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Huub Kooijman,[a]* Marijke Hogenbirk,[b] Gerrit Schat,[b] Otto S. Akkerman,[b] Friedrich Bickelhaupt[b] and Anthony L. Spek[a]

[a]Bijvoet Centre for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and [b]Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Correspondence e-mail:
h.kooijman@chem.uu.nl

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
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.

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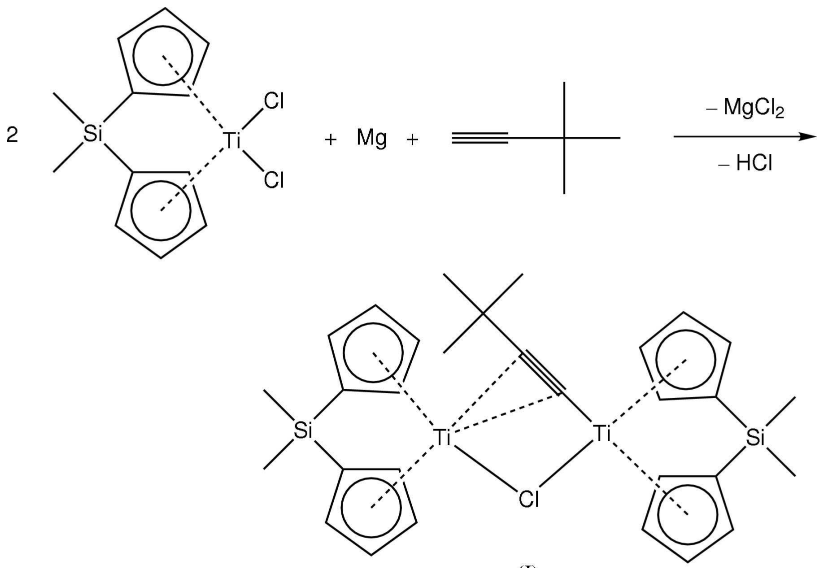
The title compound, [$Ti_2Cl(C_6H_9)(C_{12}H_{14}Si)_2$], displays an asymmetric μ_2-η^2 C≡C bridge between the two metal ions. The C—C≡C bond angle deviates markedly from linearity. The difference in the Ti—Cl bond lengths involving the bridging Cl is 0.146 (3) Å. The angles between the least-squares planes through the ring systems of the titanocene units are 55.4 (4) and 57.8 (4)°.

Comment

In order to broaden the variety of known asymmetrically substituted *ansa*-metallacyclopropene complexes, the *ansa*-titanocene $(CH_3)_2Si(C_5H_4)_2TiCl_2$ 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.



(I)

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 μ_2-η^2 bridge between the two metal ions. This bridging mode of the C≡C group is not uncommon. Recent examples are a heteronuclear Ti–Ag complex with bridging C≡C—Si$(CH_3)_3$, reported by Al-Anber *et al.* (2004), and a homonuclear Ru complex with bridging C≡C, reported by Griffith *et al.* (2003). Takahashi *et al.* (1997) published the structure of (μ_2-η^2-

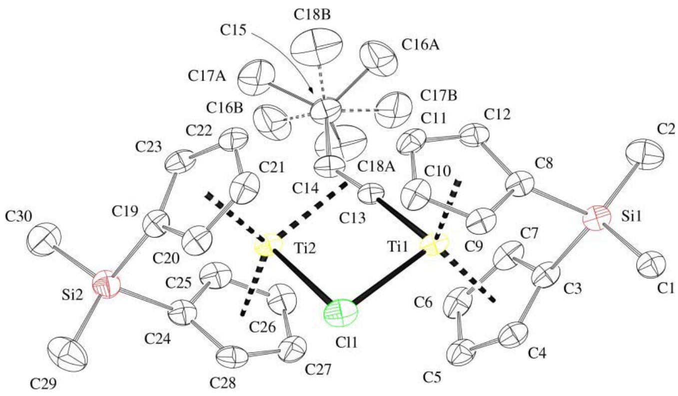


Figure 1
A view of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Disorder components with an occupation factor of less than 0.5 are drawn with dashed bonds.

propynyl)(μ_2-chloro)dizirconocene, which, compared with (I), lacks the $Si(CH_3)_2$ links between the cyclopentadienyl rings, but also shows the μ_2-η^2 bridging mode of the C≡C group.

The November 2004 release of the Cambridge Structural Database (CSD; Allen, 2002) contains 222 C—C≡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 C≡C—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 C13—Ti1 σ bond [2.043 (6) Å] is relatively small compared with 173 C≡C—Ti systems found in the CSD, with C—Ti bond lengths in the range 2.026–2.257 Å. Only four systems reported in the CSD have a C—Ti bond shorter than that found in (I).

The μ_2-Cl bridge in (I) also has an asymmetric geometry. The difference in the Ti—Cl distances is 0.146 (3) Å, with Ti1—Cl1 being the shorter bond. The angle between the least-squares planes through the Cp rings coordinated to Ti1 is 55.4 (4)°; for the rings coordinated to Ti2, this angle is 57.8 (4). For the related compound (μ_2-η^2-propynyl)(μ_2-chloro)-dizirconocene, which lacks the $Si(CH_3)_2$ 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 $Me_2Si(C_5H_4)_2TiCl_2$ [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: ^{1}H NMR (200 MHz, room temperature, C_6D_6, reference C_6D_5H = 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, $C(CH_3)_3$], 0.38 [*s*, 6H, $Si(CH_3)_2$], 0.29 [*s*, 6H, $Si(CH_3)_2$]; ^{13}C NMR (62.9 MHz, room temperature, C_6D_6, reference C_6D_6 = 128.0 p.p.m., δ, p.p.m.): 172.3 (Ti—*C*≡C), 120.9 (Ti—C≡*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 [*C*($CH_3)_3$], 33.3 [C(*C*$H_3)_3$], −5.4 ($SiCH_3$), −6.1 ($SiCH_3$); MS (EI), *m/z* (relative intensities): 584 (3) [*M*], 350 (14) [$(CH_3)_2Si(C_5H_4)_2TiCl(C{\equiv}C{-}C(CH_3)_3$], 314 (45), 269 (100), 254 (28), 234 (47), [$(CH_3)_2Si(C_5H_4)_2Ti$], 176 (24), 150 (14).

Crystal data

$[Ti_2Cl(C_6H_9)(C_{12}H_{14}Si)_2]$	Z = 2
M_r = 584.97	D_x = 1.337 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 9.381 (4) Å	Cell parameters from 25 reflections
b = 11.552 (3) Å	θ = 9.9–14.0°
c = 14.120 (4) Å	μ = 0.74 mm^{-1}
α = 80.18 (2)°	T = 298 K
β = 83.89 (3)°	Block, black
γ = 74.93 (3)°	0.3 × 0.3 × 0.2 mm
V = 1452.8 (9) Å^3	

Data collection

Enraf-Nonius CAD-4 Turbo diffractometer	θ_{max} = 25.3°
$\omega/2\theta$ scans	h = −11 → 11
Absorption correction: none	k = −13 → 13
6538 measured reflections	l = −16 → 16
5250 independent reflections	3 standard reflections
3134 reflections with $I > 2\sigma(I)$	frequency: 60 min
R_{int} = 0.081	intensity decay: 1%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.070	$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.183	$(\Delta/\sigma)_{max}$ < 0.001
S = 1.17	$\Delta\rho_{max}$ = 0.81 e Å^{-3}
5250 reflections	$\Delta\rho_{min}$ = −0.77 e Å^{-3}
326 parameters	

Table 1
Selected geometric parameters (Å, °).

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of rings C3–C7, C8–C12, C19–C23 and C24–C28, respectively. *Cg*5 is the midpoint of the C13≡C14 bond.

Ti1—Cl1	2.413 (2)	Ti2—C14	2.262 (6)
Ti1—C13	2.043 (6)	Ti2—*Cg*3	2.126 (3)
Ti1—*Cg*1	2.081 (3)	Ti2—*Cg*4	2.118 (3)
Ti1—*Cg*2	2.091 (3)	Ti2—*Cg*5	2.190 (5)
Ti2—Cl1	2.559 (2)	C13—C14	1.227 (8)
Ti2—C13	2.288 (6)		
*Cg*1—Ti1—*Cg*2	128.96 (13)	*Cg*3—Ti2—Cl1	102.27 (10)
*Cg*1—Ti1—Cl1	108.25 (11)	*Cg*4—Ti2—*Cg*5	110.88 (15)
*Cg*1—Ti1—C13	106.72 (19)	*Cg*4—Ti2—Cl1	102.93 (9)
*Cg*2—Ti1—Cl1	109.01 (10)	*Cg*5—Ti2—Cl1	97.00 (13)
*Cg*2—Ti1—C13	106.71 (18)	Ti1—Cl1—Ti2	85.72 (7)
Cl1—Ti1—C13	90.27 (17)	Ti1—C13—Ti2	102.6 (2)
*Cg*3—Ti2—*Cg*4	126.70 (13)	C13—C14—C15	140.2 (6)
*Cg*3—Ti2—*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 C16*B*–C18*B*, were set equal to those of the major disorder component atoms, C16*A*–C18*A*. 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_{iso}(H) = 1.5U_{eq}(methyl C) or 1.2U_{eq}(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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