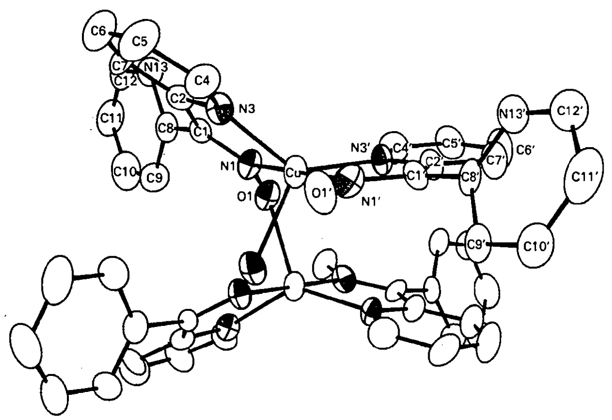

Fig. 1. A perspective view of the molecule (50% probability ellipsoids) showing the atom labeling and thermal ellipsoids. The bottom half of the dinuclear complex is related to the top half by a horizontal twofold axis.

amine oximes [*e.g.* 2·037 (5) Å (Pal *et al.*, 1986)]. In this previous study there is a bridging oxime oxygen with a Cu—O distance of 2·300 (4) Å compared with the much shorter distance [2·133 (5) Å] observed here. In the previous study, the Cu^{II} atom was in square-pyramidal coordination.

The water of hydration (O*W*) is 2·757 (9) Å from O1′($\frac{1}{2}-x$; $\frac{1}{2}-y$; $-z$) and 2·978 (9) Å from N13($\frac{1}{2}+x$; $\frac{1}{2}+y$; z) with an O1′—O*W*—N13 angle of 127·6 (3)°, allowing for hydrogen-bond formation with these ligand Lewis base atoms which are not involved in metal bonding. H-atom location for the water O atoms from difference Fourier summations was not satisfactory, and those positions reported are in reasonable hydrogen-bonding positions but are questionable.

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Structure of 10,11-μ-[(Triphenylphosphine)aurio]-9-dimethylsulfido-7,8-dicarba-*nido*-undecaborane(10) Methylene Chloride Solvate

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Abstract. $C_{22}H_{31}AuB_9PS.CH_2Cl_2$, $M_r = 737·72$, monoclinic, $P2_1/n$, $a = 15·323$ (6), $b = 12·291$ (3), $c = 17·023$ (11) Å, $\beta = 112·45$ (4)°, $V = 2962·8$ Å^3, $Z = 4$, $D_x = 1·654$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 5·273$ mm^{-1}, $F(000) = 1440$, $T = 185$ (1) K, $R = 0·0310$ for 4710 independent observed reflections. Replacement of the μ-H atom in the precursor [10,11-μ-H-9-SMe$_2$-*nido*-$C_2B_9H_{10}$] by μ-AuPPh$_3$ results in depression (> 5°) of the SMe$_2$ function from its preferred inclination to the open C_2B_3 face. However, near eclipsing of the sulfur lone pair and C(8) is retained. The Au atom bridges the B(10)—B(11) connectivity in an asymmetric manner, Au—B(10) 2·233 (6), Au—B(11) 2·357 (6) Å.

Introduction. We are currently developing the transition-metal chemistry of the monoanionic carbaborane ligand [9-SMe$_2$-*nido*-7,8-$C_2B_9H_{10}$]$^-$ (carb′$^-$), with particular reference to similarities and differences that occur with respect to the chemistry of the $[C_5H_5]^-$(Cp$^-$) ligand. As part of this program we are interested in complexes in which carb′ is ligated to metal fragments that are formally one-orbital donors, and thus we have synthesized and structurally characterized the title compound, the results of which are presented here.

Experimental. Addition of a solution of Ph$_3$PAuCl in CH_2Cl_2 to an equimolar suspension of Tl[9-SMe$_2$-

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nido-7,8-$C_2B_9H_{10}$] in the same solvent afforded an orange solution (colour attributed to minor Au^{III} coproduct) and finely divided beige solid; filtration through celite yielded a clear orange solution which was concentrated to dryness *in vacuo*; crystallization by diffusion of hexane into a methylene chloride solution at 243 K afforded colourless crystals of [10,11-$(Ph_3P)Au$-9-SMe_2-*nido*-7,8-$C_2B_9H_{10}$].CH_2Cl_2 in 70% yield; chemical characterization by IR spectroscopy (KBr disc, ν_{B-H} 2540, ν_{Au-P} 535 cm^{-1}), microanalysis (found: C, 37·2; H, 4·29%. $C_{22}H_{31}AuB_9PS.CH_2Cl_2$ requires: C, 37·4; H, 4·51%), and NMR spectroscopy [$CDCl_3$ solution: ^1H, δ 7·4–7·7 (C_6H_5), 2·35 and 2·39 (CH_3): ^{11}B, δ −10·31 [1B, B(9)], −14·20 (1B), −16·72 (2B), −17·80 (1B), −18·35 (1B), −21·12 (1B), −23·55 (1B), and −35·57 (1B): ^{31}P, δ 41·0 (br)]; crystal, 0·4 × 0·3 × 0·3 mm, mounted on an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation, graphite monochromator, ULT-1 low-temperature attachment); cell parameters and orientation matrix from least-squares refinement of the setting angles ($14 < \theta < 15°$) of 25 centred reflections; data collection by ω–2θ scans in 96 steps with ω-scan width ($0\cdot8 + 0\cdot34\tan\theta$)°; data ($h$: 0 to 18, k: 0 to 14, l: −20 to 20) measured for $1 \le \theta \le 25°$ over 122 X-ray hours; no detectable movement of crystal or decay (net intensities of $\bar{7},3,\bar{10}$ and $\bar{2}8\bar{2}$ check reflections only varied between 98·9 and 102·0% of their mean values); corrections for Lorentz and polarization effects applied (Gould & Smith, 1986); 5704 independent reflections measured, of which 4710 [$F \ge 2\cdot0\sigma(F)$] retained; structure solution *via* Patterson synthesis (Au) and iterative full-matrix least-squares refinement (on F)/ΔF synthesis (P, S, C, B, H_{cage}) (Sheldrick, 1976); cage C atoms identified on the basis of internuclear distances and refined (as B) isotropic thermal parameters; empirical absorption correction (Walker & Stuart, 1983) applied after isotropic convergence (correction factors 0·886–1·141); all non-H atoms refined with anisotropic thermal parameters; phenyl C atoms treated as regular, planar hexagon (C—C = 1·395 Å); phenyl H and methylene H atoms set in idealized positions, and CH_3 moieties treated as rigid groups; all H atoms given a group thermal parameter [$U_H = 0\cdot071$ (4) $Å^2$ at convergence]; weighting scheme $w^{-1} = \sigma^2(F) + 0\cdot000469F^2$; 335 variables, data:variable ratio > 14:1; max. shift/e.s.d. in final cycle < 0·2 (H atom); $R = 0\cdot0310$, $wR = 0\cdot0400$, $S = 1\cdot179$; max. and min. residues in final ΔF synthesis 2·38 and −1·29 e $Å^{-3}$ respectively (near Cl); scattering factors for C, H, B, P, S, and Cl inlaid in *SHELX*76. Those for Au from *International Tables for X-ray Crystallography* (1974); Fig. 1 drawn using *EASYORTEP* (Mallinson & Muir, 1985); molecular geometry calculations *via* *CALC* (Gould & Taylor, 1986).

Table 1. *Coordinates of refined atoms and equivalent isotropic thermal parameters* ($Å^2$) *in* 10,11-μ-(*triphenylphosphine*)*aurio*-9-*dimethylsulfido*-7,8-*dicarba-nido-undecaborane*(10)

$$U_{eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Au(1)	1·01420 (1)	−0·01384 (1)	0·26048 (1)	0·0245 (1)
P(1)	0·97619 (8)	0·14105 (9)	0·31099 (8)	0·0224 (7)
S(1)	1·25651 (10)	−0·12742 (12)	0·39521 (9)	0·0409 (9)
CS(1)	1·1821 (5)	−0·1163 (6)	0·4547 (4)	0·065 (5)
CS(2)	1·3061 (5)	−0·2595 (6)	0·4311 (4)	0·058 (5)
C(12)	0·81444	0·23904	0·32052	0·032 (3)
C(13)	0·72217	0·23711	0·31744	0·034 (3)
C(14)	0·67245	0·13920	0·30328	0·040 (3)
C(15)	0·71501	0·04324	0·29219	0·057 (4)
C(16)	0·80728	0·04518	0·29527	0·043 (4)
C(11)	0·85700 (20)	0·14308 (19)	0·30943 (22)	0·025 (3)
C(22)	0·97103	0·24894	0·16663	0·029 (3)
C(23)	0·98162	0·33811	0·12035	0·040 (3)
C(24)	1·00748	0·43911	0·15982	0·042 (4)
C(25)	1·02276	0·45094	0·24558	0·037 (3)
C(26)	1·01217	0·36176	0·29187	0·031 (3)
C(21)	0·98631 (24)	0·26076 (20)	0·25239 (17)	0·024 (3)
C(32)	1·02232	0·1679	0·48704	0·040 (3)
C(33)	1·08620	0·1856	0·57005	0·052 (4)
C(34)	1·18128	0·2042	0·58608	0·048 (4)
C(35)	1·21249	0·2051	0·51908	0·042 (4)
C(36)	1·14861	0·1874	0·43606	0·035 (3)
C(31)	1·05353 (17)	0·1688 (3)	0·42004 (20)	0·025 (3)
B(1)	1·1502 (4)	−0·2581 (5)	0·1306 (4)	0·034 (4)
B(6)	1·0372 (4)	−0·2460 (4)	0·1398 (4)	0·029 (3)
B(2)	1·0680 (5)	−0·1581 (5)	0·0729 (4)	0·036 (4)
B(3)	1·1885 (5)	−0·1250 (6)	0·1223 (4)	0·044 (4)
B(4)	1·2339 (4)	−0·1937 (5)	0·2194 (4)	0·036 (4)
B(5)	1·1420 (4)	−0·2703 (4)	0·2319 (4)	0·028 (3)
C(7)	1·1014 (4)	−0·0446 (4)	0·1337 (3)	0·035 (3)
C(8)	1·1916 (4)	−0·0643 (4)	0·2152 (3)	0·035 (3)
B(9)	1·1704 (4)	−0·1417 (4)	0·2810 (4)	0·026 (3)
B(10)	1·0507 (4)	−0·1837 (4)	0·2378 (3)	0·024 (3)
B(11)	1·0084 (4)	−0·1063 (5)	0·1373 (4)	0·029 (3)
H(1)	1·174 (5)	−0·329 (6)	0·101 (4)	
H(6)	0·986 (5)	−0·305 (5)	0·114 (4)	
H(2)	1·034 (5)	−0·155 (5)	−0·010 (4)	
H(3)	1·234 (5)	−0·097 (6)	0·088 (4)	
H(4)	1·295 (5)	−0·208 (6)	0·243 (4)	
H(5)	1·155 (5)	−0·358 (6)	0·268 (4)	
H(7)	1·094 (5)	0·037 (6)	0·101 (5)	
H(8)	1·252 (6)	−0·009 (5)	0·226 (5)	
H(10)	1·012 (5)	−0·213 (6)	0·273 (4)	
H(11)	0·929 (5)	−0·073 (6)	0·092 (4)	
Cl(1)	0·57964 (17)	−0·08676 (18)	−0·03513 (17)	0·0952 (18)
Cl(2)	0·76077 (21)	0·00140 (20)	0·07526 (18)	0·0989 (20)
C*M*	0·6421 (7)	0·0243 (8)	0·0131 (9)	0·122 (10)

Discussion. Table 1* lists coordinates of refined atoms and equivalent isotropic thermal parameters, and Table 2 details internuclear distances and selected interbond angles in the heteroborane, which is viewed in perspective in Fig. 1. The compound crystallizes with no unusually short contacts between molecules.

Replacement of the μ-H atom in [10,11-μ-H-9-SMe_2-*nido*-$C_2B_9H_{10}$] (carb′H) (Cowie, Hamilton, Laurie & Welch, 1988) by μ-$AuPPh_3$ in the title compound has a minimal effect on the stereochemistry of the rest of the polyhedron. Thus the

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* Lists of structure factors, calculated H-atom positions, C—Cl distances and full interbond angles, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52761 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and selected interbond angles* (°) *in* 10,11-*μ*-(*triphenylphosphine*)*aurio*-9-*dimethylsulfido*-7,8-*dicarba-nido-undecaborane*(10)

Au(1)—P(1)	2·2550 (12)	B(2)—B(11)	1·790 (9)
Au(1)—B(10)	2·233 (6)	B(2)—H(2)	1·31 (7)
Au(1)—B(11)	2·357 (6)	B(3)—B(4)	1·746 (10)
P(1)—C(11)	1·817 (3)	B(3)—C(7)	1·730 (9)
P(1)—C(21)	1·817 (3)	B(3)—C(8)	1·732 (9)
P(1)—C(31)	1·813 (4)	B(3)—H(3)	1·11 (7)
S(1)—CS(1)	1·796 (8)	B(4)—B(5)	1·773 (9)
S(1)—CS(2)	1·798 (7)	B(4)—C(8)	1·709 (9)
S(1)—B(9)	1·896 (6)	B(4)—B(9)	1·798 (9)
B(1)—B(6)	1·803 (9)	B(4)—H(4)	0·88 (7)
B(1)—B(2)	1·766 (9)	B(5)—B(9)	1·763 (8)
B(1)—B(3)	1·762 (10)	B(5)—B(10)	1·791 (8)
B(1)—B(4)	1·755 (9)	B(5)—H(5)	1·21 (7)
B(1)—B(5)	1·782 (9)	C(7)—C(8)	1·558 (8)
B(1)—H(1)	1·13 (7)	C(7)—B(11)	1·636 (8)
B(6)—B(2)	1·760 (9)	C(7)—H(7)	1·13 (8)
B(6)—B(5)	1·791 (8)	C(8)—B(9)	1·594 (8)
B(6)—B(10)	1·775 (8)	C(8)—H(8)	1·10 (9)
B(6)—B(11)	1·769 (8)	B(9)—B(10)	1·772 (8)
B(6)—H(6)	1·03 (7)	B(10)—B(11)	1·844 (8)
B(2)—B(3)	1·760 (10)	B(10)—H(10)	1·05 (7)
B(2)—C(7)	1·694 (9)	B(11)—H(11)	1·23 (7)

P(1)—Au(1)—B(10)	166·80 (15)	B(1)—B(6)—B(5)	59·5 (3)
P(1)—Au(1)—B(11)	144·99 (15)	B(2)—B(6)—B(11)	61·0 (4)
B(10)—Au(1)—B(11)	47·30 (21)	B(5)—B(6)—B(10)	60·3 (3)
Au(1)—P(1)—C(11)	114·25 (11)	B(10)—B(6)—B(11)	62·7 (3)
Au(1)—P(1)—C(21)	112·68 (11)	B(1)—B(2)—B(6)	61·5 (4)
Au(1)—P(1)—C(31)	112·71 (12)	B(1)—B(2)—B(3)	60·0 (4)
C(11)—P(1)—C(21)	106·08 (15)	B(6)—B(2)—B(11)	59·8 (4)
C(11)—P(1)—C(31)	105·83 (16)	B(3)—B(2)—C(7)	60·1 (4)
C(21)—P(1)—C(31)	104·51 (16)	C(7)—B(2)—B(11)	55·9 (3)
CS(1)—S(1)—CS(2)	98·9 (3)	B(1)—B(3)—B(2)	60·2 (4)
CS(1)—S(1)—B(9)	104·0 (3)	B(1)—B(3)—B(4)	60·0 (4)
CS(2)—S(1)—B(9)	107·6 (3)	B(2)—B(3)—C(7)	58·1 (4)
S(1)—CS(1)—HS(11)	102·6 (7)	B(4)—B(3)—C(8)	58·9 (4)
S(1)—CS(1)—HS(12)	118·5 (7)	C(7)—B(3)—C(8)	53·5 (3)
S(1)—CS(1)—HS(13)	107·0 (7)	B(1)—B(4)—B(3)	60·4 (4)
S(1)—CS(2)—HS(21)	108·7 (6)	B(1)—B(4)—B(5)	60·7 (4)
S(1)—CS(2)—HS(22)	110·8 (6)	B(3)—B(4)—C(8)	60·2 (4)
S(1)—CS(2)—HS(23)	108·9 (6)	B(5)—B(4)—B(9)	59·2 (3)
P(1)—C(11)—C(12)	121·94 (24)	C(8)—B(4)—B(9)	54·0 (3)
P(1)—C(11)—C(16)	118·06 (24)	B(1)—B(5)—B(6)	60·6 (3)
P(1)—C(21)—C(22)	118·34 (23)	B(1)—B(5)—B(4)	59·1 (4)
P(1)—C(21)—C(26)	121·61 (23)	B(6)—B(5)—B(10)	59·4 (3)
P(1)—C(31)—C(32)	122·8 (3)	B(4)—B(5)—B(9)	61·4 (4)
P(1)—C(31)—C(36)	117·2 (3)	B(9)—B(5)—B(10)	59·8 (3)
B(6)—B(1)—B(2)	59·1 (4)	B(2)—C(7)—B(3)	61·9 (4)
B(6)—B(1)—B(5)	59·9 (3)	B(2)—C(7)—B(11)	65·0 (4)
B(2)—B(1)—B(3)	59·9 (4)	B(3)—C(7)—C(8)	63·3 (4)
B(3)—B(1)—B(4)	59·5 (4)	B(3)—C(8)—B(4)	61·0 (4)
B(4)—B(1)—B(5)	60·2 (4)	B(3)—C(8)—C(7)	63·2 (4)
B(1)—B(6)—B(2)	59·4 (4)	B(4)—C(8)—B(9)	65·8 (4)
S(1)—B(9)—B(4)	108·1 (4)	B(6)—B(10)—B(5)	60·3 (3)
S(1)—B(9)—B(5)	121·2 (4)	B(6)—B(10)—B(11)	58·5 (3)
S(1)—B(9)—C(8)	114·6 (4)	B(5)—B(10)—B(9)	59·3 (3)
S(1)—B(9)—B(10)	131·0 (4)	Au(1)—B(11)—B(10)	62·83 (25)
B(4)—B(9)—B(5)	59·7 (3)	B(6)—B(11)—B(2)	59·3 (3)
B(4)—B(9)—C(8)	60·2 (4)	B(6)—B(11)—B(10)	58·8 (3)
B(5)—B(9)—B(10)	60·9 (3)	B(2)—B(11)—C(7)	59·1 (4)
Au(1)—B(10)—B(11)	69·9 (3)		

root-mean-square misfit (Gould & Taylor, 1986) of the C_2B_9 portions of the two species is only 0·028 (molecule *a* of carb′H) and 0·026 Å (molecule *b* of carb′H), rising to 0·043 and 0·045 Å respectively if S atoms are included. The poorer fit when sulfur is included reflects the fact that the S atom in the present compound is depressed below its preferred inclination to the C(7)C(8)B(9)B(10)B(11) plane. In carb′H the S—B(9) vectors are inclined at 27·1 (2) (molecule *a*) and 26·3 (2)° (molecule *b*) to the plane of the open face, these values being quite normal for a *nido* icosahedral fragment, whereas in Ph_3PAu-(carb′) the equivalent angle is only 21·9 (4)°. Presumably this arises from intramolecular steric crowding between the CS(1) methyl group and the C(31)—C(36) phenyl group [HS(11)···C(36) 2·748 (8) Å]. It is of considerable interest that the SMe_2 function does not adopt an alternate torsion about S—B(9) that would relieve this interaction. The observed torsion angle (lone pair)—S(1)—B(9)—C(8) is 4·4 (4)°, in keeping with equivalent values in carb′H [molecule *a* 27·3 (2), molecule *b* 4·0 (2)°] and in complexes of carb′ that we have so far characterized [*e.g.* $(CO)_3Mn$(carb′) 4·1 (3)° (Cowie, Hamilton, Laurie & Welch, 1990)]. Clearly, near eclipsing of the sulfur lone pair and C(8) is a highly preferred feature of the stereochemistry of the carb′ ligand.

The Au atom bridges the B(10)—B(11) connectivity asymmetrically, favouring B(10). Asymmetry in the same direction is observed for the *μ*-H atom of carb′H, although the precision of the current observation is naturally far greater. We have previously shown that the origin of this asymmetric bridging may be traced to greater negative charge on B(10) than B(11) in the anion carb′⁻. The angles at Au(1) sum to 359·09°, implying that the orbital number (Parish, Moore, Dens, Mingos & Sherman, 1989) of gold in the present compound is essentially two [one directed towards P, one towards the B(10)—B(11) connectivity]. Au—B distances compare favourably with those in the closely related compounds *μ*-$(Ph_3P)Au$-$CpNiC_2B_8H_{10}$ (Barker, Godfrey, Green, Parge, Stone & Welch, 1983), *μ*-$(Ph_3P)Au$-B_5H_8 (Alcock, Parkhill & Wallbridge, 1985), and *μ*-(*o*-tolyl$_3$P)Au-$B_{10}H_{13}$ (Wynd, McLennan, Reed & Welch, 1987).

The structural results described above provide confirmation of an important difference between the

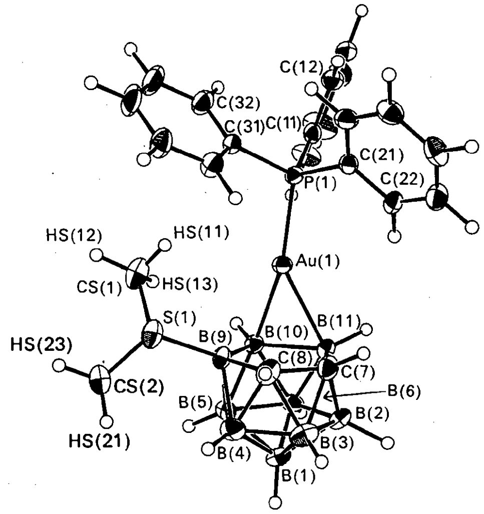

Fig. 1. Perspective view of [10,11-$(Ph_3P)Au$-9-SMe_2-*nido*-7,8-$C_2B_9H_{10}$] (50% thermal ellipsoids, except for H atoms which have an artificial radius of 0·1 Å for clarity).

chemistries of Cp^- and carb′$^-$, *viz.* that whilst protonation or addition of R_3PAu^+ to the former results in the new atom (group) adding *endo* to the five-atom face to form essentially a σ bond to carbon [for the structure of $(Ph_4C_5H)AuPPh_3$ see Baukova, Slovokhotov & Struchkov (1981)], similar treatment of carb′$^-$ affords a bridging function. Within the context of each ligand, these results are in full and simple accord with the isolobal principle (Elian, Chen, Mingos & Hoffmann, 1976; Hoffmann, 1982). Moreover, the differences between the ligands may be readily correlated with differences in the form of the highest-occupied molecular orbital of Cp^- (distorted to C_s-envelope conformation) and carb′$^-$, extended Hückel MO calculations (Howell, Rossi, Wallace, Haraki & Hoffmann, 1977) on the latter revealing a HOMO heavily localized on B(10) and B(11).

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Dichloro(η^5-cyclopentadienyl)(η^5-tris-1,2,4-trimethylsilylcyclopentadienyl)-titanium(IV)

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Abstract. $[Ti(C_5H_5)(C_{14}H_{29}Si_3)Cl_2]$, $M_r = 465{\cdot}54$, orthorhombic, *Pcab* (non-standard setting of *Pbca*), $a = 13{\cdot}82\,(1)$, $b = 18{\cdot}214\,(2)$, $c = 20{\cdot}634\,(4)$ Å, $V = 5194\,(4)$ Å^3, $Z = 8$, $D_m = 1{\cdot}18\,(1)$, $D_x = 1{\cdot}187\,(5)$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 6{\cdot}41$ cm^{-1}, $F(000) = 1968$, $T = 298$ K, $R = 0{\cdot}042$ [2267 data, $F_o > 3\sigma(F_o)$]. The Ti atom is bonded to the two cyclopentadienyl rings in a pentahapto fashion and to the two Cl atoms. The average Ti—C distances are 2·41 Å (Si_3Cp) and 2·39 Å (Cp), and the average Ti—Cl distance is 2·35 Å. The silylated cyclopentadienyl ligand shows a slight distortion toward trihapto bonding to titanium.

Introduction. The title compound was synthesized as part of studies concerning the preparation, reactivity and X-ray structures of transition-metal complexes bearing extremely bulky cyclopentadienyl ligands. The chemistry of pentamethylcyclopentadienyl (Cp*) metal complexes has received considerable attention (Wolczanski & Bercaw, 1980), and substitution of a cyclopentadienyl (Cp) ligand by the Cp* ligand in a metal complex significantly alters its thermal stability, reactivity and other properties. Many of these changes can be attributed to the increased steric bulk of the Cp* ligand. In contrast to the extensive chemistry of the Cp* ligand, the chemistry of transition-metal complexes containing polysilylated cyclopentadienyl ligands has received scant attention (Okuda & Herdtweck, 1989; Morley, Jutzi, Krüger & Wallis, 1987). Since polysilylated cyclopentadienyl ligands are more sterically demanding than the Cp* ligand, their inclusion in metallocene dihalides might lead to new and unusual modes of

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