described by the generalized equation (1), where Y = R (alkyl),[3] OR, NR_2, and SR.[4]

$$M_2Cl_2(NMe_2)_4 + 2LiY \rightarrow M_2Y_2(NMe_2)_4 + 2LiCl \quad (1)$$

We now find that employing $(THF)_3LiSn(SnMe_3)_3$[5] in eq 1 gives the new compounds $M_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ as orange, hydrocarbon-soluble, air-sensitive crystalline solids.[6]

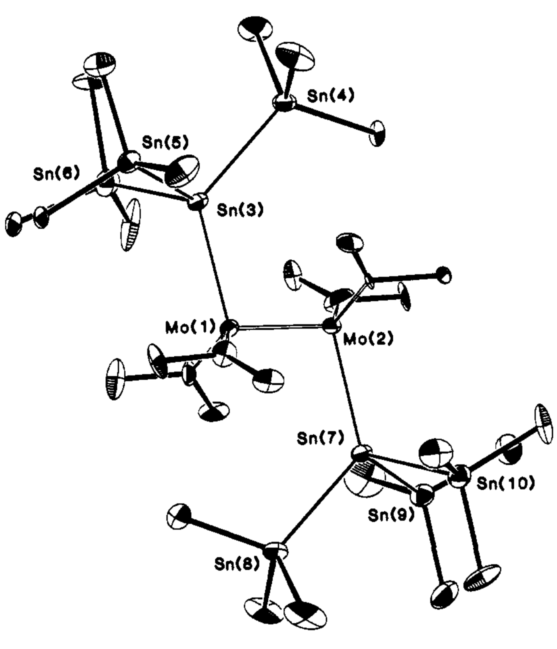


Figure 1. ORTEP view of the $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ molecule giving the atom numbering scheme used for the metal atoms. Atoms are represented by ellipsoids drawn to include 50% probability of thermal displacement. Pertinent bond distances (Å) and angles (deg) are as follows: Mo–Mo = 2.201 (2); Mo(1)–Sn(3) = 2.783 (2); Mo(2)–Sn(7) = 2.774 (2); Sn(3)–Sn(4), –Sn(5), –Sn(6) = 2.775 (2), 2.774 (2), 2.779 (2); Sn(7)–Sn(8), –Sn(9), –Sn(10) = 2.768 (2), 2.777 (2), 2.774 (2); Mo–N = 1.95 (1) (averaged); Sn(3)–Mo(1)–Mo(2) = 100.6 (1); Sn(7)–Mo(2)–Mo(1) = 100.7 (1), Mo–Mo–N = 105 (2) (averaged).

A view of the molecular structure of the molybdenum compound, deduced from a single-crystal X-ray study,[7] is shown in Figure 1. The geometry about each tin atom is close to that expected for its use of essentially tetrahedral hybrid orbitals, while the central $Mo_2Sn_2N_4$ skeleton is akin to that observed in a number of other molecules of formula $M_2X_2(NMe_2)_4$ having the anti conformation, e.g., $Mo_2X_2(NMe_2)_4$, where X = Me[8] and Cl.[2] The distance associated with the Mo≡Mo bond and the Mo–Sn and Sn–Sn bonds are all well within the range expected on the basis of previous structural studies.[9]

In toluene-d_8 and benzene-d_6, the anti conformation is apparently maintained to the exclusion of the gauche rotamer.[10]

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

(2) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

(3) Chisholm, M. H.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046.

(4) Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 286.

(5) Brown, T. L.; Wells, W. L. *J. Organomet. Chem.* **1968**, *11*, 271.

(6) Reactions were carried out by using standard procedures for the manipulation of air-sensitive materials. Preparation of $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$: $(THF_3)_3LiSn(SnMe_3)_3$ (1.05 g, 1.26 mmol) dissolved in hexane (20 mL) was added to $Mo_2Cl_2(NMe_2)_4$ (0.277 g, 0.631 mmol) suspended in hexane (20 mL). Upon addition, the mixture turned orange with the formation of an orange precipitate. After the solution stirred for 1 h at room temperature, the solution was filtered, and the solids were washed with hexane (10 mL, five times) until all the orange solids were extracted into the filtrate. The solution was then placed in a refrigerator at −15 °C, and the orange crystals, which formed over a period of 12 h, were collected by filtration and dried in vacuo (0.45 g, 44% based on Mo). $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ was prepared similarly. Satisfactory elemental analyses were obtained for both compounds. Crystals of the molybdenum compound suitable for X-ray studies were obtained by recrystallization from toluene.

(7) Crystal data for the $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$ molecule at −162 °C: space group $Pbn2_1$, $a = 14.600$ (4) Å, $b = 31.737$ (13) Å, $c = 13.545$ (4) Å, $Z = 4$, $d_{calcd} = 1.876$ g cm^{-3}. Of the 4330 unique intensities collected by using Mo Kα, $6° < 2\theta < 45°$, the 4105 reflections having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. The final residuals are $R_F = 0.046$ and $R_{wF} = 0.049$. The unit cell contains two toluene molecules. One molecule (C(41)–C(47)) is well ordered while the other (C(49)–C(57)) is disordered.

(8) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **19788** *17*, 2338.

(9) Mo–Sn = 2.753 (3) Å in $Cl_2MeSnMo(CO)_3(bpy)$: Elder, M.; Graham, W. A. G.; Hall, D.; Kumner, R. *J. Am. Chem. Soc.* **1968**, *90*, 2189. Sn–Sn = 2.77 (1) Å in $(SnPh_2)_6$: Olson, D. H.; Rundle, R. E. *Inorg. Chem.* **1963**, *2*, 1310. Mo–Mo = 2.203 (1) Å in 1,2-$Mo_2Et_2(NMe_2)_4$: ref 3. For an extensive listing of Mo≡Mo bond distances in $Mo_2X_2(NMe_2)_4$ compounds, see: Chisholm, M. H. *Transition Met. Chem.* **1978**, *3*, 321.

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Rotations about Mo–N bonds may be monitored as a function of temperature on the ^{1}H NMR time scale, which allows an estimate of $\Delta G^{\ddagger}$, the barrier to rotation, to be placed at 16.5 kcal mol^{-1}. This is comparable to that in $Mo_2Cl_2(NMe_2)_4$.

Hexane solutions of $W_2Cl_2(NMe_2)_4$ and $(THF)_3LiSi(SiMe_3)_3$[11] (2 equiv) yield an orange crystalline compound that, on the basis of spectroscopic characterization, is formulated as the silicon analogue 1,2-$W_2(Si(SiMe_3)_3)_2(NMe_2)_4$. In similar reactions, 1,2-$M_2Cl_2(NMe_2)_4$ compounds have been found to react with potassium and tetra-*n*-butylammonium salts[12] of $CpFe(CO)_2^-$ in toluene to give orange microcrystalline compounds that, on the basis of infrared[13] and ^{1}H NMR characterization, are formulated as 1,2-$M_2(Fe(Cp)(CO)_2)_2(NMe_2)_4$ compounds, where M = Mo and W. These compounds contain the connectivity Fe—M≡M—Fe, and in toluene-d_8, they exist as a mixture of anti and gauche rotamers with respect to the central $M_2Fe_2N_4$ moeity in the ratio 1:2, respectively.

This work leads us to predict that it should be possible to subtend a wide variety of metal–metal bonds from dinuclear centers containing the $(M{\equiv}M)^{6+}$ unit where M = Mo and W.[14]

Registry No. $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$, 84521-33-5; $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$, 84521-34-6; 1,2-$Wa(Si(SiMe_3)_3)_2(NMe_2)_4$, 84521-35-7; 1,2-$Mo_2(Fe(Cp)(CO)_2)_2(NMe_2)_4$, 84537-06-4; 1,2-$W_2(Fe(Cp)(CO)_2)_2(NMe_2)_4$, 84521-36-8; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6; $W_2Cl_2(NMe_2)_4$, 63301-81-5; $(THF)_3LiSn(SnMe_3)_3$, 60552-34-3; $(THF)_3LiSi(SiMe_3)_3$, 81859-95-2; $KCpFe(CO)_2$, 60039-75-0; $[Bu_4N]CpFe(CO)_2$, 65836-70-6.

Supplementary Material Available: Listings of fractional coordinates and isotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(10) ^{1}H NMR data (220 MHz, 16 °C, toluene-d_8) for $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$: δ (NMe) 3.96 (12 H), 2.50 (12 H); δ ($SnMe_3$) 0.38 ppm (54 H). $J(^{119}Sn{-}C{-}H)$ = 45.4 Hz, $J(^{117}Sn{-}C{-}H)$ = 43.6 Hz, and $J(^{117,119}Sn{-}Sn{-}C{-}H)$ = 9.4 Hz. For $W_2(Sn(SnMe_3)_3)_2(NMe_2)_4$: δ (NMe) 4.00 (12 H), 2.38 (12 H); δ ($SnMe_3$) 0.40. $J(^{119}Sn{-}C{-}H)$ = 45.6 Hz, $J(^{117}Sn{-}C{-}H)$ = 44.0 Hz, and $J(^{117,119}Sn{-}Sn{-}C{-}H)$ = 9.8 Hz.

(11) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

(12) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 213.

(13) The IR spectrum recorded as a Nujol mull shows two ν(C≡O) bands: 1950 (s) and 1892 (vs) cm^{-1} (M = Mo); 1953 (s) and 1885 (vs) cm^{-1} (M = W).

(14) We thank the National Science Foundation and the Wrubel Computing Center for support.

Stereochemistry of the Electrophilic Fragmentation–Cyclization of Allenic Sulfones and Sulfinates: Stereoselective Synthesis of Chiral α,β-Unsaturated γ-Sultines

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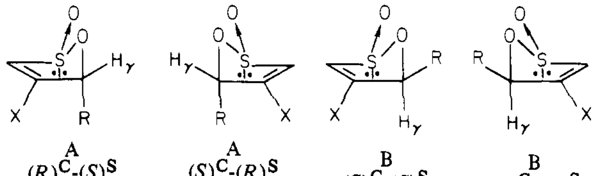
The electrophilic cyclization of a variety of functionalized allenes to heterocyclic systems[1-4] has received considerable attention due to its synthetic utility and remarkable stereoselectivity.[1a,f,2,3b,4a] In a continuation to our previous report on the electrophilic fragmentation–cyclization of allenic sulfones and sulfinates to α,β-unsaturated γ-sultines,[5] we have investigated the stereochemistry of this reaction.

Table I. Cyclization of Chiral Allenic Sulfones and Sulfinates to Chiral γ-Sultines

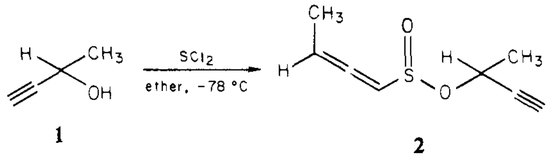
substrate	[α]^{25}D, deg	X$^+$	γ-sultine	[α]^{25}D, deg	yield, %
(−)-**2**[a]	−97.6	Br$^+$	(−)-9	−73.7 (*c* 2.7)	87
(+)-**2**[a]	+41.7	Br$^+$	(+)-9	+14.6 (*c* 1)	85
(+)-**2**[b]	+32.0	MeS$^+$	(+)-11	+20.5 (*c* 2.2)	35
(−)-**7**[c]	−47.5	Br$^+$	(+)-9	+16.9 (*c* 1.2)	87
(−)-**8**[d]	−58.5	Br$^+$	(+)-10	+15.6 (*c* 3.6)[f]	55
(−)-**7**[b]	−47.5	MeS$^+$	(+)-11	+23.7 (*c* 6.2)	80
(−)-**8**[b]	−63.5	MeS$^+$	(+)-12	+15.9 (*c* 6.1)	73

[a] In CCl_4 at 25 °C. [b] In CH_2Cl_2 at −20 °C. [c] In CCl_4 at −10 °C. [d] In CCl_4 at −20 °C. [e] In acetone. [f] Contains some 8% of sulfone.

Chart I

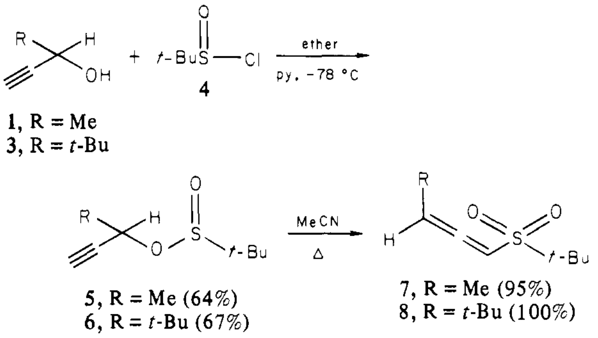


Treatment of (*R*)-(+)-1-butyn-3-ol ((+)-**1**[6], [α]^{25}D +17.7° (*c* 1.0, dioxane)) and of (*S*)-(−)-**1**,[6] [α]^{25}D −49.4° (*c* 3.2, dioxane) with sulfur dichloride, as previously described,[7] afforded sulfinates (+)-**2** ([α]^{25}D +41.7° (*c* 1.0, acetone, yield 80%)) and (−)-**2** ([α]^{25}D −97.6° (*c* 1.7, acetone, yield 80%)), respectively (eq 1).



1 **2** (1)

Racemic γ-methyl- and γ-*tert*-butylallenyl *tert*-butyl sulfones (**7**, **8**)[8] were prepared by a previously reported method[9] (eq 2).



4

1, R = Me
3, R = *t*-Bu

5, R = Me (64%)
6, R = *t*-Bu (67%)

7, R = Me (95%)
8, R = *t*-Bu (100%)

(2)

Optically active sulfones (−)-**7** ([α]^{25}D −47.5° (*c* 1.4, acetone, yield 70%)) and (−)-**8** ([α]^{25}D −58.5° (*c* 2.8, acetone, yield 66%), mp 87–88 °C) were obtained by the elegant method of kinetic resolution.[10] Treatment of optically active sulfinate **2** and sulfones

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(1) (a) Jacobs, T. L.; Macomber, R.; Zunker, D. *J. Am. Chem. Soc.* **1967**, *89*, 7001. (b) Toda, F.; Komoda, T.; Akagi, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1493. (c) Hoff, S.; Brandsma L. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 845. (d) Gelin, R.; Gelin, S.; Albrand, M. *Bull. Soc. Chim. Fr.* **1972**, 720. (e) Ollson, L.; Claeson, A. *Synthesis* **1979**, 743. (f) Beaulieu, P. L.; Morisset, V. M.; Garratt, D. G. *Tetrahedron Lett.* **1980**, *21*, 129.

(2) (a) Shingu, K.; Hagishita, S.; Nakagawa, M. *Tetrahedron Lett.* **1967**, 4371. (b) Kresze, G.; Kloinastein, L.; Runge, W. *Liebigs Ann. Chem.* **1976**, 979.

(3) (a) Macomber, R. S.; Kennedy, E. R. *J. Org. Chem.* **1976**, *41*, 3191. (b) Macomber, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 3072.

(4) (a) Musierowicz, S.; Wroblewski, A.; Krawczyk, H. *Tetrahedron Lett.* **1975**, 437. (b) Angelov, C. M.; Vachkov, K. V. *Ibid.* **1981**, *22*, 2517.

(5) (a) Braverman, S.; Reisman, D. *J. Am. Chem. Soc.* **1977**, *99*, 605. (b) Braverman, S.; Reisman, D. *Tetrahedron Lett.* **1977**, 1753.

(6) Weidmann, R.; Schoopfs, A.; Horeau, A. *Bull. Soc. Chim. Fr.* **1976**, 645.

(7) Braverman, S.; Segev, D. *J. Am. Chem. Soc.* **1974**, *96*, 1245.

(8) All new compounds gave satisfactory elemental analysis and/or IR, NMR, and mass spectra data in accord with the assigned structures.

(9) Braverman, S.; Mechoulam, H. *Tetrahedron* **1974**, *30*, 3883 and references cited therein.

(10) Cinquini, M.; Colonna, S.; Cozzi, F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 247.