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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bonding. As part of initial studies in this area, the structure of the title complex was determined.

Experimental. The preparation of the title compound (m.p. 395–396 K) will be described in a separate publication (Winter, Zhou & Dobbs, 1989); suitable crystals grown from hexane at 250 K. Experimental density D_m determined by flotation in aqueous potassium iodide. A ruby red rectangular needle, 0·20 × 0·58 × 0·18 mm, mounted on a Nicolet *R*3 automated diffractometer, Mo $K\alpha$, graphite monochromated, corrected for Lorentz and polarization effects; X-ray diffraction intensities (θ–2θ) by counter methods; scan speed 2–5° min^{-1}, variable; background-to-scan ratio 0·5; cell dimensions from 25 reflections, $20 < 2\theta < 30{\cdot}7°$; cell reduction program *TRACER*II (Lawton, 1967) run to verify that there was no lattice of higher symmetry; linear absorption coefficient 6·41 cm^{-1}, no absorption correction applied; maximum $(\sin\theta)/\lambda = 0{\cdot}59\ \text{Å}^{-1}$; h: 0–17, k: 0–22, l: 0–25; three standard reflections, less than 3% decay, 5324 data, 4633 unique data [2267 for which $F_o \geq 3\sigma(F_o)$]; structure solved by direct methods and Fourier methods; refined on F, minimizing $\sum w(|F_o| - |F_c|)^2$, 228 parameters; H atoms placed in calculated positions, C—H = 0·96 Å, isotropic thermal parameters allowed to refine; $R = 0{\cdot}0482$, $wR = 0{\cdot}0298$ where $w = 1/\sigma^2(F_o)$; max. shift/e.s.d. = 0·001; 040 reflection omitted due to extinction; maximum residual electron density 0·48 e Å^{-3}, 0·103 Å from Ti; principal computing employed *SHELX*76 (Sheldrick, 1976) and *SHELXTL* (Sheldrick, 1983) programs; neutral-atom scattering factors taken from *International Tables for X-ray Crystallography* (1974) and corrected for anomalous dispersion.

Atomic parameters are listed in Table 1,* and bond distances and angles are listed in Table 2. Fig. 1 shows the molecule and the numbering scheme.

Table 1. *Atomic parameters*

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

	x	y	z	U_{eq}(Å^2)
Ti	0·12617 (7)	0·18003 (5)	0·33188 (5)	0·0544 (4)
Cl(1)	0·2560 (1)	0·24922 (8)	0·37475 (8)	0·0882 (6)
Cl(2)	0·2300 (1)	0·09752 (7)	0·27959 (8)	0·0993 (8)
C(1)	0·0572 (4)	0·1874 (2)	0·4374 (2)	0·042 (2)
C(2)	−0·0121 (4)	0·1539 (2)	0·3964 (2)	0·041 (2)
C(3)	0·0236 (3)	0·0846 (2)	0·3735 (2)	0·039 (2)
C(4)	0·1165 (3)	0·0744 (2)	0·4049 (2)	0·039 (2)
C(5)	0·1379 (4)	0·1373 (2)	0·4436 (2)	0·044 (2)
Si(1)	0·0418 (1)	0·27303 (8)	0·48925 (8)	0·0601 (6)
C(6)	0·0554 (4)	0·3611 (2)	0·4454 (3)	0·098 (3)
C(7)	−0·0808 (3)	0·2695 (3)	0·5272 (3)	0·094 (3)
C(8)	0·1360 (3)	0·2688 (3)	0·5549 (2)	0·088 (3)
Si(2)	−0·0548 (1)	0·01850 (7)	0·32493 (8)	0·0581 (6)
C(9)	−0·1797 (3)	0·0578 (2)	0·3225 (2)	0·071 (2)
C(10)	−0·0101 (4)	0·0025 (3)	0·2410 (2)	0·084 (2)
C(11)	−0·0638 (3)	−0·0716 (2)	0·3677 (2)	0·081 (3)
Si(3)	0·1991 (1)	−0·00800 (8)	0·41386 (7)	0·0531 (6)
C(12)	0·1551 (4)	−0·0558 (2)	0·4878 (2)	0·086 (3)
C(13)	0·2038 (3)	−0·0744 (2)	0·3449 (2)	0·074 (2)
C(14)	0·3234 (3)	0·0271 (3)	0·4315 (3)	0·094 (3)
C(15)	0·0001 (6)	0·2047 (4)	0·2565 (4)	0·087 (4)
C(16)	0·0105 (5)	0·2669 (4)	0·2948 (3)	0·078 (3)
C(17)	0·1013 (6)	0·2965 (3)	0·2798 (4)	0·084 (3)
C(18)	0·1466 (5)	0·2512 (5)	0·2345 (4)	0·103 (4)
C(19)	0·0817 (8)	0·1950 (4)	0·2196 (3)	0·107 (4)

Table 2. *Bond distances* (Å) *and selected angles* (°)

Ti—Cp(1)*	2·083 (1)	Ti—Cp(2)*	2·076 (1)
Ti—Cl(1)	2·364 (2)	C(3)—Si(2)	1·904 (5)
Ti—Cl(2)	2·342 (2)	C(4)—C(5)	1·426 (6)
Ti—C(1)	2·380 (5)	C(4)—Si(3)	1·896 (5)
Ti—C(2)	2·377 (5)	Si(1)—C(6)	1·851 (5)
Ti—C(3)	2·402 (4)	Si(1)—C(7)	1·869 (5)
Ti—C(4)	2·447 (4)	Si(1)—C(8)	1·880 (5)
Ti—C(5)	2·438 (5)	Si(2)—C(9)	1·870 (4)
Ti—C(15)	2·379 (8)	Si(2)—C(10)	1·861 (5)
Ti—C(16)	2·376 (7)	Si(2)—C(11)	1·868 (5)
Ti—C(17)	2·402 (6)	Si(3)—C(12)	1·859 (5)
Ti—C(18)	2·407 (8)	Si(3)—C(13)	1·868 (5)
Ti—C(19)	2·412 (7)	Si(3)—C(14)	1·868 (5)
C(1)—C(2)	1·415 (7)	C(15)—C(16)	1·39 (1)
C(1)—C(5)	1·447 (6)	C(15)—C(19)	1·37 (1)
C(1)—Si(1)	1·904 (5)	C(16)—C(17)	1·40 (1)
C(2)—C(3)	1·436 (6)	C(17)—C(18)	1·40 (1)
C(3)—C(4)	1·450 (7)	C(18)—C(19)	1·40 (1)

Cl(1)—Ti—Cl(2)	92·83 (6)	Cp(1)—Ti—Cp(2)	129·7 (2)
Cl(1)—Ti—C(4)	103·3 (1)	Cl(2)—Ti—C(15)	105·6 (2)
Cl(1)—Ti—C(5)	76·5 (1)	Cl(2)—Ti—C(16)	133·8 (2)
Cl(1)—Ti—C(15)	134·4 (2)	Cl(2)—Ti—C(17)	116·6 (2)
Cl(1)—Ti—C(16)	106·0 (2)	Cl(2)—Ti—C(18)	83·6 (2)
Cl(1)—Ti—C(17)	78·8 (2)	Cl(2)—Ti—C(19)	77·6 (2)
Cl(1)—Ti—C(18)	86·3 (2)	C(1)—Ti—C(2)	34·6 (2)
Cl(1)—Ti—C(19)	119·5 (2)	C(1)—Ti—C(3)	58·5 (2)
Cl(2)—Ti—C(1)	134·7 (1)	C(1)—Ti—C(4)	57·3 (2)
Cl(2)—Ti—C(2)	128·5 (1)	C(1)—Ti—C(5)	34·9 (2)
Cl(2)—Ti—C(3)	93·6 (1)	C(1)—Ti—C(15)	107·1 (2)
Cl(2)—Ti—C(4)	79·2 (1)	C(1)—Ti—C(16)	89·2 (2)
Cl(2)—Ti—C(5)	100·9 (1)	C(1)—Ti—C(17)	107·6 (2)
Cl(1)—Ti—C(1)	86·1 (1)	C(1)—Ti—C(18)	141·3 (2)
Cl(1)—Ti—C(2)	120·5 (1)	C(1)—Ti—C(19)	140·3 (3)
Cl(1)—Ti—C(3)	134·4 (1)	C(1)—C(2)—C(3)	110·1 (4)
C(1)—C(5)—C(4)	107·3 (4)	C(3)—Si(2)—C(11)	110·2 (2)
C(1)—Si(1)—C(6)	115·1 (2)	C(4)—Ti—C(5)	33·9 (1)
C(1)—Si(1)—C(7)	108·0 (2)	C(4)—Ti—C(15)	120·7 (2)
C(1)—Si(1)—C(8)	107·1 (2)	C(4)—Ti—C(16)	133·2 (2)
C(2)—Ti—C(3)	35·0 (1)	C(4)—Ti—C(17)	164·1 (2)
C(2)—Ti—C(4)	56·9 (2)	C(4)—Ti—C(18)	160·6 (2)
C(2)—Ti—C(5)	57·3 (2)	C(4)—Ti—C(19)	131·8 (2)
C(2)—Ti—C(15)	79·4 (2)	C(4)—C(3)—Si(2)	131·2 (3)

Discussion. The title compound is a monomolecular complex of titanium bonded to a Cp and 1,2,4-tris(trimethylsilyl)cyclopentadienyl (Si_3Cp) ligand in a pentahapto (η^5) manner and to two Cl atoms. The Ti—C distances average 2·41 Å (Si_3Cp) and 2·39 Å (Cp) and the distances of titanium to the planes of the cyclopentadienyl ligands are 2·082 Å (Cp) and 2·076 Å (Si_3Cp). Interestingly, there is a slight distortion toward trihapto bonding in the Si_3Cp ligand. Ti—C(1) (2·380 Å), Ti—C(2) (2·377 Å), and

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52456 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (*cont.*)

C(2)—Ti—C(16)	76·9 (2)	C(4)—Si(3)—C(12)	104·7 (2)
C(2)—Ti—C(17)	108·2 (2)	C(4)—Si(3)—C(13)	117·4 (2)
C(2)—Ti—C(18)	132·0 (2)	C(4)—Si(3)—C(14)	107·6 (2)
C(2)—Ti—C(19)	110·9 (3)	C(5)—Ti—C(15)	136·6 (2)
C(2)—C(1)—C(5)	107·6 (4)	C(5)—Ti—C(16)	124·2 (2)
C(2)—C(1)—Si(1)	127·9 (4)	C(5)—Ti—C(17)	135·6 (2)
C(2)—C(3)—C(4)	105·6 (4)	C(5)—Ti—C(18)	162·4 (2)
C(2)—C(3)—Si(2)	122·3 (3)	C(5)—Ti—C(19)	163·9 (2)
C(3)—Ti—C(4)	34·8 (2)	C(5)—C(1)—Si(1)	123·6 (3)
C(3)—Ti—C(5)	58·0 (2)	C(5)—C(4)—Si(3)	117·2 (3)
C(3)—Ti—C(15)	86·4 (2)	C(6)—Si(1)—C(7)	109·1 (2)
C(3)—Ti—C(16)	101·5 (2)	C(6)—Si(1)—C(8)	108·5 (2)
C(3)—Ti—C(17)	135·6 (2)	C(7)—Si(1)—C8	108·9 (2)
C(3)—Ti—C(18)	139·2 (2)	C(9)—Si(2)—C(10)	110·0 (2)
C(3)—Ti—C(19)	105·9 (2)	C(9)—Si(2)—C(11)	106·7 (2)
C(3)—C(4)—C(5)	109·4 (4)	C(10)—Si(2)—C(11)	108·9 (2)
C(3)—C(4)—Si(1)	132·7 (3)	C(12)—Si(3)—C(13)	109·5 (2)
C(3)—Si(2)—C(9)	107·3 (2)	C(12)—Si(3)—C(14)	107·5 (2)
C(3)—Si(2)—C(10)	113·6 (2)	C(13)—Si(3)—C(14)	109·7 (2)
C(15)—Ti—C(16)	34·0 (2)	C(16)—Ti—C(19)	56·3 (3)
C(15)—Ti—C(17)	55·7 (3)	C(16)—C(15)—C(19)	109·6 (7)
C(15)—Ti—C(18)	55·8 (3)	C(16)—C(17)—C(18)	108·9 (6)
C(15)—Ti—C(19)	33·3 (3)	C(17)—Ti—C(18)	33·7 (3)
C(15)—C(16)—C(17)	106·2 (6)	C(17)—Ti—C(19)	55·6 (3)
C(15)—C(19)—C(18)	108·2 (7)	C(17)—C(18)—C(19)	107·0 (7)
C(16)—Ti—C(17)	34·1 (3)	C(18)—Ti—C(19)	33·7 (3)
C(16)—Ti—C(18)	56·8 (2)		

* Cp(1) is the centroid of the Cp ligand and Cp(2) is the centroid of the Si_3Cp ligand.

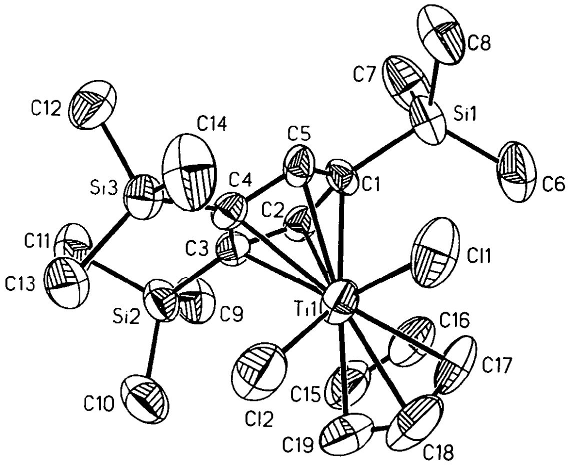

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the title molecule, with thermal ellipsoids at the 50% probability level.

Ti—C(3) (2·402 Å) comprise the short bonds, while Ti—C(4) (2·447 Å) and Ti—C(5) (2·438 Å) constitute the long ones. The ring C—C bond distances average 1·435 Å (Si_3Cp) and 1·392 Å (Cp), and the Ti—Cl distances are 2·342 and 2·364 Å. The Ti atom lies at the center of a distorted tetrahedron with a Cp—Ti—Cp′ angle of 129·7° and a Cl—Ti—Cl′ angle of 92° (Table 2). The C atoms of the cyclopentadienyl rings are planar to within 0·017 (5) (Si_3Cp) and 0·012 (1) Å (Cp). The Si atoms of the trimethylsilyl groups are bent out of the plane of the Si_3Cp ligand by 7·4 (2) [Si(1)], 6·7 (2) [Si(2)], and 9·2 (2)° [Si(3)]. There are no significant intermolecular contacts.

The structural features of the title complex are normal. Comparisons can be made with the structures of $Cp^{\ddagger}_2TiCl_2$ (McKenzie, Sanner & Bercaw, 1975) and $Cp^*CpTiCl_2$ (Rogers, Benning, Kurihara, Moriarty & Rausch, 1985). The CpTiCp′ (129·71°) and ClTiCl′ (92·83°) angles are very similar to those in $Cp^*CpTiCl_2$ (CpTiCp′ 132; ClTiCl′ 94·44°) and $Cp^{\ddagger}_2TiCl_2$ (CpTiCp′ 137·4; ClTiCl′ 92·94°). The Ti–Cp centroid distance (2·08 Å) and Ti—Cl distances (av. 2·35 Å) are also very similar to the related distances in $Cp^*CpTiCl_2$ (Ti–Cp centroid av. 2·085; Ti—Cl 2·35 Å) and $Cp^{\ddagger}_2TiCl_2$ (Ti–Cp centroid av. 2·13; Ti—Cl 2·35 Å). The presence of the bulky Si_3Cp ligand does not perturb the major structural features of the titanocene skeleton. As noted above, the Si_3Cp ligand shows a distortion toward trihapto bonding to titanium. This distortion probably arises from Si···Cl non-bonded repulsions, as close contacts of 3·81 [Si(1)···Cl(1)] and 3·40 Å [Si(3)···Cl(2)] are observed. These contacts are well within the sum of covalent radii of silicon and chlorine of about 3·85 Å (Bondi, 1964). The silicon···chlorine close contacts account for the larger bending out of the plane of the cyclopentadienyl ring of Si(1) and Si(3) relative to Si(2). A zirconium complex that features an η^3-fluorenyl ligand has been structurally characterized (Kowala & Wunderlich, 1976).

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