Methyltriphenylphosphonium Undecahydro-1,2-dicarba-3-thalla-*closo*-dodecaborate–Tetrahydrofuran, [PPh₃Me]⁺[3,1,2-TlC₂B₉H₁₁]⁻ · ½(C₄H₈O), at 173 K

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Abstract. $C_{19}H_{18}P^+ \cdot C_2H_{11}B_9Tl^- \cdot \frac{1}{2}(C_4H_8O)$, monoclinic, $P2_1/c$, $a = 12.3755$ (17), $b = 14.4518$ (18), $c = 15.3769$ (16) Å, $\beta = 98.416$ (10)°, $Z = 4$, $D_m = 1.58$ (1) (293 K), $D_x = 1.587$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 60.7$ cm⁻¹. The structure has been refined to $R = 0.028$ on 3183 observed reflections. The anion may be formally regarded as an ion pair, $[Tl^+C_2B_9H_{11}^{2-}]^-$, and provides evidence for a progressive opening of the metallacarbaborane cage as electron density on the metal increases. The parameters of the essentially uncoordinated cage confirm that the framework distortions in related compounds are produced by coordination of a metal-ligand group, and provide a useful base for the assessment of these distortions.

Introduction. As part of a systematic study of the molecular geometries of $3,1,2\text{-}MC_2B_9H_{11}$ metallacarbaboranes, we have undertaken a single-crystal X-ray study of the $d^{10}s^2$ (Tl^I) title complex. This salt of the $[3,1,2\text{-}TlC_2B_9H_{11}]^-$ ion, originally reported by Spencer, Green & Stone (1972), completes the series of transition-metal ions in isoelectronic $3,1,2\text{-}MC_2B_9H_{11}$ complexes from d^6 (Re^I) (Zalkin, Hopkins & Templeton, 1966), through d^8 (Au^{III}) (Colquhoun, Greenhough & Wallbridge, 1976) and d^{10} (Hg^{II}) (Colquhoun, Greenhough & Wallbridge, 1977a) to $d^{10}s^2$ (Tl^I). The crystal data and preliminary metal–cage distances have been given previously (Colquhoun, Greenhough & Wallbridge, 1977a).

The lattice parameters were derived by least-squares calculations from the setting angles of 15 reflections ($2\theta = 25$–30°) measured on a Syntex $P2_1$ computer-controlled diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and a low-temperature device (N₂ stream) in operation at 173 K. Intensities were measured out to $2\theta = 52°$ by the θ–2θ scan with a variable scan range and speed, and a crystal $0.005 \times 0.012 \times 0.012$ mm. 4401 measurements included 3279 intensities with $I > 3\sigma(I)$ (variances based on counting

statistics) which were classified as observed and used in the structure analysis. Periodic remeasurement of the intensities of four reflections showed no significant change over the 270 h X-ray exposure, whereas crystals exposed to the air at room temperature during this period exhibited marked signs of deterioration. Lorentz and polarization corrections were carried out and systematic absences $h0l$, $l = 2n$ and $0k0$, $k = 2n$ confirmed the space group $P2_1/c$. The crystal was found to be bounded by (010), (100), (011), (0$\bar{1}$1), (10$\bar{2}$), (1$\bar{1}$2) and (11$\bar{2}$) and the inverse planes, accurate

Table 1. *Atomic coordinates* ($\times 10^4$, *for* Tl *and* P $\times 10^5$) *with e.s.d.'s in parentheses*

	x	y	z
Tl	23730 (2)	17778 (2)	−5142 (1)
P	28235 (9)	81267 (10)	5488 (8)
C(1)	4014 (4)	2487 (4)	887 (3)
C(2)	2916 (4)	2946 (3)	1029 (3)
B(4)	3918 (5)	1348 (5)	895 (4)
B(5)	4635 (5)	1943 (5)	1827 (4)
B(6)	3986 (5)	3011 (4)	1887 (4)
B(7)	1976 (5)	2188 (4)	1150 (4)
B(8)	2589 (5)	1107 (4)	1112 (3)
B(9)	3697 (5)	1063 (4)	1985 (4)
B(10)	3726 (5)	2115 (4)	2595 (4)
B(11)	2623 (5)	2809 (5)	2082 (4)
B(12)	2439 (5)	1588 (4)	2150 (3)
C(21)	1886 (4)	8055 (4)	1332 (3)
C(22)	1843 (4)	8758 (4)	1936 (3)
C(23)	1078 (5)	8729 (4)	2513 (3)
C(24)	368 (5)	7992 (5)	2477 (4)
C(25)	394 (5)	7300 (5)	1882 (4)
C(26)	1158 (5)	7332 (4)	1306 (4)
C(31)	3140 (4)	6970 (3)	241 (3)
C(32)	3534 (5)	6345 (4)	896 (3)
C(33)	3791 (5)	5455 (4)	687 (4)
C(34)	3680 (5)	5182 (4)	−184 (4)
C(35)	3312 (5)	5800 (4)	−838 (4)
C(36)	3032 (4)	6692 (4)	−632 (3)
C(41)	2219 (4)	8766 (3)	−393 (3)
C(42)	2781 (4)	9146 (4)	−964 (3)
C(43)	2408 (5)	9633 (4)	−1694 (3)
C(44)	1282 (5)	9747 (4)	−1860 (3)
C(45)	633 (5)	9380 (4)	−1303 (4)
C(46)	1093 (4)	8888 (4)	−566 (3)
C(50)	4054 (4)	8679 (4)	1027 (3)

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measurement of interfacial distances being used in *ABSCOR* (Alcock, 1970), which gave maximum and minimum transmission factors for the correction of $|F_o|$ of 0·778 (002) and 0·529 ($\bar{2}$94).

The Tl and P atoms were located from a Patterson synthesis and successive least-squares refinement and Fourier synthesis, followed by a difference synthesis, allowed all atoms, except the solvent, to be located and refined anisotropically, except for H which were only positionally refined at this stage. A further difference synthesis contained large peaks around the centre of symmetry at $0,\frac{1}{2},0$ which were identified as disordered tetrahydrofuran (THF) of solvation. The solvent atoms were all treated as $\frac{1}{2}$C and included in the model. Least-

squares refinement on all parameters, except the assigned isotropic temperature factors for H and THF, with anomalous scattering components for Tl and P (Cromer & Liberman, 1970) gave $R = 0\cdot030$ ($R = \sum |\varDelta F|/\sum |F_o|$) for the observed reflections. Despite overlap of the centrosymmetrically related $\frac{1}{2}$THF molecules, a reasonable geometry was obtained from the refinement, and further refinement including the solvent U values clearly indicated which C was in fact an O atom. Numerous relatively large $\varDelta F$ values and peaks in a difference synthesis were improved first by using the scattering factors for Tl$^+$ (Cromer & Mann, 1968), and then by including H atoms for the solvent at calculated positions. A sensible extinction correction could not be computed, and five reflections thought to be badly affected were deleted. Symmetry-related pairs of reflections were averaged, and the final refinement included all parameters except those for the calculated H atoms and the solvent population parameter set at 0·5. The final value of R was 0·028 for 3183 observed reflections, the function minimized being $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[1 + \sigma(F_o)^2 + 0\cdot0001F_o^2]$. The final R_w $\{= [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\}$ was 0·027. A difference synthesis calculated after the final cycle showed only random fluctuations up to $\pm0\cdot3$ e Å^{-3}, except in the region of Tl$^+$ where one peak of $\pm0\cdot6$ and another of $-0\cdot5$ e Å^{-3} were present. Final positional and (for H) thermal parameters are given in Tables 1 and 2.*

Table 2. *Hydrogen and THF solvent positional coordinates* ($\times 10^3$, *for* C *and* O $\times 10^4$) *and thermal parameters* ($\times 10^2$)

	x	y	z	U (Å^2)
H(1)	436 (4)	282 (3)	50 (3)	3·2 (1·3)
H(2)	272 (4)	357 (3)	72 (3)	4·5 (1·5)
H(4)	445 (4)	89 (3)	50 (3)	3·8 (1·4)
H(5)	556 (4)	191 (3)	203 (3)	3·9 (1·4)
H(6)	443 (4)	369 (3)	207 (3)	4·5 (1·5)
H(7)	108 (3)	237 (3)	99 (3)	2·4 (1·2)
H(8)	212 (3)	44 (3)	91 (3)	2·7 (1·2)
H(9)	401 (4)	42 (3)	231 (3)	4·1 (1·4)
H(10)	398 (3)	220 (3)	331 (3)	2·0 (1·2)
H(11)	213 (3)	337 (3)	239 (2)	1·7 (1·1)
H(12)	188 (4)	131 (3)	261 (3)	3·9 (1·4)
H(22)	231 (4)	924 (3)	195 (3)	3·9 (1·4)
H(23)	111 (4)	926 (4)	288 (3)	5·8 (1·7)
H(24)	−6 (4)	794 (3)	282 (3)	4·4 (1·5)
H(25)	−5 (5)	678 (4)	188 (4)	6·5 (1·7)
H(26)	121 (4)	683 (4)	92 (3)	6·2 (1·7)
H(32)	355 (3)	654 (3)	147 (3)	1·8 (1·1)
H(33)	409 (4)	504 (3)	114 (3)	4·1 (1·4)
H(34)	375 (4)	451 (4)	−37 (3)	5·8 (1·7)
H(35)	320 (5)	557 (4)	−141 (4)	7·1 (1·9)
H(36)	276 (4)	714 (3)	−106 (3)	4·0 (1·5)
H(42)	362 (3)	904 (3)	−86 (3)	2·6 (1·2)
H(43)	288 (4)	987 (4)	−203 (3)	5·4 (1·6)
H(44)	93 (4)	1014 (4)	−235 (3)	6·0 (1·7)
H(45)	−16 (5)	938 (4)	−138 (4)	6·8 (1·9)
H(46)	63 (4)	860 (3)	−22 (3)	4·3 (1·5)
H(501)	387 (4)	929 (3)	117 (3)	4·2 (1·4)
H(502)	457 (3)	866 (3)	65 (3)	2·7 (1·2)
H(503)	429 (4)	833 (3)	152 (3)	4·3 (1·4)
THF				
O(1)	9938 (7)	5198 (6)	986 (5)	5·6 (0·2)
C(61)	9195 (13)	5562 (12)	276 (10)	6·4 (0·4)
C(62)	9659 (19)	5434 (16)	−590 (14)	9·2 (0·7)
C(63)	10651 (15)	4940 (14)	−304 (11)	7·8 (0·5)
C(64)	10743 (13)	4709 (12)	559 (9)	5·1 (0·4)
H(611)	907	622	39	8·0
H(612)	850	520	25	8·0
H(621)	911	508	−102	8·0
H(622)	975	606	−85	8·0
H(631)	1067	437	−67	8·0
H(632)	1128	536	−41	8·0
H(641)	1065	404	62	8·0
H(642)	1149	490	86	8·0

Discussion. Interatomic separations for the anion are given in Table 3 according to the atomic labels shown in Fig. 1. There are no unusual intermolecular contact distances.

The metal–cage distances, the shortest of which considerably exceeds the sum of the covalent radii, have been discussed in terms of a progressive opening of the metallacarbaborane cage as electron density on the metal increases (Colquhoun, Greenhough & Wallbridge, 1977*a*). Since the C$_2$B$_9$H$_{11}$ cage itself can be regarded essentially as 7,8-C$_2$B$_9$H$_{11}^{2-}$, the structure provides the best data so far for the parameters of an uncoordinated cage, and confirmation is provided that the framework distortions in 1,2-C$_2$B$_9$H$_{11}$ metalla-carbaboranes (Mingos, Forsyth & Welch, 1977; Colquhoun, Greenhough & Wallbridge, 1976, 1977*b*, 1978) are produced by coordination of a metal-ligand system to the 7,8-C$_2$B$_9$H$_{11}^{2-}$ anion. Furthermore, the framework geometry provides both a reference point for the assessment of such distortions and a con-

figuration for MO calculations which have so far been performed on an anion with an idealized undistorted icosahedral framework with C—B, C—C and B—B all 1·75 Å (Mingos, 1977; Mingos, Forsyth & Welch, 1977).

Table 4 illustrates both the progressive cage opening in the isoelectronic 18 e $d^6-d^8-d^{10}-d^{10}s^2$ complexes and the framework distortions associated with the coordination of $d^6-d^{10}s^2$ metal ions in $3,1,2\text{-}MC_2B_9H_{11}$ complexes. While some of the individual measurements are not significantly different, the overall trends

in the cage parameters given are easily recognized. Indeed, the trend in all the given quantities in Table 4 is retained even when the parameters of either of the recently reported d^8 metallacarbaboranes, $3,3\text{-}(PEt_3)_2$-$3,1,2\text{-}PtC_2B_9H_{11}$ (Mingos, Forsyth & Welch, 1977) and $[(1,2\text{-}C_2B_9H_{11})_2Au]^-[(Et_2NCS)_2Au]^+$ (Colquhoun, Greenhough & Wallbridge, 1977b), are substituted for the d^8 values given. In addition, the cage parameters for all three d^8 compounds may be so arranged side by side in Table 4 that not only is a progressive trend across these three sets of values apparent, but also the overall trends throughout the table remain. Other cage parameters, such as the B—B bond distances in the lower pentagonal girdle and the two C—B(6) distances, do not exhibit discernible or convincing trends; the most marked distortions occur in the parameters of the C_2B_3 face and the non-planarity of both this and the lower B_5 pentagonal girdle.

Table 3. *Interatomic distances* (Å) *for the anion with e.s.d.'s in parentheses*

Tl—C(1)	2·921 (5)	C(1)—C(2)	1·555 (8)
Tl—C(2)	2·910 (5)	C(1)—B(4)	1·650 (9)
Tl—B(4)	2·743 (6)	C(2)—B(7)	1·628 (8)
Tl—B(7)	2·741 (6)	B(7)—B(8)	1·742 (9)
Tl—B(8)	2·659 (6)	B(4)—B(8)	1·761 (9)
C(1)—B(6)	1·719 (8)	B(9)—B(5)	1·762 (9)
C(2)—B(6)	1·730 (8)	B(11)—B(12)	1·784 (9)
C(1)—B(5)	1·724 (7)	B(11)—B(6)	1·780 (9)
C(2)—B(11)	1·722 (8)	B(5)—B(6)	1·749 (9)
B(7)—B(11)	1·779 (8)	B(12)—B(9)	1·783 (9)
B(4)—B(5)	1·791 (8)	B(6)—B(10)	1·750 (9)
B(7)—B(12)	1·784 (8)	B(12)—B(10)	1·807 (8)
B(4)—B(9)	1·786 (8)	B(9)—B(10)	1·784 (9)
B(8)—B(12)	1·776 (8)	B(11)—B(10)	1·782 (8)
B(8)—B(9)	1·773 (8)	B(5)—B(10)	1·763 (9)
C(1)—H(1)	0·92 (5)	B(7)—H(7)	1·13 (4)
C(2)—H(2)	1·03 (5)	B(8)—H(8)	1·14 (4)
B(4)—H(4)	1·16 (5)	B(9)—H(9)	1·14 (5)
B(5)—H(5)	1·16 (4)	B(10)—H(10)	1·11 (4)
B(6)—H(6)	1·13 (5)	B(11)—H(11)	1·09 (5)
		B(12)—H(12)	1·14 (5)
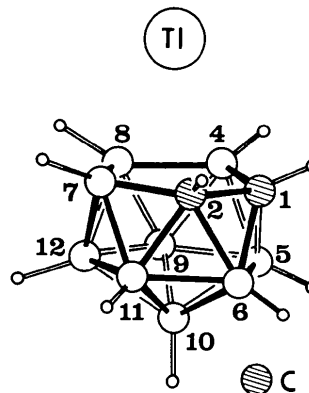
Fig. 1. Structure of $[3,1,2\text{-}TlC_2B_9H_{11}]^-$.

Table 4. *Metal–cage distances and framework distortions in* $Tl^+ . 7,8\text{-}C_2B_9H_{11}^{2-}$ *and* $3,1,2\text{-}MC_2B_9H_{11}$ *systems*

	d^6 Re^I	d^7 Ni^{III}	d^8 Au^{III}	d^9 Cu^{II}	d^{10} Hg^{II}	$d^{10}s^2$ Tl$^+$. 7,8-$C_2B_9H_{11}^{2-}$
M—B(8) (Å)	2·35	2·16	2·20	2·13	2·20	2·66
M—B(4), B(7) (Å)*	2·34	2·11	2·22	2·23	2·52	2·74
M—C (Å)*	2·31	2·15	2·79	2·58	2·90	2·92
C_2B_3 face dihedral angle (acute °)	0·2	5·1	17·2	8·0	5·2	3·6
Lower B_5 girdle dihedral angle (acute °)	0·8	5·1	9·2	4·2	0·5	0·3
C—C (Å)	1·61	1·59	1·46	1·53	1·54	1·56
Facial C—B (Å)*	1·71	1·72	1·82	1·69	1·60	1·64
B(7)—B(11), B(12); B(4)—B(5), B(9) (Å)*	1·77	1·80	1·84	1·82	1·78	1·77
B(7)—B(8)—B(4) (°)	106	105	98	99	101	105
C—B(5), B(11) (Å)*	1·73	1·70	1·62	1·71	1·69	1·72
Reference	(a)	(b)	(c)	(d)	(e)	This work

References: (a) $[(3\text{-}CO)_3\text{-}3,1,2\text{-}ReC_2B_9H_{11}]^-$ (Zalkin, Hopkins & Templeton, 1966). (b) $[(CH_3)_4N]^+[Ni(1,2\text{-}C_2B_9H_{11})_2]^-$ (Hansen, Hazell, Hyatt & Stucky, 1973). (c) $3\text{-}(Et_2NCS)_2\text{-}3,1,2\text{-}AuC_2B_9H_{11}$ (Colquhoun, Greenhough & Wallbridge, 1976). (d) $(Et_4N)_2^+[Cu(1,2\text{-}C_2B_9H_{11})_2]^{2-}$ (Wing, 1967). (e) $3\text{-}PPh_3\text{-}3,1,2\text{-}HgC_2B_9H_{11}$ (Colquhoun, Greenhough & Wallbridge, 1978).

* Mean values.

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6-Chloro-4,5-diethyl-1,2,3-oxathiazine 2,2-Dioxide

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Abstract. $C_7H_{10}ClNO_3S$, monoclinic, $P2_1/c$, $a = 7.970(4)$, $b = 14.55(1)$, $c = 17.77(1)$ Å, $\beta = 92.2(1)°$, $V = 2059$ Å^3, $Z = 8$, $D_x = 1.44$ g cm^{-3}. The structure has been determined by Patterson and trial methods. Block-diagonal least-squares refinement led to $R = 0.070$, $R_w = 0.075$ for the 1393 observed reflections. The compound contains a novel six-membered ring in which three hetero-atoms, O, S and N, are adjacent to each other. Analysis of the relationship between the two crystallographically independent molecules in the asymmetric unit has shown that the structure found is a superstructure of a simpler structure which would have a unit cell with b halved and contain four molecules in the space group $P2/c$.

Introduction. Reaction of 3-hexyne (I) with chlorosulfonyl isocyanate (II) yielded a novel adduct (III).

$$Et—C≡C—Et \;+\; ClO_2S—N=C=O \;\longrightarrow\;$$

(I)   (II)

(III)

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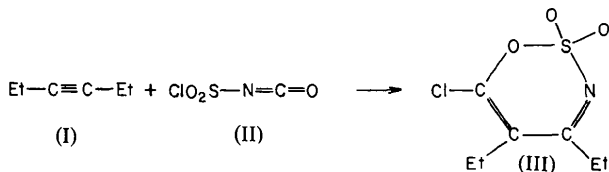
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Initially structure (III) was postulated as the only one which could account for the UV, IR and NMR spectra of the compound together with those obtained after reduction with LiAlH$_4$. Since the ring structure containing three adjacent hetero-atoms was most unusual an X-ray analysis was undertaken which confirmed this structure completely (Moriconi et al., 1970). The mechanisms of this and related reactions have since been discussed in detail (Moriconi & Shimakawa, 1972). In the present paper we present the detailed results of the X-ray analysis after further refinement.

The compound was crystallized from pentane and formed transparent, needle-shaped crystals which were very unstable in air, and had to be sealed in capillaries for X-ray work. Density determination could not be made. Two crystals were used for data collection. The first, for rotation about the c (needle) axis, measured 0.16 × 0.14 mm in cross-section and 1.0 mm in length. The second, for rotation about the b axis, was 0.40 × 0.40 mm in cross-section and 0.36 mm in length. The reciprocal-lattice levels $hk0–hk11$, and $h0l–h10l$ were recorded using Ni-filtered Cu $K\alpha$ radiation and the equi-inclination Weissenberg technique. Intensities were estimated visually against a time-based standard scale from multiple-film packs and corrected for Lorentz–polarization effects. Cylindrical absorption corrections