37685-63-5; I, 107-19-7; III, 90108-85-3; IV, 90132-10-8; V, 624-67-9; VII, 90108-87-5; VIII, 90108-88-6; IX, 90108-89-7; XI, 82648-21-3; XII, 82648-22-4; XIII, 90108-90-0; XIV, 90108-91-1; XV, 90108-92-2; XVI, 90108-93-3; $[(EtO)_2DCC{\equiv}CCD(OEt)_2]Co_2(CO)_6$, 90109-01-6; $HC{\equiv}CPh$, 536-74-3; $HC{\equiv}C$-*n*-Bu, 693-02-7; $HC{\equiv}CC(CH_3){=}CH_2$, 78-80-8; $HC{\equiv}C$-*t*-Bu, 917-92-0; $HC{\equiv}CMe$, 74-99-7; $MeC{\equiv}CPh$, 673-32-5; $PhC{\equiv}CPh$, 501-65-5; $MeC{\equiv}C$-*n*-Pr, 764-35-2; $MeC{\equiv}CMe$, 503-17-3; $EtC{\equiv}CEt$, 928-49-4; $HC{\equiv}CCO_2Et$, 623-47-2; $(EtO)_2CHC{\equiv}CCN$, 73542-39-9; $PhC{\equiv}CCHO$, 2579-22-8; $(EtO)_2CHC{\equiv}CCHO$, 74149-25-0; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $OHCC{\equiv}CCHO$, 21251-20-7; $OHCC{\equiv}CCN$, 90108-94-4; $CF_3C{\equiv}CCF_3$, 692-50-2; $Co_2(CO)_8$, 10210-68-1.

Communications

Crystal Structure of (μ-Trithio)bis[tricyclohexylgermanium(IV)]: Corrigendum[†]

Richard E. Marsh* and Kirby J. Slagle

Arthur Amos Noyes Laboratory of Chemical Physics
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

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Summary: The crystal structure of $[(C_6H_{11})_3Ge]_2S_3$, which has been described and refined[1] in the triclinic space group $P1$, can be better described in space group $P\bar{1}$. Least-squares refinement in $P\bar{1}$ led to an R of 0.052 for 3394 reflections, compared to an R of 0.070 obtained for the $P1$ refinement. In the $P\bar{1}$ description, the central S atom is disordered between two centrosymmetrically related sites; as a result of this disorder, the S–S distances, which are calculated at 1.973 (3) and 2.051 (3) Å, may well be equal at about 2.01 Å. Other distances and angles are now normal.

The crystal structure of $[(C_6H_{11})_3Ge]_2S_3$ has been described[1] in the triclinic space group $P1$ (a = 9.004 (7), b = 9.808 (4), c = 11.815 (5) Å; α = 83.14 (3), β = 84.64 (5), γ = 66.92 (5)°; Z = 1) and refined to an R of 0.063 for 3185 reflections with $I > 1.9\sigma(I)$, R = 0.070 for all 3395 measured reflections. Three considerations led us to investigate the possibility of higher symmetry: (1) the molecule has potential symmetry that space group $P1$ cannot satisfy; (2) averaging the coordinates (Table I[1]) of the two pairs of chemically equivalent heavy atoms Ge(1), Ge(2) and S(1), S(3) gives nearly identical values ($\bar{x}$ = 0.193, $\bar{y}$ = 0.128, $\bar{z}$ = −0.197); (3) most convincing of all, the authors noted that the highest peak in a final difference map (1.2 e·Å^{-3}) "was in the vicinity of the sulfur atoms, at 1.92, 2.21, and 2.04 Å from the S(1), S(2) and S(3) atoms, respectively". By triangulation, this peak must be related to the central atom S(2) by the same point that relates Ge(1) to Ge(2) and S(1) to S(3), suggesting that the space group might be $P\bar{1}$ with S(2) disordered between two centrosymmetrically related sites. Further study showed that every remaining atom in Table I[1] has a chemically equivalent mate approximately related by the same center of symmetry.

Reformulating the structure in $P\bar{1}$ required a shift of origin to x = 0.19, y = 0.13, and z = −0.20 and an averaging of symmetry-related coordinates. (This averaging was confusing because of inconsistencies in the atom numbering system, which does not conform to Figure 1 of ref 1.) Atom S(2) was assigned a population parameter of 0.5. The hydrogen atoms were placed in assumed positions so as to complete tetrahedra with C–H = 0.95 Å, as in ref 1, and were not further adjusted. Initial least-squares refinement led to an R of 0.065 for the 3395 reflections in the supplementary table, but one reflection ($70\bar{2}$) was a statistical outlier; when it was removed from the refinement, convergence was reached at R = 0.052 for all 3394 reflections and R = 0.050 for 3188 reflections with $I > 1.9\sigma(I)$, compared to 0.070 and 0.063 for the $P1$ refinement.[1] The principal features of a final difference map were about 0.5 and −0.9 e·Å^{-3} in height and formed a familiar clover-leaf pattern about the Ge atom, suggesting that the U_{ij} terms were not able to completely compensate for systematic errors such as absorption. There were similar but smaller features about S(1,3), but no indications of additional disorder. The final $P\bar{1}$ coordinates are given in Table I. Coordinates assigned to the H atoms and U_{ij}

Table I. Coordinates (×10^5 for Ge; ×10^4 for S and C) and U_{eq} Values (×10^4) (Space Group $P\bar{1}$)

	x	y	z	U_{eq}, Å^2
Ge(1,2)	19399 (6)	12777 (5)	−19726 (4)	419 (1)
S(1,3)	1903 (2)	−226 (2)	−351 (1)	656 (3)
S(2)[a]	73 (3)	−920 (3)	−537 (2)	575 (5)
C(11,61)	95 (5)	1635 (5)	−2894 (4)	481 (10)
C(12,66)	−1465 (6)	2863 (6)	−2494 (4)	604 (13)
C(13,65)	−2858 (6)	3163 (6)	−3258 (5)	737 (16)
C(14,64)	−2440 (7)	3511 (6)	−4499 (5)	734 (15)
C(15,63)	−921 (7)	2272 (7)	−4906 (5)	758 (16)
C(16,62)	475 (6)	2000 (6)	−4162 (4)	611 (13)
C(21,41)	1884 (5)	3155 (5)	−1489 (4)	491 (10)
C(22,46)	2355 (7)	4078 (6)	−2466 (4)	640 (13)
C(24,45)	2280 (9)	5532 (6)	−2093 (6)	906 (18)
C(23,44)	3248 (8)	5318 (6)	−1069 (5)	756 (15)
C(25,43)	2770 (7)	4430 (7)	−103 (5)	742 (14)
C(26,42)	2876 (7)	2948 (6)	−456 (4)	672 (13)
C(31,51)	3981 (5)	112 (5)	−2785 (4)	448 (9)
C(32,56)	5483 (6)	−174 (6)	−2160 (4)	595 (12)
C(33,55)	7031 (6)	−1081 (7)	−2830 (5)	741 (16)
C(34,54)	6989 (7)	−2521 (6)	−3142 (5)	715 (15)
C(35,53)	5488 (7)	−2238 (6)	−3767 (5)	733 (15)
C(36,52)	3952 (6)	−1366 (5)	−3087 (5)	643 (13)

[a] Half-populated site.

Table II. 206 Reflections, $I \leqslant 1.9\sigma(I)$

	$P\bar{1}$	$P1$
ΣF_o	222.4	218.4
$\Sigma\lvert F_c\rvert$	186.0	463.7
$\Sigma\lvert\Delta F\rvert$	99.4	270.8
R	0.45	1.24

[†] Contribution No. 6978.

[1] Brisse, F.; Vanier, M.; Olivier, M. J.; Gareau, Y.; Steliou, K. *Organometallics* **1983**, 878–882.

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values for the heavier atoms have been submitted as supplementary material.

Of particular interest are the 206 reflections coded as having $I \leq 1.9\sigma(I)$; some statistics for these reflections are given in Table II. (The $70\bar{2}$ reflection is excluded, being a severe outlier with $F_o = 0.6$ and $F_c = 13.6$ for both refinements.) For the $P1$ description, the average value of $|F_c|$ is over twice that of F_o and the R index is a striking 1.24, clear evidence of the inappropriateness of the noncentrosymmetric description. On the other hand, the numbers are quite reasonable for the $P\bar{1}$ description. The message is clear and we repeat it:[2] if there is possible ambiguity between a centrosymmetric and a noncetrosymmetric description of a structure, the weak reflections are the ones most able to provide a choice. The common practice of deleting these reflections from the data set is a dangerous one and should be strongly discouraged.

The $P\bar{1}$ refinement has led to a considerably more reasonable molecular structure. For example, the Ge–C bond lengths are statistically equal at 1.970 (3) Å whereas they ranged from 1.896 to 2.050 Å for the $P1$ refinement, and the range of C–C distances is between 1.486 (9) and 1.544 (7) Å compared with 1.427–1.614 Å. Nevertheless, the two S–S distances, at 1.973 (3) and 2.051 (3) Å, remain severely disparate. It is probable that the disparity is related to the disorder of the central atom S(2). In particular, atom S(1,3) has a large anisotropic "temperature" factor, with its principal axis (U = 0.094 (1) A^2) oriented along the S(2)···S(2)′ direction; this atom may well occupy alternative sites that depend upon which S(2) site is occupied. Because of this situation, no reliable value can be assigned to either S–S distance; they could well be equal at about 2.01 Å. The Ge–S distance, for which we obtain the value 2.281 (2) Å, is less seriously in doubt because the bond is directed approximately perpendicular to the principal axis of S(1,3); possibly it should be lengthened slightly.

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Registry No. $[(C_6H_{11})_3Ge]_2S_3$, 85185-49-5.

Supplementary Material Available: Tables of coordinates and isotropic B's, assigned to the hydrogen atoms, and anisotropic U's (2 pages). Ordering information is given on any current masthead page.

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(2) Marsh, R. E. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1985–1988.

Synthesis and Characterization of New, Air-Stable *closo*-1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$

Narayan S. Hosmane* and Narayan N. Sirmokadam

Department of Chemistry, Southern Methodist University
Dallas, Texas 75275

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Summary: The *closo*-osmacarborane, 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$, has been synthesized by the reaction of Os$_3$(CO)$_{12}$ with either *closo*-Sn[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_4$ or *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$. The reaction of Os$_3$(CO)$_{12}$ with the *closo*-stannacarborane yielded the osmacarborane in gram quantities in almost quantitative yields, while *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$ produced the osmacarborane in much lower yields.

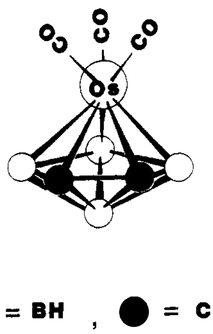

Figure 1. Proposed structure of 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$.

Although several hundred metallacarborane derivatives containing transition metals or main-group metals have been synthesized,[1,2] insertion of osmium metal into a carborane cage framework has never been reported. However, Shore et al. demonstrated the insertion of one BH unit into an osmium–carbonyl bond of (μ-H)$_2$Os$_3$(CO)$_{10}$ to produce (μ-H)$_3$(CO)$_9$Os$_3$BCO in 85% yield.[3]

We have recently reported the synthesis of the carborane *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$[4] and the stannacarborane *closo*-Sn[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_4$.[5] We report herein the reaction of Os$_3$(CO)$_{12}$ with these new carboranes to produce the first osmacarborane having a pentagonal-bipyramidal geometry (Figure 1). This compound is isoelectronic and isostructural with known metallacarboranes[1,2] of the types C$_2$B$_4$H$_6$MLn, C$_2$B$_3$H$_5$(MLn)$_2$ [MLn = Fe(CO)$_3$, CoCp, Ni(PPh$_3$)$_2$, Pt(PEt$_3$)$_2$, GaR, BeNMe$_3$, AlR, Sn, Pb], C$_3$B$_3$H$_5$CH$_3$Mn(CO)$_3$, and C$_4$BH$_3$R$_2$[Mn(CO)$_3$]$_2$.

The reaction of Os$_3$(CO)$_{12}$ with *closo*-Sn[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_4$, in a molar ratio of 1:3, in the absence of a solvent at 150 °C produced 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$ as an air-stable, volatile (bp 148–149 °C at 10 torr of argon), colorless liquid; in addition, the side products, carbon monoxide and metallic tin (Sn^0), were produced in almost quantitative yields. The fact that this compound is obtained in gram quantities as a single volatile carborane product is in contrast with the results of the gas-phase reaction of Sn(CH$_3$)$_2$C$_2$B$_4$H$_4$ with (η^5-C$_5$H$_5$)Co(CO)$_2$ which produced a mixture of (η^5-C$_5$H$_5$)CoSn(CH$_3$)$_2$C$_2$B$_4$H$_4$, 1,2,3-(η^5-C$_5$H$_5$)Co(CH$_3$)$_2$C$_2$B$_4$H$_4$, and (η^5-C$_5$H$_5$)$_2$Co$_2$(CH$_3$)$_2$C$_2$B$_4$H$_4$ in low yields.[6] The reaction of Os$_3$(CO)$_{12}$ with *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$ at 140 °C also produced the same *closo*-osmacarborane (Figure 1) in very low yield (<3%). The other detectable gaseous products were carbon monoxide and, presumably, hydrogen.

The electron-impact mass spectrum of 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$ exhibited an intense parent grouping [^{192}Os(^{12}C^{16}O)$_3$(^{12}CH$_3$)$_6$^{28}Si$_2$^{12}C$_2$^{11}B$_4$H$_4$$^+$] with the major cutoff at m/e 494 and strong groups with local cutoffs at m/e 479, 466, 451, 423, 409, 395, 338, 323, 309 that correspond to the fragments Os(CO)$_3$(CH$_3$)$_5$Si$_2$C$_2$B$_4$H$_4$$^+$, Os(CO)$_2$(CH$_3$)$_6Si_2C_2B_4H_4$$^+$, Os(CO)$_2$(CH$_3$)$_5Si_2C_2B_4H_4$$^+$, Os(CO)(CH$_3$)$_5Si_2C_2B_4H_4$$^+$, Os(CO)(CH$_3$)$_4Si_2C_2B_4H_5$$^+$, Os-

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(1) "Metal Interactions with Boron Clusters", Grimes, R. N., Ed. Plenum Press: New York, 1982 and references therein.

(2) Grimes, R. N. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982, Vol. 1, and references therein.

(3) Shore, S. G.; Jan, D. Y.; Hsu, L. Y.; Hsu, W. L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

(4) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N., submitted for publication.

(5) Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics*, in press.

(6) Wong, K.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053.

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