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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
Disorder in main residue
R factor = 0.070
wR factor = 0.183
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

$(\mu_2-\eta^2-2\text{-tert-Butylethyn-1-yl})(\mu_2\text{-chloro})\text{bis}\{[\text{bis}(\eta^5\text{-cyclopentadienyl})\text{dimethylsilane}]\text{titanium}\}$

The title compound, $[\text{Ti}_2\text{Cl}(\text{C}_6\text{H}_9)(\text{C}_{12}\text{H}_{14}\text{Si})_2]$, displays an asymmetric $\mu_2-\eta^2$ C \equiv C bridge between the two metal ions. The C—C \equiv C bond angle deviates markedly from linearity. The difference in the Ti—Cl bond lengths involving the bridging Cl is 0.146 (3) Å. The angles between the least-squares planes through the ring systems of the titanocene units are 55.4 (4) and 57.8 (4)°.

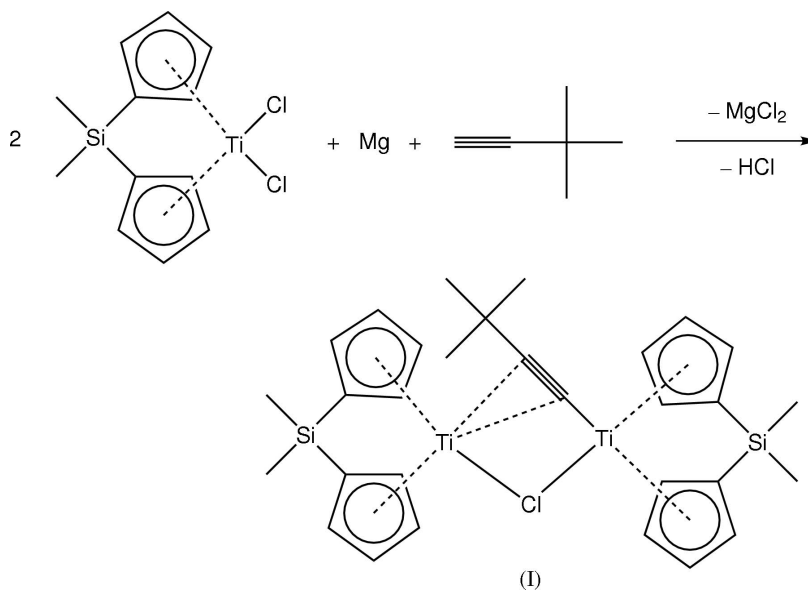
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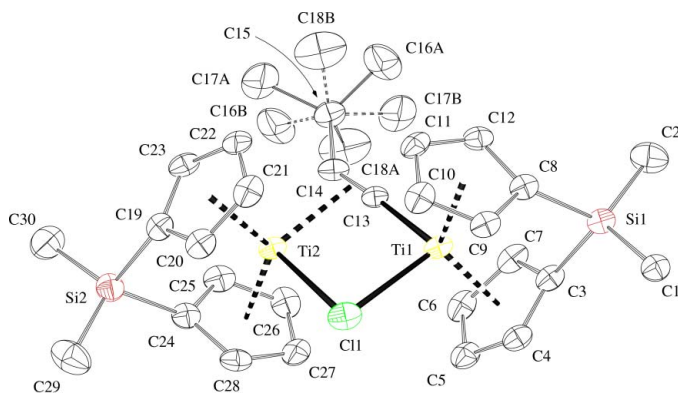
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Comment

In order to broaden the variety of known asymmetrically substituted *ansa*-metallacyclopropene complexes, the *ansa*-titanocene $(\text{CH}_3)_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ was treated with magnesium in tetrahydrofuran in the presence of *tert*-butylacetylene. Unexpectedly, the title compound, (I), was obtained and we present its structure here.



The structure of (I) is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The distance of 3.383 (2) Å between the Ti ions is large enough to be considered as non-bonding (in the metal, the Ti—Ti distance is 2.90 Å; Hull, 1921). The *tert*-butylacetylene group acts as a $\mu_2-\eta^2$ bridge between the two metal ions. This bridging mode of the C \equiv C group is not uncommon. Recent examples are a heteronuclear Ti—Ag complex with bridging C \equiv C—Si(CH₃)₃, reported by Al-Anber *et al.* (2004), and a homonuclear Ru complex with bridging C \equiv C, reported by Griffith *et al.* (2003). Takahashi *et al.* (1997) published the structure of $(\mu_2-\eta^2-$


Figure 1

A view of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Disorder components with an occupation factor of less than 0.5 are drawn with dashed bonds.

propynyl)(μ_2 -chloro)dizirconocene, which, compared with (I), lacks the $\text{Si}(\text{CH}_3)_2$ links between the cyclopentadienyl rings, but also shows the μ_2 - η^2 bridging mode of the $\text{C}\equiv\text{C}$ group.

The November 2004 release of the Cambridge Structural Database (CSD; Allen, 2002) contains 222 $\text{C}-\text{C}\equiv\text{C}$ groups involved in a μ_2 - η^2 bridge between two metal ions. The length of the triple bond in (I) [1.227 (8) Å] is in good agreement with the range observed in the CSD (1.05–1.37 Å, mean value 1.224 Å, standard deviation of sample 0.035 Å), but the $\text{C}\equiv\text{C}-\text{C}$ bond angle [140.2 (6)°] is among the most extreme deviations from linearity (observed CSD range 139–180°, mean value 164°, standard deviation of sample 8°). The length of the $\text{C}13-\text{Ti}1$ σ bond [2.043 (6) Å] is relatively small compared with 173 $\text{C}\equiv\text{C}-\text{Ti}$ systems found in the CSD, with $\text{C}-\text{Ti}$ bond lengths in the range 2.026–2.257 Å. Only four systems reported in the CSD have a $\text{C}-\text{Ti}$ bond shorter than that found in (I).

The μ_2 -Cl bridge in (I) also has an asymmetric geometry. The difference in the $\text{Ti}-\text{Cl}$ distances is 0.146 (3) Å, with $\text{Ti}1-\text{Cl}1$ being the shorter bond. The angle between the least-squares planes through the Cp rings coordinated to $\text{Ti}1$ is 55.4 (4)°; for the rings coordinated to $\text{Ti}2$, this angle is 57.8 (4). For the related compound (μ_2 - η^2 -propynyl)(μ_2 -chloro)dizirconocene, which lacks the $\text{Si}(\text{CH}_3)_2$ links between the cyclopentadienyl rings, the slightly lower values of 51.5 (4) and 55.6 (3)°, respectively, were found.

Experimental

Experiments were performed using a high-vacuum sealed glass apparatus (Vreugdenhil & Blomberg, 1963). Solvents were dried before use by distillation from a liquid Na–K alloy. At room temperature, a solution of *tert*-butylacetylene (0.21 mmol) in tetrahydrofuran (12.1 ml) was added to $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}_2$ [62.2 mg, 0.20 mmol, prepared according to the procedures reported by Bajgur *et al.* (1985)]. After stirring for 7 h, an intense dark-purple mixture was formed. Although there was still some unreacted magnesium remaining, the solvent was removed by distillation with liquid nitrogen. The residue was extracted twice with 10 ml of toluene. NMR analysis of the product mixture revealed that two products had

been formed in a 3.5:1 ratio. Crystals of (I), suitable for X-ray diffraction studies, were obtained by cooling a saturated solution of the reaction product in toluene. The crystals were isolated in a glove box under a nitrogen atmosphere and sealed into Lindemann glass capillaries. Spectroscopic analysis: ^1H NMR (200 MHz, room temperature, C_6D_6 , reference $\text{C}_6\text{D}_5\text{H} = 7.17$ p.p.m., δ , p.p.m.): 5.62 (*m*, 12H, C_5H_4), 5.31 (*m*, 4H, C_5H_4), 1.22 [*s*, 9H, $\text{C}(\text{CH}_3)_3$], 0.38 [*s*, 6H, $\text{Si}(\text{CH}_3)_2$], 0.29 [*s*, 6H, $\text{Si}(\text{CH}_3)_2$]; ^{13}C NMR (62.9 MHz, room temperature, C_6D_6 , reference $\text{C}_6\text{D}_6 = 128.0$ p.p.m., δ , p.p.m.): 172.3 ($\text{Ti}-\text{C}\equiv\text{C}$), 120.9 ($\text{Ti}-\text{C}\equiv\text{C}$), 119.3 (C_5H_4), 117.5 (C_5H_4), 102.7 (C_5H_4), 102.6 (C_5H_4 , bridgehead), 101.2 (C_5H_4), 38.8 [$\text{C}(\text{CH}_3)_3$], 33.3 [$\text{C}(\text{CH}_3)_3$], -5.4 ($\text{Si}(\text{CH}_3)_2$), -6.1 ($\text{Si}(\text{CH}_3)_2$); MS (EI), *m/z* (relative intensities): 584 (3) [*M*], 350 (14) [$(\text{CH}_3)_2\text{Si}(\text{C}_5\text{H}_4)_2\text{TiCl}(\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_3$], 314 (45), 269 (100), 254 (28), 234 (47), [$(\text{CH}_3)_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Ti}$], 176 (24), 150 (14).

Crystal data

$[\text{Ti}_2\text{Cl}(\text{C}_6\text{H}_9)(\text{C}_{12}\text{H}_{14}\text{Si})_2]$
 $M_r = 584.97$
 Triclinic, $P\bar{1}$
 $a = 9.381$ (4) Å
 $b = 11.552$ (3) Å
 $c = 14.120$ (4) Å
 $\alpha = 80.18$ (2)°
 $\beta = 83.89$ (3)°
 $\gamma = 74.93$ (3)°
 $V = 1452.8$ (9) Å³

$Z = 2$
 $D_x = 1.337$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.9$ – 14.0 °
 $\mu = 0.74$ mm⁻¹
 $T = 298$ K
 Block, black
 $0.3 \times 0.3 \times 0.2$ mm

Data collection

Enraf-Nonius CAD-4 Turbo diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 6538 measured reflections
 5250 independent reflections
 3134 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.081$

$\theta_{\text{max}} = 25.3$ °
 $h = -11 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -16 \rightarrow 16$
 3 standard reflections
 frequency: 60 min
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.183$
 $S = 1.17$
 5250 reflections
 326 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.81$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.77$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

$\text{Cg}1$, $\text{Cg}2$, $\text{Cg}3$ and $\text{Cg}4$ are the centroids of rings $\text{C}3-\text{C}7$, $\text{C}8-\text{C}12$, $\text{C}19-\text{C}23$ and $\text{C}24-\text{C}28$, respectively. $\text{Cg}5$ is the midpoint of the $\text{C}13=\text{C}14$ bond.

$\text{Ti}1-\text{Cl}1$	2.413 (2)	$\text{Ti}2-\text{Cl}1$	2.262 (6)
$\text{Ti}1-\text{C}13$	2.043 (6)	$\text{Ti}2-\text{Cg}3$	2.126 (3)
$\text{Ti}1-\text{Cg}1$	2.081 (3)	$\text{Ti}2-\text{Cg}4$	2.118 (3)
$\text{Ti}1-\text{Cg}2$	2.091 (3)	$\text{Ti}2-\text{Cg}5$	2.190 (5)
$\text{Ti}2-\text{Cl}1$	2.559 (2)	$\text{C}13-\text{C}14$	1.227 (8)
$\text{Ti}2-\text{C}13$	2.288 (6)		
$\text{Cg}1-\text{Ti}1-\text{Cg}2$	128.96 (13)	$\text{Cg}3-\text{Ti}2-\text{Cl}1$	102.27 (10)
$\text{Cg}1-\text{Ti}1-\text{Cl}1$	108.25 (11)	$\text{Cg}4-\text{Ti}2-\text{Cg}5$	110.88 (15)
$\text{Cg}1-\text{Ti}1-\text{C}13$	106.72 (19)	$\text{Cg}4-\text{Ti}2-\text{Cl}1$	102.93 (9)
$\text{Cg}2-\text{Ti}1-\text{Cl}1$	109.01 (10)	$\text{Cg}5-\text{Ti}2-\text{Cl}1$	97.00 (13)
$\text{Cg}2-\text{Ti}1-\text{C}13$	106.71 (18)	$\text{Ti}1-\text{Cl}1-\text{Ti}2$	85.72 (7)
$\text{Cl}1-\text{Ti}1-\text{C}13$	90.27 (17)	$\text{Ti}1-\text{C}13-\text{Ti}2$	102.6 (2)
$\text{Cg}3-\text{Ti}2-\text{Cg}4$	126.70 (13)	$\text{C}13-\text{C}14-\text{Cl}1$	140.2 (6)
$\text{Cg}3-\text{Ti}2-\text{Cg}5$	111.61 (15)		

The *tert*-butyl group displayed conformational disorder, which could be described with a two-site model. The site-occupancy ratio

refined to 0.715 (8):0.285 (8). The displacement parameters of the minor disorder component, atoms C16B–C18B, were set equal to those of the major disorder component atoms, C16A–C18A. H atoms were introduced in calculated positions, with C–H = 0.93–0.97 Å, and refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$ or $1.2U_{\text{eq}}(\text{cyclopentadienyl C})$.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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References

- Al-Anber, M., Walfort, B., Stein, T. & Lang, H. (2004). *Inorg. Chim. Acta*, **357**, 1675–1681.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bajgur, C. S., Tikkanen, W. R. & Petersen, J. L. (1985). *Inorg. Chem.* **24**, 2539–2546.
- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
- Griffith, C. S., Koutsantonis, G. A., Skelton, B. W. & White, A. H. (2003). *J. Organomet. Chem.* **670**, 198–204.
- Hull, A. W. (1921). *Phys. Rev.* **18**, 88–89.
- Sheldrick, G. M. (1985). *SHELXS86*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *HELENA*. University of Utrecht, The Netherlands.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Takahashi, T., Nishihara, Y., Sun, W. H., Fischer, R. & Nakajima, K. (1997). *Organometallics*, **16**, 2216–2219.
- Vreugdenhil, A. D. & Blomberg, C. (1963). *Recl Trav. Chim. Pays-Bas*, **83**, 453–460.