

For both compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local program; program(s) used to refine structures: *ORFLS* (Busing, Martin & Levy, 1962); molecular graphics: *ORTEPII* (Johnson, 1976).

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1059). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.
- Blackstock, S. C. & Kochi, J. K. (1987). *J. Am. Chem. Soc.* **109**, 2484–2496.
- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Faller, J. & Ma, Y. (1988). *Organometallics*, **7**, 559–561.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Legzdins, P., Phillips, E. C., Rettig, S. J., Sánchez, L., Trotter, J. & Yee, V. C. (1988). *Organometallics*, **7**, 1877–1878.
- Legzdins, P., Rettig, S. J. & Sánchez, L. (1985). *Organometallics*, **4**, 1470–1471.
- Masnovi, J. M., Kochi, J. K., Hilinski, E. F. & Rentzepis, P. M. (1985). *J. Phys. Chem.* **89**, 5387–5395.
- Phillips, E. C. (1989). PhD thesis, Univ. of British Columbia, Vancouver, Canada.

Acta Cryst. (1995). **C51**, 2501–2503

A Trigonal Prismatic Cluster Compound of Tin and Lithium: Structure of $[\{\text{Sn}(\text{OCMe}_2\text{C}_6\text{H}_4)_2\}_3\text{Li}_2\text{O}]\cdot 2\text{HOcMe}_2\text{Ph}$

GLEN D. SMITH, PHILLIP E. FANWICK AND
IAN P. ROTHWELL

*Department of Chemistry, 1393 Brown Building,
Purdue University, West Lafayette, IN 47907, USA*

(Received 11 June 1993; accepted 5 September 1995)

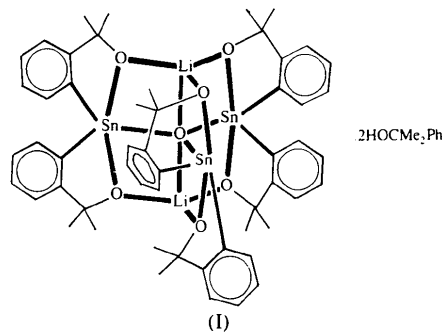
Abstract

The structure of the title compound, $\mu_3\text{-oxo-}2:3:4\kappa^3\text{O-hexakis}[\mu\text{-}2\text{-phenyl-}2\text{-propanolato}(2\text{-})]\text{-}1:2\kappa^2\text{O}, 2\kappa\text{C}^2\text{-}; 1:3\kappa^2\text{O}, 3\kappa\text{C}^2\text{-}; 1:4\kappa^2\text{O}, 4\kappa\text{C}^2\text{-}; 2\kappa\text{C}^2\text{-}; 2:5\kappa^2\text{O}; 3\kappa\text{C}^2\text{-}; 3:5\kappa^2\text{O};$

$4\kappa\text{C}^2\text{-}; 4:5\kappa^2\text{O}$ -dilithiumtritin bis(2-phenyl-2-propanol), contains a prismatic cluster of three $[\text{Sn}(\text{OCMe}_2\text{C}_6\text{H}_4)_2]$ units held together by one equivalent of Li_2O through Sn—O—Sn and O—Li—O bridges. A central triangular Sn_3O unit is sandwiched by two capping O_3Li units. The Sn—O(oxo) distances are 2.100(2) and 2.088(4) Å, while the Li—O(oxo) distances are 2.342(9) Å. A crystallographic twofold axis passes through a unique Sn atom and the central oxo group of the cluster.

Comment

Recent work by our group has shown that Sn^{IV} metal centers have the ability to intramolecularly activate the aromatic C—H bonds of certain specific types of aryl-substituted alkoxide and aryloxy ligation (Smith, Visciglio, Fanwick & Rothwell, 1992). The reaction generates a series of five- and six-membered oxametalacyclic ring compounds of tin. During one of our studies of the thermal reactivity of the tetraalkoxy derivative of tin $[\text{Sn}(\text{OCMe}_2\text{Ph})_4]$, we noticed the formation of a few crystals of a material that was completely insoluble in most organic solvents. A view of this compound, (I), is shown in Fig. 1.



The thermolysis of the liquid tetraalkoxide $[\text{Sn}(\text{OC}_3\text{Me}_2\text{Ph})_4]$ typically leads to the dinuclear compound $[\text{Sn}(\text{OCMe}_2\text{C}_6\text{H}_4)_2]_2$ along with eliminated 2-phenylpropan-2-ol (Smith, Visciglio, Fanwick & Rothwell, 1992). The compound analyzed in this report contains three formally neutral Sn^{IV} units, $[\text{Sn}(\text{OCMe}_2\text{C}_6\text{H}_4)_2]$, containing two five-membered metalacycles formed by cyclometalation of the *ortho*-CH bond of each of the 2-phenyl-2-propanolato groups. The three tin-containing units are held together by one equivalent of Li_2O . The origin of the lithium oxide presumably stems from water contamination in the initial synthesis of the precursor $[\text{Sn}(\text{NMe}_2)_4]$, obtained from SnCl_4 and LiNMe_2 . A twofold axis of symmetry is present and passes through unique Sn(2) and O(B). Two molecules of 2-phenylpropan-2-ol per cluster unit are also present but are omitted from the *ORTEP* (Johnson, 1965) view for clarity.

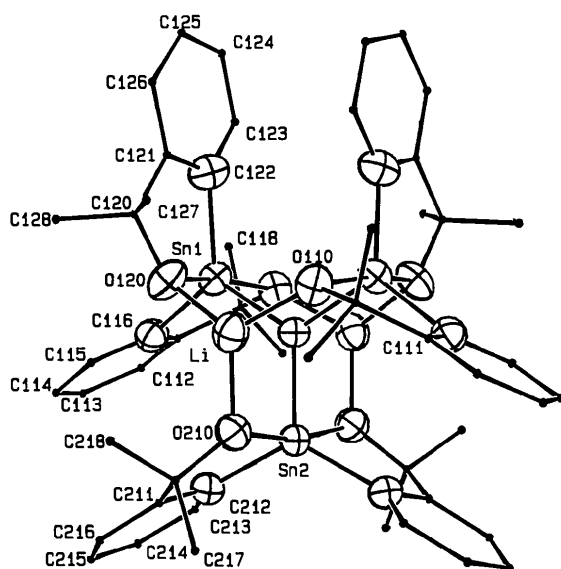


Fig. 1. View of the molecule emphasizing the central coordination sphere. H atoms are omitted for clarity.

The solid-state structure of $[\{\text{Sn}(\text{OCMe}_2\text{C}_6\text{H}_4)_2\}\text{Li}_2\text{O}]\cdot 2\text{HOCMe}_2\text{Ph}$ (Fig. 1) is best described as a trigonal prism built up of three triangular units stacked on top of one another. The central triangle consists of an Sn₃O unit in which the O atom bridges all three Sn atoms. The local coordination about each Sn atom is distorted trigonal bipyramidal, with the O atoms of the cyclometalated alkoxy groups being in mutually *trans* axial positions. These alkoxy O atoms are each bound to a Li atom, making up the top and bottom LiO₃ triangles of the central prismatic core. The two Li atoms are positioned above and below the central oxide O atom, resulting in a locally trigonal-bipyramidal geometry around O(B). The Li—O(B) distances of 2.342(9) Å are longer than the Sn—O(alkoxy) distances of 2.090(3)–2.107(5) Å; hence, the Li atoms are positioned slightly above or below the plane of the three O atoms in the LiO₃ triangles.

Experimental

Crystal data

[Sn₃Li₂(C₉H₁₀O)₆O].
2C₉H₁₂O

$M_r = 1463.42$

Monoclinic

$P2_1/n$

$a = 11.130(1) \text{ \AA}$

$b = 13.157(7) \text{ \AA}$

$c = 23.077(2) \text{ \AA}$

$\beta = 95.68(1)^\circ$

$V = 3362.8(9) \text{ \AA}^3$

$Z = 2$

$D_x = 1.45 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25
reflections

$\theta = 18\text{--}21^\circ$

$\mu = 1.162 \text{ mm}^{-1}$

$T = 239 \text{ K}$

Plate

$0.60 \times 0.50 \times 0.38 \text{ mm}$

Colorless

Data collection

CAD-4 diffractometer

ω - 2θ scans

Absorption correction:

refined from ΔF (DI-
FABS; Walker & Stuart,
1983)

$T_{\min} = 0.41$, $T_{\max} = 0.65$

4651 measured reflections

4651 independent reflections

3354 observed reflections

$[F > 3\sigma(F)]$

$\theta_{\max} = 22.5^\circ$

$h = -12 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 24$

3 standard reflections

frequency: 83.33 min

intensity decay: insignificant

Refinement

Refinement on F

$R = 0.033$

$wR = 0.042$

$S = 1.244$

3354 reflections

389 parameters

H-atom parameters not
refined

$w = 1/[\sigma^2(F) + (0.02F)^2 + 1 - f]$

$(\Delta/\sigma)_{\max} = 0.27$

$\Delta\rho_{\max} = 0.53 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.69 \text{ e \AA}^{-3}$

Atomic scattering factors

from Cromer & Waber
(1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Sn(1)	0.27037 (3)	0.23086 (3)	0.32894 (2)	3.171 (7)
Sn(2)	1/4	-0.00828 (4)	1/4	3.47 (1)
O(B)	1/4	0.1504 (4)	1/4	3.0 (1)
O(110)	0.0826 (3)	0.2160 (3)	0.3238 (2)	3.80 (8)
O(120)	0.4543 (3)	0.2262 (3)	0.3173 (2)	4.16 (9)
O(210)	0.4374 (3)	0.0085 (3)	0.2538 (2)	4.09 (9)
C(110)	0.0382 (5)	0.1904 (5)	0.3779 (2)	4.5 (1)
C(111)	0.1388 (5)	0.1414 (5)	0.4189 (2)	4.1 (1)
C(112)	0.1140 (7)	0.0943 (5)	0.4708 (3)	5.7 (2)
C(113)	0.2086 (7)	0.0537 (6)	0.5071 (3)	6.3 (2)
C(114)	0.3258 (7)	0.0574 (6)	0.4934 (3)	5.9 (2)
C(115)	0.3510 (6)	0.1051 (5)	0.4422 (3)	4.5 (1)
C(116)	0.2569 (5)	0.1460 (4)	0.4057 (2)	3.8 (1)
C(117)	-0.0674 (6)	0.1168 (6)	0.3642 (3)	6.6 (2)
C(118)	-0.0029 (7)	0.2885 (6)	0.4055 (3)	6.9 (2)
C(120)	0.5157 (6)	0.3193 (5)	0.3298 (3)	5.0 (1)
C(121)	0.4246 (6)	0.4082 (5)	0.3270 (3)	4.7 (1)
C(122)	0.3025 (5)	0.3883 (4)	0.3244 (2)	4.0 (1)
C(123)	0.2188 (6)	0.4673 (5)	0.3233 (3)	5.1 (1)
C(124)	0.2575 (7)	0.5668 (5)	0.3246 (3)	6.7 (2)
C(125)	0.3783 (8)	0.5869 (5)	0.3269 (3)	7.8 (2)
C(126)	0.4631 (7)	0.5104 (5)	0.3286 (3)	6.7 (2)
C(127)	0.6055 (6)	0.3335 (6)	0.2845 (3)	7.1 (2)
C(128)	0.5817 (7)	0.3127 (7)	0.3915 (3)	7.2 (2)
C(210)	0.5026 (5)	-0.0593 (4)	0.2935 (3)	4.3 (1)
C(211)	0.4229 (5)	-0.0969 (4)	0.3387 (3)	4.2 (1)
C(212)	0.2981 (5)	-0.0820 (4)	0.3297 (3)	4.0 (1)
C(213)	0.2224 (6)	-0.1181 (5)	0.3696 (3)	5.1 (2)
C(214)	0.2714 (7)	-0.1706 (5)	0.4187 (3)	5.9 (2)
C(215)	0.3941 (7)	-0.1865 (5)	0.4271 (3)	6.3 (2)
C(216)	0.4698 (6)	-0.1515 (5)	0.3883 (3)	5.3 (2)
C(217)	0.5429 (7)	-0.1506 (6)	0.2589 (3)	6.7 (2)
C(218)	0.6121 (6)	-0.0013 (6)	0.3220 (3)	6.1 (2)
C(310)	0.1481 (7)	0.3398 (7)	0.6181 (4)	8.0 (2)
C(311)	0.2052 (6)	0.3952 (5)	0.5697 (3)	5.5 (2)
C(312)	0.1570 (8)	0.4813 (7)	0.5454 (4)	7.9 (2)
C(313)	0.211 (1)	0.5291 (8)	0.5001 (4)	11.0 (3)
C(314)	0.311 (1)	0.493 (1)	0.4808 (4)	12.6 (4)
C(315)	0.359 (1)	0.411 (1)	0.5067 (5)	14.8 (4)
C(316)	0.3059 (9)	0.3612 (8)	0.5495 (5)	11.6 (3)
C(317)	0.211 (1)	0.2418 (7)	0.6246 (5)	14.2 (3)
C(318)	0.0288 (9)	0.305 (1)	0.6019 (5)	12.8 (3)
C(319)	0.176 (1)	0.385 (1)	0.6717 (4)	20.3 (4)
Li	0.4600 (9)	0.1507 (8)	0.2482 (4)	4.0 (2)

Table 2. Selected geometric parameters (Å, °)

Sn(1)—O(B)	2.100 (2)	Sn(2)—C(212)	2.102 (5)
Sn(1)—O(110)	2.090 (3)	O(B)—Li	2.342 (9)
Sn(1)—O(120)	2.092 (3)	O(110)—C(110)	1.427 (6)
Sn(1)—C(116)	2.113 (5)	O(120)—C(120)	1.419 (7)
Sn(1)—C(122)	2.107 (5)	O(120)—Li	1.884 (9)
Sn(2)—O(B)	2.088 (4)	O(210)—C(210)	1.425 (6)
Sn(2)—O(210)	2.091 (3)	O(210)—Li	1.89 (1)
O(B)—Sn(1)—O(110)	83.2 (1)	C(212)—Sn(2)—C(212')	125.0 (3)
O(B)—Sn(1)—O(120)	84.07 (9)	Sn(1)—O(B)—Sn(1')	119.5 (2)
O(B)—Sn(1)—C(116)	116.8 (2)	Sn(1)—O(B)—Sn(2)	120.3 (1)
O(B)—Sn(1)—C(122)	117.2 (2)	Sn(1)—O(B)—Li	89.5 (2)
O(110)—Sn(1)—O(120)	167.3 (1)	Sn(2)—O(B)—Li	90.1 (3)
O(110)—Sn(1)—C(116)	81.0 (2)	Li—O(B)—Li'	180 (1)
O(110)—Sn(1)—C(122)	105.2 (2)	Sn(1)—O(110)—C(110)	113.8 (3)
O(120)—Sn(1)—C(116)	104.1 (2)	Sn(1)—O(120)—C(120)	114.0 (3)
O(120)—Sn(1)—C(122)	81.3 (2)	Sn(1)—O(120)—Li	103.9 (3)
C(116)—Sn(1)—C(122)	126.0 (2)	C(120)—O(120)—Li	124.9 (4)
O(B)—Sn(2)—O(210)	83.95 (9)	Sn(2)—O(210)—C(210)	113.8 (3)
O(B)—Sn(2)—C(212)	117.5 (1)	Sn(2)—O(210)—Li	103.9 (3)
O(210)—Sn(2)—O(210')	167.9 (2)	C(210)—O(210)—Li	126.8 (4)
O(210)—Sn(2)—C(212)	81.1 (2)		

One Sn-atom position was solved using the Patterson heavy-atom method. The remaining atoms were located using *DIRDIF* (Beurskens *et al.*, 1984) and in succeeding difference Fourier syntheses. It was not possible to differentiate the hydroxy and the two methyl groups of the 2-phenylpropanol solvent molecule. Hence, these three atoms were refined as C atoms without attached H atoms. All other H atoms were located and included in the structure-factor calculations, but their positions were not refined. The structure was refined by full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as per the Killean & Lawrence (1969) method with the terms 0.20 and 1.0. Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). The highest peak in the final difference Fourier map had a height of 0.53 \AA^{-3} with an estimated error based on ΔF (Cruickshank, 1945) of 0.08. All calculations were performed on a VAX computer using *SDP* (Enraf-Nonius, 1985).

We thank the National Science Foundation (grant CHE-8915573) for support of this research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A., Noordik, J. H., Beurskens, G., Parthasarathi, V., Bruins Slot, H. J., Haliwanger, R. C., Strumpel, M. & Smiths, J. M. M. (1984). *DIRDIF*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.2. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Cruickshank, D. W. T. (1949). *Acta Cryst.* **2**, 154–157.
- Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delf, The Netherlands.

- Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.
- Omae, I. (1989). *J. Organomet. Chem. Lib.* **21**, 237.
- Smith, G. D., Visciglio, V. M., Fanwick, P. E. & Rothwell, I. P. (1992). *Organometallics*, **11**, 1064–1071.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1995). **C51**, 2503–2508

Three α,β -Unsaturated (Carbene)pentacarbonylchromium Complexes

EHMKE POHL, BORIS O. KNEISEL AND
REGINE HERBST-IRMER*

*Institut für Anorganische Chemie, Universität
Göttingen, Tammannstrasse 4, 37077 Göttingen,
Germany*

ARMIN DE MEIJERE, FRANK FUNKE AND FRANK STEIN

*Institut für Organische Chemie, Universität Göttingen,
Tammannstrasse 2, 37077 Göttingen, Germany*

(Received 21 February 1995; accepted 10 May 1995)

Abstract

The syntheses and crystal structures of [(2*E*)-1-amino-3-dimethylamino-3-phenylpropen-1-ylidene]pentacarbonylchromium, $[\text{Cr}(\text{C}_{11}\text{H}_{14}\text{N}_2)(\text{CO})_5]$, pentacarbonyl[(2*E*)-3-dibenzylamino-1-ethoxy-6,6-dimethylhept-2-en-4-ynylidene]chromium, $[\text{Cr}(\text{C}_{25}\text{H}_{29}\text{NO})(\text{CO})_5]$, and pentacarbonyl[(4-dibenzylamino-5,5-dimethyl-2,5-dihydro-2-furylidene)chromium, $[\text{Cr}(\text{C}_{20}\text{H}_{21}\text{NO})(\text{CO})_5]$, are reported. All compounds show significant π delocalization over the carbene fragment.

Comment

α,β -Unsaturated (carbene)chromium complexes have become important reagents in synthetic organic chemistry. With appropriate substituents at the carbene C atom and/or the vinyl terminus, they react with alkynes in a number of ways to give various ring systems. The addition of ammonia to (alkynylcarbene)chromium complexes leads either to [(*Z*)-2-aminoethynyl]carbene complexes or to (1-aminoethynyl)carbene complexes; this can be controlled by temperature variations (Stein, Duetsch, Pohl, Herbst-Irmer & de Meijere, 1993).

The reaction of (1-ethoxy-3-phenylpropynylidene)-pentacarbonylchromium, (1), with ammonia afforded exclusively the substitution product (2) in 96% yield at