Organometallics 1984, 3, 1500–1504

Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 12.[1] Crystal and Molecular Structures of Tetrakis(η^1-indenyl) Derivatives of Germanium and Tin: Meso Diastereoisomers with S_4 Symmetry

Jerry L. Atwood,*[2a] A. D. McMaster,[2b] Robin D. Rogers,[2a] and Stephen R. Stobart*[2b]

Departments of Chemistry, University of Alabama, University, Alabama 35486, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Received May 23, 1984

An X-ray crystallographic analysis of $Ge(\eta^1\text{-}C_9H_7)_4$ (1) and $Sn(\eta^1\text{-}C_9H_7)_4$ (2) reveal molecular structures corresponding to the meso diastereoisomer, belonging to the point-group S_4. Diastereotopic effects observed in ^{13}C NMR spectra of 2 and of *n*-butyltri-1-indenyltin are temperature dependent in a manner clearly establishing that nondegenerate intramolecular metallotropism in these compounds provides a mechanism for intraconversion between all possible stereoisomers. Compound 1 crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 11.115$ (4) Å, $b = 11.259$ (4) Å, $c = 11.319$ (4) Å, $\alpha = 114.26$ (3)°, $\beta = 95.11$ (3)°, $\gamma = 90.65$ (3)°, and $D_{\text{calcd}} = 1.38$ g cm^{-3} for $Z = 2$. Least-squares refinement based on 1537 independent observed reflections led to a final R value of 0.020. Compound 2 belongs to the monoclinic space group $P2_1/c$ with $a = 11.684$ (4) Å, $b = 22.254$ (5) Å, $c = 11.432$ (4) Å, $\beta = 117.04$ (4)°, and $D_{\text{calcd}} = 1.45$ g cm^{-3} for $Z = 4$. The final R value based on 1342 independent observed reflections was 0.032. Although not isostructural both compounds are structurally identical. Coordination about the metal center is almost exactly tetrahedral in both molecules with mean Ge–C and Sn–C bond lengths of 2.00 (1) and 2.19 (1) Å, respectively.

Introduction

In concluding the present series we wish to discuss the results of a determination by X-ray diffraction of the crystal and molecular structures of tetrakis(η^1-indenyl)germanium (1) and tetrakis(η^1-indenyl)tin (2). These two molecules belong to a wider general class of stereochemically nonrigid metallocyclopolyenyl derivatives, the most familiar examples of which are the fluxional η^1-cyclopentadienyl (η^1-C_5H_5) family.[3] In previous papers we have been concerned with characterization of the dynamic properties of such systems by variable-temperature nuclear magnetic resonance spectroscopy; this has led inter alia to (a) mechanistic definition[4] of the degenerate rearrangement behavior of η^1-cyclopentadienyl compounds, (b) analysis[5] of nondegenerate rearrangement via facile reversible isomerization in η^1-methylcyclopentadienyl analogues, and (c) identification of stereomutation characteristics synonymous with metalloptropic rearrangement in η^1-indenyl analogues.[6] Although low-energy interconversions in the fluid state between equivalent or nonequivalent configurations so represented have been subjected to continuing investigation for nearly 25 years,[3] the corresponding equilibrium geometry adopted in either gas or solid phase has been determined by diffraction methods for rather few examples for which such behavior is typical.[7] In several cases also the data are of poor quality or have been disputed.[7b,c,f]

Recently the structure of germylcyclopentadiene (3, M = GeH_3) has been determined both for the gaseous molecule (by electron diffraction) and for the crystal (by X-ray crystallography). The important conclusion of this elegant study[7h] is that in both phases the geometry is the same: the C_5 ring is planar (to within 1°, gas phase, and 4°, crystal) with alternating long–short–medium–short–long C–C bond distances. This situation parallels exactly that described by Cotton et al.[7d,e] for the η^1-C_5H_5 group in $[Mo(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)NO]$ and $[Ti(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)_2]$, by Day et al.[7g] in $[Mn(\eta^1\text{-}C_5Cl_5)(CO)_5]$, and by the present authors[7i] in $[Hf(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)_2]$. Conflicting electron diffraction studies of[7b,c] $Me_3MC_5H_5$ (M = Si or Ge) and an X-ray structure determination[7f] for $\{(\eta^1\text{-}C_5H_5)_2Sn[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2\}$ have claimed to distinguish an "envelope" conformation possessing fold angles across the C^2C^5 axis of 22, 24, and 27°, respectively. These latter claims have provoked substantial criticism,[7e] and indeed subsequent X-ray data from the same source suggest[7j] that in $Sn(\eta^1\text{-}C_5H_5)_4$ the greatest deviation from planarity for any of the four C_5 units is only 5.9°. The corresponding indenyl systems that may be represented as 4 appear to have been completely ignored in terms of structural characterization

---

(1) McMaster, A. D.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.*, submitted for publication as part 11.

(2) (a) University of Alabama. (b) University of Victoria.

(3) Wilkinson, G. *J. Organomet. Chem.* **1975**, *100*, 273. Cotton, F. A. *Ibid.* **1975**, *100*, 29. Larrabee, R. B. *Ibid.* **1974**, *74*, 313. Cotton, F. A. in "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L., Cotton, F. A., Eds.; Academic Press: New York, 1975.

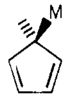
(4) Bonny, A.; Holmes-Smith, R. D.; Hunter, G.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 1855.

(5) Holmes-Smith, R. D.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1980**, 159.

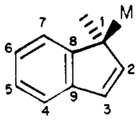
(6) McMaster, A. D.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 2109.

(7) (a) Bentham, J. E.; Rankin, D. W. H. *J. Organomet. Chem.* **1971**, *30*, C54. (b) Veniaminov, N. N.; Ustynyuk, Yu. A.; Alekseev, N. V.; Ronova, I. A.; Struchkov, Yu. T. *Ibid.* **1970**, *22*, 551. (c) Veniaminov, N. N.; Ustynyuk, Yu, A.; Struchkov, Yu. T.; Alekseev, N. V.; Ronova, I. A. *Zh. Strukt. Khim.* **1970**, *11*, 127. Veniaminov, N. N.; Ustynyuk, Yu. A.; Alekseev, N. V.; Ronova, I. A.; Struchkov, Yu. T. *Dokl. Akad. Nauk SSSR* **1971**, *199*, 346. (d) Calderon, J. L.; Cotton, F. A.; Legzdins, P. *J. Am. Chem. Soc.* **1969**, *91*, 2528. (e) Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Takats, J. *J. Am. Chem. Soc.* **1971**, *93*, 3592. (f) Biryhkov, B. P.; Struchkov, Yu, T. *Zh. Strukt. Khim.* **1969**, *10*, 95. (g) Day, V. W.; Stutts, B. R.; Reimer, K. J.; Shaver, A. *J. Am. Chem. Soc.* **1974**, *96*, 4008. (h) Barrow, M. J.; Ebsworth, E. A. V.; Harding, M. M.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 603. (i) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 692. (j) Kulishov, V. I.; Bokü, N. G.; Prikhot'ko, A. F.; Struchkov, Yu. T. *J. Struct. Chem.* (*Engl. Transl.*) **1975**, *16*, 231.

0276-7333/84/2303-1500$01.50/0



3



4

although the geometry of the five-membered ring in the bicyclic framework is potentially interesting in relation to localization of the C^2C^3 double bond compared with C^8C^9 which is benzenoid in type. By contrast with cyclopentadienylmetal chemistry not many indenylmetal compounds have been reported and apart from the complex structure of diindenylmagnesium (which displays[8] terminal and bridging indenyl groups exhibiting η^5, η^2 and possibly η^1 bonding modes for the C_5 ring–metal interaction) all available X-ray data refer[9] to η^5-indenyl derivatives. Consequently and also developing our interest[6] in diastereoisomerism in metal poly(η^1-indenyl) systems we have completed a crystallographic study of the tetraindenyl compounds 1 and 2.

Experimental Section

X-ray Data Collection, Structure Determination, and Refinement for $Ge(\eta^1\text{-}C_9H_7)_4$. Details for synthesis of $M(C_9H_7)_4$ (M = Ge, 1; M = Sn, 2) have been given previously.[6,10] Crystals suitable for X-ray diffraction were obtained from benzene solution as colorless lozenges and sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta/\lambda)^2$ values for 15 reflections ($2\theta > 25°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P\bar{1}$ from the choices of $P1$ and $P\bar{1}$ by the successful solution and refinement of the structure.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[11] A summary of the data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[12] Neutral atom scattering for Ge and C were taken from Cromer and Waber,[13] and the scattering for germanium was corrected for real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[14] Scattering factors for H were from ref 15.

The position of the germanium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the germanium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.064$. The hydrogen atoms of the indenyl rings were placed at calculated positions 1.08 Å from the bonded carbon atom and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.020$ and $R_w = 0.022$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.[16]

X-ray Data Collection, Structure Determination, and Refinement for $Sn(\eta^1\text{-}C_9H_7)_4$ (2). Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 25°$) accurately centered on the diffractometer are given in Table I. The space group was uniquely determined to be $P2_1/c$ from the systematic absences.

Table I. Crystal Data, Summary of Intensity Data Collection, and Structure Refinement

compd	$Ge(\eta^1\text{-}C_9H_7)_4$	$Sn(\eta^1\text{-}C_9H_7)_4$
mol wt	533.2	579.3
space group	$P\bar{1}$	$P2_1/c$
cell constants		
a, Å	11.115 (4)	11.684 (4)
b, Å	11.259 (4)	22.254 (5)
c, Å	11.319 (4)	11.432 (4)
α, deg	114.26 (3)	
β, deg	95.11 (3)	117.04 (4)
γ, deg	90.65 (3)	
cell vol, Å^3	1284.5	2647.6
molecules/unit cell	2	4
D(calcd), g cm^{-3}	1.38	1.45
μ(calcd), cm^{-1}	12.90	9.95
transmissn factor range	0.69–0.78	0.68–0.72
radiatn	Mo Kα	Mo Kα
max cryst dimens, mm	0.20 × 0.30 × 0.60	0.30 × 0.40 × 0.40
scan width	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
std reflctns	400, 040	040, 002
decay of stds	±2%	±2%
reflctns measd	1837	2190
2θ range, deg	≤36	≤36
reflctns collected	1537	1342
no. of parameters varied	334	334
GOF	0.75	2.58
R	0.020	0.032
R_w	0.022	0.037

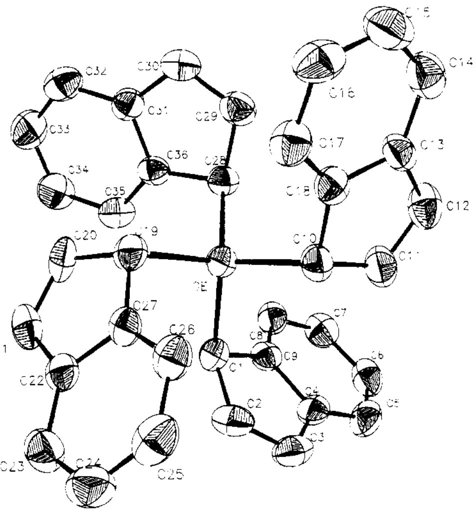


Figure 1. Molecular structure of $Ge(\eta^1\text{-}C_9H_7)_4$ (1), with the atoms represented by their 50% probability ellipsoids for thermal motion.

Data were collected as described for the previous compound. The intensities were corrected for Lorentz and polarization effects but not for absorption. Neutral atom scattering factors were obtained as noted above, and that of tin was corrected for the real and imaginary components of anomalous dispersion.

The position of the tin atom was revealed by the inspection of a Patterson map, and the subsequent calculation of a difference Fourier map allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic thermal parameters led to a reliability index of $R = 0.070$. The hydrogen atoms of the indenyl rings were placed at calculated positions 1.08 Å from the bonded carbon atom and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.032$ and $R_w = 0.037$. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme

---

[8] Atwood, J. L.; Smith, K. D. *J. Am. Chem. Soc.* **1974**, *96*, 994.

[9] Shakir, R.; Atwood, J. L. *Acta Crystallogr. Sect. B* **1981**, *B37*, 1656.

[10] Zimmer, H.; Sparmann, H. W. *Naturwissenschaften* **1953**, *40*. 220. Lesbre, M.; Mazerolles, P.; Manuel, G. *C. R. Hebd. Seances Acad. Sci., Ser. B* **1962**, *255*, 544.

[11] Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

[12] SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

[13] Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

[14] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[15] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

[16] See paragraph at the end of paper regarding supplementary material.

Table II. Final Fractional Coordinates for $Ge(\eta^1\text{-}C_9H_7)_4$ (1)

atom	*x/a*	*y/b*	*z/c*
Ge	0.17358 (4)	-0.19716 (4)	0.19930 (4)
C(1)	0.1013 (3)	-0.0520 (4)	0.1629 (4)
C(2)	0.0870 (4)	0.0622 (4)	0.2883 (4)
C(3)	-0.0301 (5)	0.0840 (4)	0.3028 (4)
C(4)	-0.1044 (5)	-0.0079 (4)	0.1885 (5)
C(5)	-0.2296 (5)	-0.0253 (5)	0.1570 (5)
C(6)	-0.2746 (4)	-0.1174 (5)	0.0368 (6)
C(7)	-0.1981 (5)	-0.1915 (4)	-0 0525 (4)
C(8)	-0.0740 (4)	-0.1773 (4)	-0.0210 (5)
C(9)	-0.0265 (4)	-0.0870 (4)	0.1002 (5)
C(10)	0.0946 (4)	-0.2136 (4)	0.3433 (4)
C(11)	-0.0366 (4)	-0.2532 (5)	0.3038 (4)
C(12)	-0.0631 (4)	-0.3670 (5)	0.3067 (4)
C(13)	0.0446 (4)	-0.4152 (5)	0.3492 (4)
C(14)	0.0652 (5)	-0.5301 (5)	0.3644 (4)
C(15)	0.1792 (6)	-0.5509 (5)	0.4088 (5)
C(16)	0.2734 (4)	-0.4591 (6)	0.4372 (4)
C(17)	0.2560 (4)	-0.3439 (5)	0.4217 (4)
C(18)	0.1420 (4)	-0.3227 (4)	0.3760 (4)
C(19)	0.3509 (3)	-0.1501 (4)	0.2584 (4)
C(20)	0.4110 (3)	-0.1239 (5)	0.1573 (4)
C(21)	0.4409 (3)	0.0037 (5)	0.2005 (5)
C(22)	0.4112 (3)	0.0713 (5)	0.3322 (5)
C(23)	0.4249 (4)	0.2021 (5)	0 4170 (6)
C(24)	0.3926 (4)	0.2402 (4)	0.5421 (6)
C(25)	0.3489 (4)	0.1498 (6)	0.5826 (4)
C(26)	0.3336 (3)	0.0194 (5)	0.4989 (5)
C(27)	0.3627 (3)	-0.0205 (4)	0.3721 (4)
C(28)	0.1509 (3)	-0.3632 (4)	0.0393 (4)
C(29)	0.1905 (4)	-0.4757 (4)	0.0678 (4)
C(30)	0.2877 (4)	-0.5265 (4)	0.0072 (4)
C(31)	0.3197 (4)	-0.4575 (4)	-0.0694 (4)
C(32)	0.4139 (4)	-0.4724 (4)	-0.1467 (5)
C(33)	0.4203 (4)	-0.3945 (5)	-0.2141 (4)
C(34)	0.3341 (5)	-0.3044 (5)	-0.2067 (4)
C(35)	0.2413 (4)	-0.2877 (4)	-0.1280 (4)
C(36)	0.2343 (4)	-0.3631 (4)	-0.0577 (4)
H(1)[C(1)]	0.1583	-0.0331	0.1049
H(2)[C(2)]	0.1577	0.1161	0.3547
H(3)[C(3)]	-0.0625	0.1552	0.3825
H(4)[C(5)]	-0.2866	0.0293	0.2230
H(5)[C(6)]	-0.3670	-0.1306	0.0127
H(6)[C(7)]	-0.2356	-0.2592	-0.1437
H(7)[C(8)]	-0.0185	-0.2340	-0.0891
H(8)[C(10)]	0.1102	-0.1239	0.4214
H(9)[C(11)]	-0.0977	-0.1994	0.2755
H(10)[C(12)]	-0.1479	-0.4138	0.2828
H(11)[C(14)]	-0.0054	-0.5990	0.3423
H(12)[C(15)]	0.1937	-0.6368	0.4198
H(13)[C(16)]	0.3575	-0.4782	0.4688
H(14)[C(17)]	0.3274	-0.2759	0.4452
H(15)[C(19)]	0.3891	-0.2247	0.2771
H(16)[C(20)]	0.4263	-0.1941	0.0667
H(17)[C(21)]	0.4796	0.0478	0.1477
H(18)[C(23)]	0.4590	0.2702	0.3870
H(19)[C(24)]	0.4012	0.3381	0.6053
H(20)[C(25)]	0.3283	0.1820	0.6775
H(21)[C(26)]	0.3004	-0.0464	0.5323
H(22)[C(28)]	0.0612	-0.3717	0.0045
H(23)[C(29)]	0.1481	-0.5097	0.1268
H(24)[C(30)]	0.3331	-0.6033	0.0145
H(25)[C(32)]	0.4783	-0.5400	-0.1553
H(26)[C(33)]	0.4907	-0.4023	-0.2711
H(27)[C(34)]	0.3394	-0.2495	-0.2606
H(28)[C(35)]	0.1773	-0.2205	-0.1229

Table III. Final Fractional Coordinates for $Sn(\eta^1\text{-}C_9H_7)_4$ (2)

atom	*x/a*	*y/b*	*z/c*
Sn	0.19299 (6)	0.41249 (3)	0.31897 (7)
C(1)	0.3820 (9)	0.4225 (5)	0.492 (1)
C(2)	0.485 (1)	0.3986 (6)	0.459 (1)
C(3)	0.535 (1)	0.3483 (6)	0.526 (1)
C(4)	0.475 (1)	0.3331 (6)	0.611 (1)
C(5)	0.491 (1)	0.2865 (5)	0.695 (1)
C(6)	0.419 (1)	0.2851 (6)	0.763 (1)
C(7)	0.332 (1)	0.3304 (7)	0.744 (1)
C(8)	0.315 (1)	0.3775 (5)	0.663 (1)
C(9)	0.387 (1)	0.3795 (5)	0.593 (1)
C(10)	0.150 (1)	0.3178 (5)	0.271 (1)
C(11)	0.161 (1)	0.2869 (5)	0.388 (1)
C(12)	0.046 (2)	0.2745 (5)	0.376 (1)
C(13)	-0.052 (1)	0.2907 (5)	0.246 (1)
C(14)	-0.182 (2)	0.2854 (6)	0.190 (2)
C(15)	-0.251 (1)	0.3025 (7)	0.063 (3)
C(16)	-0.194 (2)	0.3236 (6)	-0.011 (1)
C(17)	-0.059 (1)	0.3313 (5)	0.047 (1)
C(18)	0.010 (1)	0.3134 (5)	0.176 (1)
C(19)	0.188 (1)	0.4582 (5)	0.148 (1)
C(20)	0.219 (1)	0.5219 (6)	0.181 (1)
C(21)	0.336 (1)	0.5357 (5)	0.189 (1)
C(22)	0.387 (1)	0.4831 (6)	0.158 (1)
C(23)	0.502 (1)	0.4754 (7)	0.151 (1)
C(24)	0.526 (1)	0.419 (1)	0.113 (1)
C(25)	0.438 (2)	0.3720 (7)	0.082 (1)
C(26)	0.324 (1)	0.3797 (6)	0.088 (1)
C(27)	0.299 (1)	0.4356 (6)	0.127 (1)
C(28)	0.0463 (9)	0.4517 (6)	0.367 (1)
C(29)	-0.078 (1)	0.4550 (7)	0.240 (1)
C(30)	-0.105 (1)	0.5128 (8)	0.207 (1)
C(31)	-0.013 (1)	0.5507 (6)	0.302 (1)
C(32)	0.001 (1)	0.6132 (9)	0.314 (2)
C(33)	0.098 (2)	0.6403 (6)	0.421 (2)
C(34)	0.185 (1)	0.6029 (8)	0.522 (2)
C(35)	0.177 (1)	0.5406 (6)	0.513 (1)
C(36)	0.079 (1)	0.5156 (5)	0.404 (1)
H(1)[C(1)]	0.3934	0.4661	0.5212
H(2)[C(2)]	0.5115	0.4179	0.3956
H(3)[C(3)]	0.6031	0.3238	0.5186
H(4)[C(5)]	0.5574	0.2544	0.7089
H(5)[C(6)]	0.4298	0.2512	0.8246
H(6)[C(7)]	0.2797	0.3273	0.7936
H(7)[C(8)]	0.2503	0.4104	0.6535
H(8)[C(10)]	0.2096	0.2982	0.2380
H(9)[C(11)]	0.2429	0.2778	0.4685
H(10)[C(12)]	0.0252	0.2553	0.4449
H(11)[C(14)]	-0.2314	0.2697	0.2384
H(12)[C(15)]	-0.3474	0.3025	0.0185
H(13)[C(16)]	-0.2478	0.3321	-0.1052
H(14)[C(17)]	-0.0139	0.3502	-0.0042
H(15)[C(19)]	0.1019	0.4522	0.0691
H(16)[C(20)]	0.1619	0.5514	0.1993
H(17)[C(21)]	0.3796	0.5764	0.2102
H(18)[C(23)]	0.5669	0.5095	0.1713
H(19)[C(24)]	0.6084	0.4125	0.1077
H(20)[C(25)]	0.4623	0.3326	0.0558
H(21)[C(26)]	0.2600	0.3466	0.0661
H(22)[C(28)]	0.0401	0.4267	0.4375
H(23)[C(29)]	-0.1298	0.4195	0.1897
H(24)[C(30)]	-0.1824	0.5269	0.1255
H(25)[C(32)]	-0.0635	0.6386	0.2450
H(26)[C(33)]	0.1074	0.6857	0.4276
H(27)[C(34)]	0.2563	0.6205	0.6056
H(28)[C(35)]	0.2426	0.5149	0.5832

was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table III.

Discussion

The molecular structures and atom labeling schemes for $Ge(\eta^1\text{-}C_9H_7)_4$ (1) and $Sn(\eta^1\text{-}C_9H_7)_4$ (2) are presented in Figures 1 and 2, respectively. The title compounds are not crystallographically isostructural, crystallizing in different space groups. They are, however, structurally identical. A comparison of the bonding parameters about the central metal atom in each compound is given in Table IV.

Coordination about the metal center is almost exactly tetrahedral in both molecules with mean Ge–C and Sn–C bond lengths of 2.00 (1) and 2.19 (1) Å, respectively. These distances compare closely with unperturbed gas-phase values of 1.945 ($GeMe_4$, microwave spectroscopy)[17] or 2.18

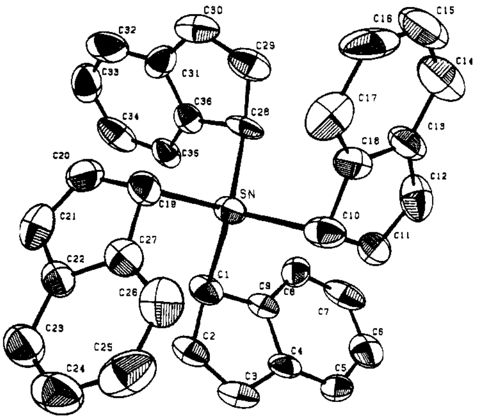


Figure 2. Molecular structure of $Sn(\eta^1\text{-}C_9H_7)_4$ (2).

Table IV. Bond Distances (Å) and Angles (deg) for $M(C_9H_7)_4$ (M = Ge, Sn)

atoms	dist (M = Ge)	dist (M = Sn)
M-C(1)	2.002 (4)	2.205 (9)
M-C(10)	1.990 (4)	2.18 (1)
M-C(19)	2.016 (4)	2.18 (1)
M-C(28)	1.991 (4)	2.200 (9)

atoms	angle (M = Ge)	angle (M = Sn)
C(1)-M-C(10)	109.0 (2)	110.1 (4)
C(1)-M-C(19)	108.3 (2)	111.3 (4)
C(1)-M-C(28)	109.9 (2)	108.3 (4)
C(10)-M-C(19)	108.4 (2)	108.4 (4)
C(10)-M-C(28)	110.6 (2)	109.3 (4)
C(19)-M-C(28)	110.6 (2)	109.4 (4)
M-C(1)-C(2)	109.9 (3)	109.3 (7)
M-C(1)-C(9)	111.9 (3)	107.5 (7)
M-C(10)-C(11)	111.1 (3)	108.1 (8)
M-C(10)-C(18)	112.7 (3)	107.1 (7)
M-C(19)-C(20)	109.8 (3)	108.1 (8)
M-C(19)-C(27)	108.3 (3)	108.4 (7)
M-C(28)-C(29)	111.0 (3)	107.3 (7)
M-C(38)-C(36)	110.7 (3)	108.9 (6)

Å ($SnMe_4$, electron diffraction);[18] in $Sn(\eta^1\text{-}C_5H_5)_4$ the mean Sn–C bond length determined crystallographically was substantially longer at 2.27 Å. Each of the four indenyl groups is attached identically to the metal center through the (saturated) C^1 atom, in accord with expectations for the η^1 mode of bonding and with the characterization using NMR spectroscopy of the intramolecular rearrangement behavior of 1, 2, and related molecules.[1,3,6] Bond distances and angles within the indenyl fragments are represented in Figure 3 for both compounds. The bicyclic skeletons are planar to within 0.08 (1) and 0.09 Å (2), and the M–C^1 bond meets the C_5 ring at an average angle of 122° in 1 and 117° in 2. There is clear evidence for localization of double-bond character between C^2 and C^3 (mean distance 1.336 Å for 1 and 1.34 Å for 2) compared with C^8C^9 so that within the cyclopentadienyl ring the overall shape may be described as long–short–medium–medium–long.

Earlier we have analyzed the diastereoisomerism in poly(η^1-indenyl)metal derivatives that arises from asymmetry at the C^1 carbon atom in the mono-1-substituted indene. At slow rates of metallotropic rearrangement all three isomers of 1 or 2 were detected by ^{13}C NMR spectroscopy, in approximately statistical equilibrium distribution in solution. As the rate of the stereospecific[1] metallotropic shift becomes faster, the indenyl C^1 and C^3 positions are progressively averaged and the diastereomers are simultaneously scrambled.[6] The structure of the crystalline solid for each compound is that of a single stereoisomer; the molecular arrangement reported here conforms to S_4 point-group symmetry and represents[6] the meso modification.

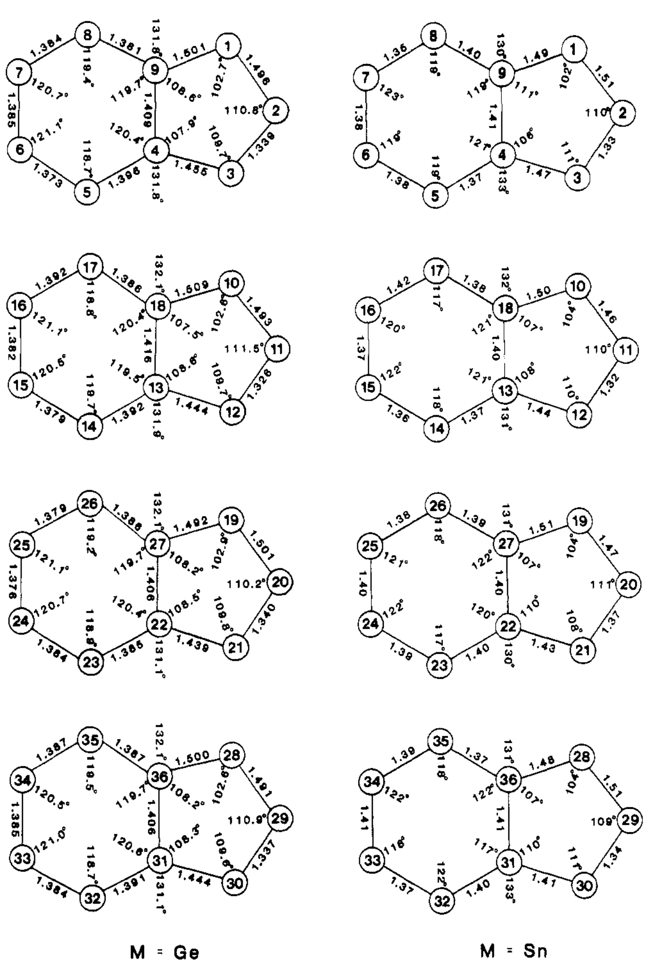


Figure 3. Bond distances (Å) and angles (deg) associated with the (η^1-C_9H_7) ligands for A, $Ge(\eta^1\text{-}C_9H_7)_4$ (1), and B, $Sn(\eta^1\text{-}C_9H_7)_4$ (2).

While a number of species MR_4 have been shown to possess molecular structures belonging to the point-group S_4, invariably the ground-state geometry so adopted is attained through conformational distortion of a configuration belonging to a higher symmetry group, normally[19] D_{2d}. Illustrative examples of structures having S_n symmetry are usually contrived in this way, and the rarity of molecules for which the highest possible symmetry corresponds to such a point group has frequently been acknowledged.[20] Over 20 years ago and in a most elegant way McCasland and co-workers delineated[21] the configurational logistics of substances whose optical inactivity can be attributed only to fourfold alternating axial molecular symmetry, i.e., belonging to the point-group S_4. Nevertheless so far as we are aware only once before has a real example representing this situation been structurally characterized: the bis[*N*,*N*,*N*^{1},*N*^{1}-tetrapropyl(*trans*-1,2-cyclohexylenedioxy)diacetamido]manganese(II) cation, for which X-ray data were published[22] in 1977. By comparison

---

(17) Laurie, V. W. *J. Chem. Phys.* **1959**, *30*, 1210.

(18) Brockway, L. O.; Jenkins, H. O. *J. Am. Chem. Soc.* **1936**, *58*, 2036.

(19) Karipides, A.; Iroff, L. D.; Mislow, K. *Inorg. Chem.* **1979**. *18*, 907.

(20) Cotton, F. A. "Chemical Applications of Group Theory", 2nd ed.; Wiley-Interscience: New York, 1971. Orchin, M. M.; Jaffe, H. H. *J. Chem. Educ.* **1970**, *47*, 372. Mislow, K. "Introduction to Stereochemistry"; W. A. Benjamin: New York, 1965. Farina, M.; Morandi, C. *Tetrahedron* **1974**, *30*, 1819 and references therein.

(21) McCasland, G. E.; Horvat, R.; Roth, M. R. *J. Am. Chem. Soc.* **1959**, *81*, 2399.

the dissymmetric geometry of compounds 1 and 2 is much more easily recognizable, and for this reason we feel that the common structure for these two molecules should be regarded as pedagogically significant. Crystallization of each as the pure meso isomer results from continuous depletion from solution of the least soluble component in the equilibrium diastereomer distribution.

Acknowledgment. We thank the NSERC (S.R.S., Canada) and NSF (J.L.A., U.S.A.) and the Research Corp. (S.R.S., Cottrell Foundation) for financial support for this study.

Registry No. 1, 80865-56-1; 2, 7770-22-1.

Supplementary Material Available: Tables of best plane results, thermal parameters, and observed and calculated structure factor for 1 and 2 (22 pages). Ordering information is given on any current masthead page.

---

(22) Neupert-Laves, K.; Dobler, M. *Helv. Chim. Acta* **1977**, *60*, 1861.

Preparation, Structure, and Ligand Substitution Reactions of (Cycloocta-1,5-diene)-(methyl *trans*-β-(phenylsulfonyl)acrylate)nickel

H. Michael Büch, Paul Binger,* and Carl Krüger

Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim-Ruhr, West Germany

Received February 16, 1984

The title compound was synthesized from bis(cycloocta-1,5-diene)nickel [Ni(cod)$_2$] and methyl *trans*-β-(phenylsulfonyl)acrylate (sma) in 88% yield and characterized by mass, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Its structure was determined by X-ray diffraction. The compound crystallizes from THF/Et$_2$O/pentane in the monoclinic space group C^5_{2h}—$P2_1/c$ with a = 8.428 (1) Å, b = 17.645 (4) Å, c = 12.168 (1) Å, β = 104.35 (1)°, and Z = 4. The structure was refined to R = 0.062 using 2616 unique data ($I < 2.0\sigma(I)$). The 16-electron complex is trigonal planar with the midpoints of the three coordinated C=C double bonds occupying vertices of a triangle centered at the nickel atom. Two of the double bonds are arranged perpendicular to the coordination plane, a conformation which has not yet been observed in d^{10} tris(olefin) complexes. Intramolecular distances indicate an anomalously short nonbonded contact between nickel and sulfur. Selective ligand substitution reactions can be achieved at room temperature or below. Treatment of the complex with diphosphines, 2,2′-bipyridine, 1,4-diazabuta-1,3-dienylbis(2,6-xylene), ethylenebis(dimethylamine), or an excess of 1,6-dimethylcycloocta-1,5-diene results in the liberation of the cod ligand, giving new NiL$_2$(sma) complexes. Maleic anhydride (mah) replaces the vinyl sulfone to give Ni(cod)(mah). When (cycloocta-1,5-diene)(dimethyl fumarate)nickel [Ni(cod)(fdm)] is treated with methyl *trans*-β-(phenylsulfonyl)acrylate (sma), the title compound is obtained in quantitative yield. Thus the coordinating ability of activated olefins increases in the order fdm < sma < mah.

Introduction

A wide variety of stoichiometric and catalytic reactions of unsaturated substrates are promoted or catalyzed by nickel(0) compounds.[1,2] A fascinating feature of these reactions is that they can be controlled by variation of the ligands attached to the nickel. For example, the so-called "naked nickel" (e.g., Ni(cod)$_2$ where cod = cycloocta-1,5-diene) catalyzes the cyclodimerization of methylenecyclopropane,[3] whereas the presence of phosphine-modified nickel(0) results in cyclotrimerization.[4] On the other hand, addition of special α,β-unsaturated carboxylic acid derivatives to nickel(0) leads to a remarkable enhancement of the cyclodimerization.[5] Unsaturated ligands such as these attract special attention since in some cases they act not only as controlling factors but also as cosubstrates.[6] It was therefore thought worthwhile to look for new ligands that might be able to play both parts.

It has recently been demonstrated that vinyl sulfones are useful synthons in organic chemistry. They can be used as ethylene,[7] acetylene,[8] or ketene[9] equivalents in Diels–Alder cycloadditions and 1,3-diyl trapping reactions.

We now have found that one chelating cod ligand in Ni(cod)$_2$ can be smoothly replaced by vinyl sulfones to give new thermally stable Ni(cod)(olefin) complexes whose behavior as catalysts is under investigation. In this paper we report the synthesis and structure of the title compound together with some related chemistry.

Experimental Section

General Remarks. All manipulations were carried out in oxygen-free, rigorously dried solvents under high-purity argon. The NMR spectrometers used were Bruker WP 80 FT (^{1}H and ^{31}P), Varian XL 100 FT (^{13}C), and Bruker WH 400 FT (^{1}H). ^{31}P positive chemical shifts are downfield from 85% H$_3$PO$_4$. IR spectra were run on a Nicolet FT IR 7199 spectrometer. The mass spectra were obtained on an Atlas-CH 5 spectrometer. Melting points were determined with a Büchi SMP-20 apparatus in ca-

---

(1) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1975; Vols. 1 and 2.

(2) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

(3) Binger, P. *Angew. Chem.* **1972**, *84*, 352.

(4) Binger, P.; McMeeking, J. *Angew. Chem.* **1973**, *85*, 1053.

(5) Binger, P. *Synthesis* **1973**, 427.

(6) Binger, P.; Cetinkaya, B; Doyle, M. J.; Germer, A.; Schuchardt, U. *Fundam. Res. Homogeneous Catal.* [*Proc. Int. Workshop*] **1979**, *3*, 271.

(7) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853.

(8) De Luchi, O.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1982**, 914.

(9) Little, R. D.; Myong, S. O. *Tetrahedron Lett.* **1980**, *21*, 3339.

0276-7333/84/2303-1504$01.50/0