

Dichlorobis(cumylcyclopentadienyl)-
titanium(IV)Roberto Centore,^{a*} Zsolt Csok^b and Angela Tuzi^a^aDipartimento di Chimica, Università degli Studi di Napoli 'Federico II', Complesso di Monte S. Angelo, Via Cinthia, 80126 Napoli, Italy, and ^bDipartimento di Chimica, Università degli Studi di Salerno, Via S. Allende, 84081 Salerno, Italy
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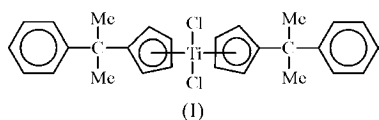
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The title compound, [Ti(C₁₄H₁₅)₂Cl₂], belongs to a class of complexes that are potentially active as pre-catalysts in the stereospecific polymerization of olefins. In the crystal structure, molecules lie on C₂ axes with pseudo-tetrahedral coordination around the Ti atoms. Conformational features of the compound are discussed, in conjunction with calculations that demonstrate the existence of other energetically favorable conformations in addition to that found in the reported crystal structure.

Comment

In view of possible applications in the area of polymerization of hydrocarbon monomers, we synthesized a new particularly fluxional titanocene, [Ti(cCp)₂Cl₂] [cCp = cumylcyclopentadienyl, C₆H₅C(CH₃)₂C₅H₄], (I).



The synthesis, the ¹H NMR spectrum and the X-ray structure are reported in this paper, together with some consideration of the conformations of the complex in solution.

The molecule (Fig. 1) possesses crystallographic twofold symmetry. This seems to be a fairly general feature for group IV metallocenes of formula [M(CpR)₂Cl₂] [CpR = C₅H₄C(Me)₂R; R = alkyl or aryl, and M = Ti, Zr and Hf] (Shan *et al.*, 1994; Dorado *et al.*, 1998; Grimmond *et al.*, 1999), and several structural and conformational features look very similar across this class of complexes.

The metal center adopts a pseudo-tetrahedral geometry with respect to the chloride ligands and cyclopentadienyl (Cp) ring centroids [Cg1—Ti—Cg2 = 131.36 (5)°; Cg1 and Cg2 are the Cp ring centroids]. The Cp rings are inclined [the dihedral angle between the mean planes is 53.71 (9)°] in a staggered conformation, while the ring substituents are mutually disposed in a pseudo-*trans* manner. The *gem*-dimethyl groups

are oriented laterally, leaving the bulky phenyl rings in a distal disposition, that is, oriented away from the metal core and roughly perpendicular to the cyclopentadienyl ring [the dihedral angle between the mean planes is 81.1 (1)°]. As generally found in this class of complexes, the metal is not equidistant from the five Cp ring C atoms. In particular, the Ti—C1 and Ti—C5 distances are longer than the other Ti—C distances; this effect could be a consequence of contacts between *gem*-methyl groups and chloride ligands, each Cl atom lying, in projection, between two methyl groups [C1ⁱ...C8 = 3.687 (3) Å and C1ⁱ...C7 = 3.518 (4) Å; symmetry code as in Table 1]. Another possible consequence of these contacts is the fact that atom C6 lies slightly, but significantly, out of the plane of the Cp ring [0.266 (4) Å].

We have examined some basic conformational features of the title complex, searching in particular for energetically feasible conformations having different steric encumbrances around the Cl atoms, which are possible polymerization sites. The analysis was carried out using the *MOLDRAW* software (Ugliengo *et al.*, 1993) and taking into consideration only non-bonded interactions. The following conformational degrees of freedom were explored: (i) rotation of each Cp ring around the axis from Ti to the center of the Cp ring (ψ rotations); (ii) rotations around the C1—C6 and C1ⁱ—C6ⁱ bonds (χ rotations).

Starting from the pseudo-*trans* crystallographic conformation (C1—Cg1—Cg2—C1ⁱ = -178°), we performed ψ rotations and then, in some of the energy minima found, the χ angles were varied so as to minimize the non-bonded energy. In this way, several conformational minima were found, with energies comparable to or even lower than that calculated for the crystallographic conformation (but within a few kcal mol⁻¹), corresponding to pseudo-*gauche* and pseudo-*cis* arrangements of the Cp groups. Interconversion between these conformations is always possible through the basic conformational degrees of freedom of the molecule (the torsion angles around the C6—C9 and C6ⁱ—C9ⁱ bonds in addition to the ψ and χ rotations). As an example, the two pseudo-*cis* conformers shown in Figs. 2 and 3 are characterized, respectively, by a low and a high steric encumbrance around the Cl atoms. Conformer *A* (Fig. 2) has a lower energy than the crystallographic conformer, while conformer *B* (Fig. 3) has a higher energy, probably because in *A* there is less

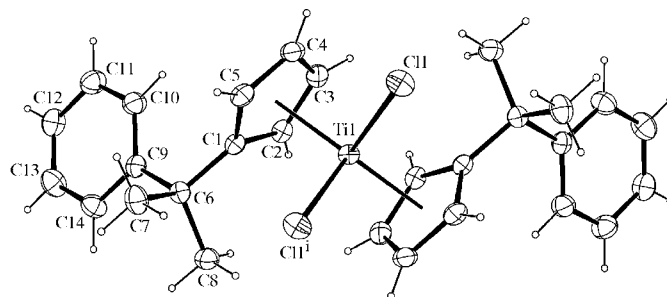


Figure 1

An *ORTEP*-3 (Farrugia, 1997) view of the molecular structure of [Ti(cCp)₂Cl₂]. Displacement ellipsoids are drawn at the 30% probability level.

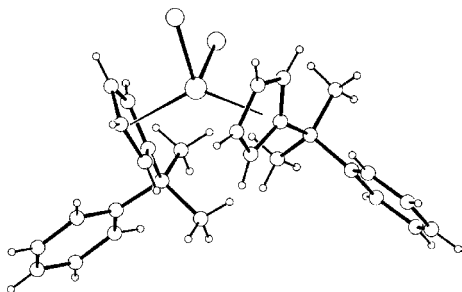


Figure 2
A model of the calculated *A* conformer of [Ti(cCp)₂Cl₂].

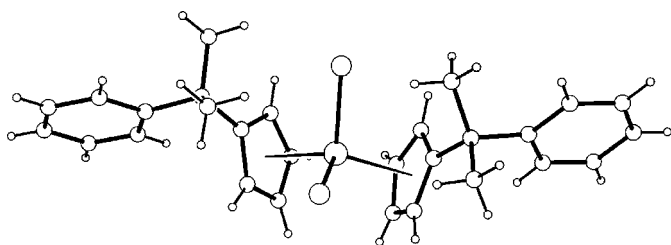


Figure 3
A model of the calculated *B* conformer of [Ti(cCp)₂Cl₂].

steric encumbrance around the Cl atoms, the two *gem*-methyl groups being oriented away from the Cl atoms. Clearly, in solution, a continuous interconversion between these (and other) conformers can be expected.

Experimental

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over sodium benzophenone (benzene) or calcium hydride (diethyl ether and dichloromethane). 6,6-Dimethylfulvene was synthesized according to the method of Stone & Little (1984). Compound (I) was synthesized in two steps: (i) 6,6-dimethylfulvene (36.8×10^{-3} mol) was added to a solution of phenyllithium (36.8×10^{-3} mol) in diethyl ether (25 ml) pre-cooled to 195 K, and the mixture was left overnight to reach room temperature. The resulting precipitate [PhC(CH₃)₂CpLi] was filtered off and dried under vacuum to give a white solid (yield 6 g, 85.7%). ¹H NMR (400 MHz, 298 K, THF-*d*₈): δ 1.61 (*s*, 6H, CH₃), 5.57 (*s*, 4H, Cp), 6.94 (*t*, *J*_{HH} = 7.4 Hz, 1H, *p*-Ph), 7.08 (*t*, *J*_{HH} = 7.4 Hz, 2H, *m*-Ph), 7.30 (*m*, 2H, *o*-Ph). (ii) A benzene solution (45 ml) of TiCl₄ (6×10^{-3} mol) was added to a suspension of PhC(CH₃)₂CpLi (13.1×10^{-3} mol) in benzene (100 ml) at room temperature. The reaction mixture was stirred overnight at 353 K and filtered through celite. The filtrate was concentrated until precipitation of a red material took place. The precipitate was filtered off and dried under vacuum, and after slow crystallization from CH₂Cl₂ afforded dark red needles. ¹H NMR (400 MHz, 298 K, CD₂Cl₂): δ 1.77 (*s*, 6H, CH₃), 6.15 (*t*, *J*_{HH} = 2.5 Hz, 2H, Cp), 6.47 (*t*, *J*_{HH} = 2.5 Hz, 2H, Cp), 7.15–7.27 (unresolved multiplet, 5H, Ph). The molecular structure of this product was identified by comparison of the ¹H NMR spectrum with that of cCpTiCl₃ (Sassmannshausen *et al.*, 1999) (the same patterns and different chemical shifts). Crystals of [Ti(cCp)₂Cl₂] suitable for structure determination were obtained by slow crystallization from dichloromethane solution at room temperature. The selected crystal was sealed in a Lindemann capillary under an inert atmosphere (N₂).

Crystal data

[Ti(C₁₄H₁₅)₂Cl₂]
M_r = 485.29
Monoclinic, *C2/c*
a = 18.816 (5) Å
b = 6.645 (3) Å
c = 19.12 (2) Å
β = 101.77 (3)°
V = 2340 (3) Å³
Z = 4

D_x = 1.378 Mg m⁻³
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 13.9–14.8°
μ = 0.61 mm⁻¹
T = 298 K
Prism, red
0.50 × 0.20 × 0.13 mm

Data collection

Nonius MACH3 diffractometer
Non-profiled *ω* scans
Absorption correction: *ψ* scan
(North *et al.*, 1968).
*T*_{min} = 0.859, *T*_{max} = 0.923
2877 measured reflections
2792 independent reflections
2233 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.045
*θ*_{max} = 27.9°
h = -24 → 24
k = 0 → 8
l = 0 → 25
1 standard reflection
frequency: 120 min
intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.046
wR(*F*²) = 0.128
S = 1.07
2792 reflections
170 parameters
H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F*_o²) + (0.0819*P*)² + 0.4482*P*]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/*σ*)_{max} < 0.001
Δ*ρ*_{max} = 0.61 e Å⁻³
Δ*ρ*_{min} = -0.78 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1–C2	1.408 (3)	C3–C4	1.401 (4)
C1–C5	1.419 (3)	C3–Ti1	2.325 (3)
C1–Ti1	2.495 (3)	C4–C5	1.404 (3)
C2–C3	1.409 (3)	C4–Ti1	2.388 (3)
C2–Ti1	2.386 (2)	C5–Ti1	2.452 (3)
C7–C6–C8	109.5 (2)	C11 ¹ –Ti1–C11	91.96 (5)
C6–C1–C5–C4	-167.0 (2)	C1–C6–C9–C14	163.7 (2)
C2–C1–C6–C8	54.1 (3)		

Symmetry code: (i) -*x*, *y*, $\frac{1}{2}$ - *z*.

Reflections corresponding to lattice centering were not collected. Methyl H atoms were positioned geometrically and treated as riding on their parent atoms (C–H = 0.96 Å). All other H atoms were located in difference maps and their coordinates were refined. For all H atoms, *U*_{iso}(H) was set at *U*_{eq}(carrier atom).

Data collection: *MACH3 Software* (Enraf–Nonius, 1996); cell refinement: *CELLFIT* (Centore, 2002); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON92* (Spek, 1992); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1100). Services for accessing these data are described at the back of the journal.

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