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The dimeric mixed-ligand titanacarborane sandwich [1-(Cp)-1-Ti-2-(Me)-3-($SiMe_3$)-2,3-$C_2B_4H_4$]$_2$

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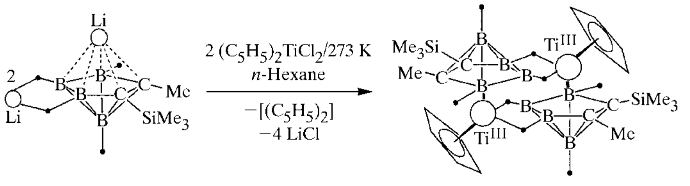
The title dimer, bis[1-cyclopentadienyl-2-methyl-1-titana-3-trimethylsilyl-2,3-dicarba-*closo*-hexaborane(6)], [Ti(C_5H_5)($C_6H_{16}B_4Si$)]$_2$, reveals that the centrosymmetric molecule consists of two bent-sandwich titanacarboranes bridged by the B—H—Ti bonds. The average bond distances are Ti—B 2.445 (3), Ti—C(cage) 2.334 (2) and Ti—C(Cp) 2.376 (3) Å, and the corresponding bond angles are Cp—Ti—Cp 163.2 (1) and Cp—Ti—Cb (Cb = C_2B_3 face) 139.9 (1)°; the Ti—H separations are 2.10 (2) and 2.19 (2) Å.

Comment

Group four (titanium group) organometallic compounds have been the subject of numerous structural, spectroscopic and synthetic investigations (Abel *et al.*, 1995; Cardin *et al.*, 1986; Jordan, 1988; Jordan *et al.*, 1990; Corbin *et al.*, 1986). Interest in the design of novel molecular magnetic materials (Miller & Epstein, 1994) has made the study of electron spin–electron spin interactions in dinuclear and polynuclear transition metal complexes a topic of intense research (VanVleck, 1932; Kahn, 1993; Mabbs & Collison, 1992). However, only a relatively small number of symmetrical Ti^{III} dimers have been completely characterized by electron paramagnetic resonance (Mabbs & Collison, 1992), magnetic susceptibility measurements and crystal structure determinations (Samuel *et al.*, 1992; Xin *et al.*, 1994; Grimes, 1995; Hosmane & Maguire, 1990, 1991, 1993). Although our recent paper on this subject described the synthesis and reactivity studies on the dimeric mixed-ligand titanacarborane sandwich [1-(Cp)-1-Ti-2-(Me)-3-($SiMe_3$)-2,3-$C_2B_4H_4$)]$_2$, (II) (Cp = η^5-C_5H_5), we were unable to grow a suitable single crystal of this complex and hence its structure was not reported (Hosmane *et al.*, 1997). After allowing a benzene solution of (II) to stand for several months at room temperature *in vacuo*, suitable crystals were obtained and were subsequently used for X-ray analysis.

The driving force for the formation of (II) is most likely the stability of the Ti^{III} product, as well as the formation of dihydrofulvalene. When the 'C atoms adjacent' bis(trimethylsilyl)carborane (Cb) was reacted with $TiCl_3$, only the monomeric full-sandwich chlorotitanacarborane was formed, irrespective of the stoichiometry used in the reaction. Replacement of an $SiMe_3$ group with the smaller Me group afforded the [(Cb*)$_2$Ti]$_2^{2-}$ dimer exclusively (Hosmane *et al.*, 1997). In the same way, replacement of one of the Cb ligands with the smaller, isolobal and isoelectronic π-donor Cp ligand also resulted in dimer formation, giving the mixed-ligand dimer (II).



(I) (II)

The crystal structure (Fig. 1) reveals that (II) is a bent-sandwich complex, similar to those found in the Cp system (Corbin *et al.*, 1986; Samuel *et al.*, 1992; Jungst *et al.*, 1977; Peterson & Dahl, 1975; Pattiasina *et al.*, 1987). The (ring centroid)—Ti—(ring centroid) bond angle of 139.9 (1)° is within the range 130–144° found in the titanocenes (Corbin *et al.*, 1986; Samuel *et al.*, 1992; Jungst *et al.*, 1977; Peterson & Dahl, 1975; Pattiasina *et al.*, 1987), and similar to the analogous angles of 144.6 and 138.8° found by Jordan for the mixed-ligand complexes [(Cp*)Ti($NCMe_2$)($C_2B_9H_{11}$)] and [(Cp*)Ti($NCMe_2$)(MeCN)($C_2B_9H_{11}$)], respectively (Kreuder *et al.*, 1995). A comparison of the distances between Ti and the centroids of the Cp and C_2B_3 carborane rings reveals a surprising insensitivity to either the formal charge on the metals or the nature of the other ligands present. The average Ti—Cp distance of 2.060 (3) Å is close to the average of 2.054 (4) Å found in [Cp_2TiCl]$_2$ (Jungst *et al.*, 1977) and is also close to the analogous distances found in a number of substituted titanocenes (Corbin *et al.*, 1986; Peterson & Dahl, 1975; Pattiasina *et al.*, 1987). The average Ti—C_2B_3(centroid) distance of 1.983 (3) Å is close to the values of 2.02 and 1.91 Å found in the Cp*Ti($C_2B_9H_{11}$) mixed-ligand sandwich compounds of Jordan (Kreuder *et al.*, 1995), as well as the Ti—C_2B_3(centroid) distance of 1.917 Å reported by Grimes for the cyclooctatetraene (COT) titanacarborane 1-(η^8-C_8H_8)-1-Ti-2,3-(Et)$_2$-2,3-$C_2B_4H_4$ (Swisher *et al.*, 1984). The latter compound is of interest in that it, as well as its cyclopentadienide analogues (Koon & Helmholdt, 1984), is not bent but has a linear ring centroid—Ti—ring centroid arrangement. It is not clear whether the linear structures found in the COT complexes are a result of the size of the [C_8H_8]$^{2-}$ ligand or the fact that it is a ten-electron donor. In the same way, while both steric and electronic effects are operative in determining the geometry of (II), the relative importance of the two effects is not apparent. However, the influence of steric factors is readily seen in some of the structural features of known titanacarborane bent-sandwich complexes (Hosmane *et al.*, 1997). Nonetheless, substitution of an $SiMe_3$ group by a sterically less demanding Me allows additional coordination to form the dimeric structure as found for (II). This is similar to what is found in the titanocenes where the substitution of a Cp ligand in $[Cp_2TiCl]_2$ by Cp* (Cp* = η^5-C_5Me_5) resulted in the isolation of the $[(Cp^*)_2TiCl]$ monomer (Jungst *et al.*, 1977; Peterson & Dahl, 1975; Pattiasina *et al.*, 1987). Other properties may also be affected. For example, steric crowding by the $SiMe_3$ groups has been used to account for the lack of reactivity of the coordinated Cl and tetrahydrofuran (thf) in the zirconacarborane anion, $[1\text{-Cl-1-thf-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}1,1'\text{-}commo\text{-}Zr(2,3\text{-}C_2B_4H_4)_2]^-$ (Thomas *et al.*, 1995). It may well be that the use of different cage-carbon substituents and the locations of the cage-C atoms in the bonding face could be used to control the reactivities of these d^0 or d^1 bent-sandwich metallacarboranes.

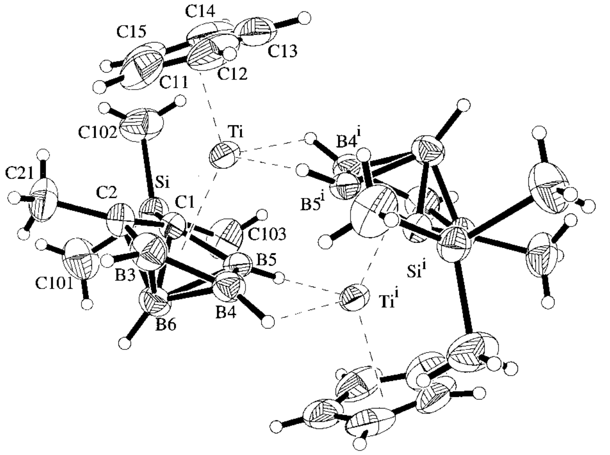


Figure 1
Displacement ellipsoid drawing of the title compound with ellipsoids shown at the 50% probability level [symmetry code: (i) $1 - x, -y, -z$].

Experimental

The reaction of Cp_2TiCl_2 with the unsolvated 'C atoms adjacent' dilithium compounds, *closo-exo*-Li-1-Li-2-(Me)-3-$(SiMe_3)$-2,3-$C_2B_4H_4$ (Hosmane *et al.*, 1993), produced the corresponding mixed-ligand sandwich titanacarborane, $[commo\text{-}1\text{-Cp-}1\text{-}Ti^{III}\text{-}2\text{-(Me)-}3\text{-}(SiMe_3)\text{-}2,3\text{-}C_2B_4H_4]_2$, (II), in 54% yield as shown in the scheme above (Hosmane *et al.*, 1997).

Crystal data

$[Ti(C_5H_5)(C_6H_{16}B_4Si)]_2$
$M_r = 545.02$
Monoclinic, $P2_1/c$
$a = 8.2310\ (16)$ Å
$b = 10.655\ (2)$ Å
$c = 17.042\ (3)$ Å
$\beta = 102.26\ (3)^\circ$
$V = 1460.5\ (5)$ Å^3
$Z = 2$
$D_x = 1.239$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3$–25°
$\mu = 0.640$ mm^{-1}
$T = 293\ (2)$ K
Rectangular, black
0.32 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.862$, $T_{max} = 0.938$
3263 measured reflections
3164 independent reflections
2365 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 26.96^\circ$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 21$
3 standard reflections every 250 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.089$
$S = 1.026$
3164 reflections
170 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.2584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ti—C1	2.330 (2)	Ti—C12	2.384 (2)
Ti—C2	2.339 (2)	Ti—B3	2.406 (3)
Ti—C15	2.371 (2)	Ti—B5	2.414 (2)
Ti—C13	2.371 (2)	Ti—B5^i	2.415 (2)
Ti—C11	2.375 (2)	Ti—B4	2.484 (2)
Ti—C14	2.378 (2)	Ti—B4^i	2.505 (3)
C1—Ti—C2	37.26 (7)	C2—Ti—C14	116.45 (9)
C1—Ti—C15	113.91 (9)	C15—Ti—C14	34.29 (10)
C2—Ti—C15	83.89 (10)	C13—Ti—C14	33.80 (9)
C1—Ti—C13	142.58 (8)	C11—Ti—C14	56.58 (10)
C2—Ti—C13	136.68 (8)	C1—Ti—C12	108.54 (8)
C15—Ti—C13	56.68 (11)	C2—Ti—C12	110.61 (9)
C1—Ti—C11	94.64 (8)	C15—Ti—C12	56.47 (11)
C2—Ti—C11	80.92 (9)	C13—Ti—C12	34.28 (9)
C15—Ti—C11	34.10 (11)	C11—Ti—C12	33.79 (10)
C13—Ti—C11	56.62 (9)	C14—Ti—C12	56.41 (10)
C1—Ti—C14	148.00 (9)		

Symmetry code: (i) $1 - x, -y, -z$.

The H atoms on C atoms were refined using a riding model with U_{iso} values equal to 1.5 times those of the preceding C atoms for the methyl groups and 1.3 times for the rings. The C—H distances are 0.97 and 0.96 Å for the CH_2 and CH_3 groups, respectively. The H atoms attached to B atoms were located in a difference map and freely refined.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4-PC Software*; data reduction: *CAD-4-PC Software*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL97* (Sheldrick, 1997); molecular graphics: *SHELXTL97*; software used to prepare material for publication: *SHELXTL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1105). Services for accessing these data are described at the back of the journal.

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