

## Synthesis and Ring Inversion of the First Ditellurolene Chelate, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{Te}_2\text{C}_6\text{H}_4)]$

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$[(\text{cp})_2\text{Ti}(\text{Te}_2\text{C}_6\text{H}_4)]$  (**1**) (cp =  $\eta^5\text{-C}_5\text{H}_5$ ) was obtained from (i)  $[(\text{cp})_2\text{TiCl}_2]$  and  $o\text{-(LiTe)}_2\text{C}_6\text{H}_4$ , or (ii)  $[(\text{cp})_2\text{TiPh}_2]$  and Te, and was shown by temperature-dependent  $^1\text{H}$  n.m.r. spectroscopy to exist in toluene solution in an envelope conformation, the five-membered  $\text{TiTe}_2\text{C}_2$  chelate ring undergoing rapid inversion at room temperature.

Titanocene metallacycles containing *O,O*-,<sup>1</sup> *S,S*-,<sup>2,3</sup> and *Se,Se*-co-ordinated<sup>4,5</sup> benzene-1,2-diolato, -dithiolato, or -diselenolato chelate ligands have been synthesized. Their structures in the solid state and in solution have been determined by *X*-ray structure analysis<sup>6</sup> and by temperature-dependent  $^1\text{H}$  n.m.r. spectroscopy.<sup>3,5,7</sup> We now report on the synthesis and spectroscopic characterization of titanocene-

benzene-1,2-ditellurolate (**1**), the first example of a tellurium analogue of the dithiolene chelates.

The reaction of titanocene dichloride  $[(\text{cp})_2\text{TiCl}_2]$  with dilithium benzene-1,2-ditellurolate<sup>8</sup> in tetrahydrofuran (THF) at  $-78^\circ\text{C}$  afforded the metallacycle (**1**) as a dark-green solid which is sensitive towards air and moisture (Scheme 1). With exclusion of air, moisture, and light and under an argon

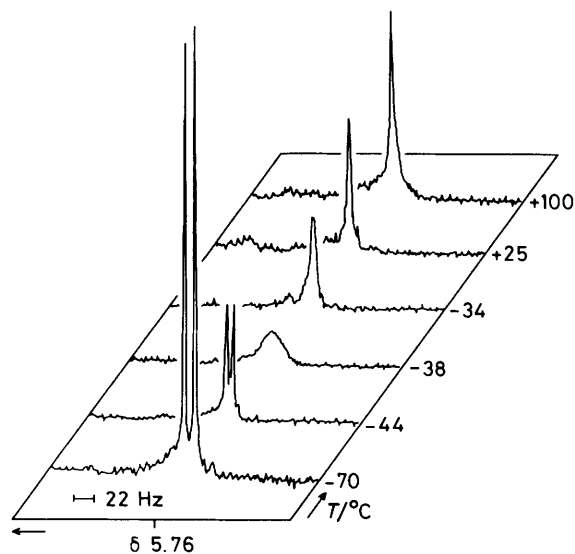
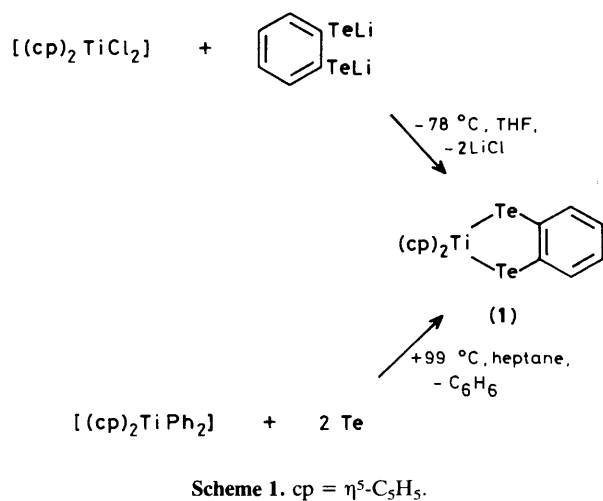


Figure 1. Temperature-dependent  $^1\text{H}$  n.m.r. spectrum (cp region) of (1) in  $\text{CD}_3\text{C}_6\text{D}_5$ .

atmosphere,  $o\text{-(LiTe)}_2\text{C}_6\text{H}_4$  (8.00 mmol) was stirred for 2 h at  $-78^\circ\text{C}$  with  $[(\text{cp})_2\text{TiCl}_2]$  (8.00 mmol) in dry THF (150 ml). After warming to  $20^\circ\text{C}$  during 15 h, the deep-green solution was filtered and evaporated *in vacuo* to dryness. The residue was recrystallized from dry toluene to yield compound (1) (54.7%) [satisfactory elemental analyses were obtained; i.r. (KBr):  $\omega$  (CC, cp) 1440,  $\delta$  (CH, cp) 1018,  $\gamma$  (CH, cp) 812,  $\gamma$  (CH,  $o\text{-C}_6\text{H}_4$ ) 735  $\text{cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{CD}_3\text{C}_6\text{D}_5$ ):  $\delta$  8.28–6.88 (m, 4 H,  $o\text{-C}_6\text{H}_4$ ), and 5.76 (s, 10 H, cp)].

Another route (Scheme 1), starting from diphenyltitanocene and elemental tellurium, also led to the ditelluroene chelate (1).  $[(\text{cp})_2\text{TiPh}_2]$  (1.96 mmol) was refluxed for 12 days at  $99^\circ\text{C}$  with Te (4.23 mmol) in dry heptane (200 ml). After evaporation *in vacuo* to dryness the residue was extracted with dry benzene and the deep-green solution was evaporated to dryness again. The remaining solid was recrystallized from dry toluene and gave a 54% yield of (1), with analytical and spectroscopic results in agreement with the data given above.

Complex (1) is thermally relatively stable, but decomposes without melting above  $180^\circ\text{C}$ . In the mass spectrum [ $m/z$

Table 1.  $^1\text{H}$  N.m.r. data<sup>a</sup> and activation parameters of  $[(\text{cp})_2\text{Ti}(\text{X}_2\text{C}_6\text{H}_4)]$ , X = Te (1), Se (2), and S (3).

	$\delta$ (cp)	$T_c/^\circ\text{C}$	$\Delta\nu/\text{Hz}$	$\Delta G_c^\ddagger/\text{kJ/mol}$
(1)	5.76	-38	10.0	51
(2)	5.58	-9	13.5	57
(3)	5.55	-20	25.0	53

<sup>a</sup> Solvent:  $\text{CD}_3\text{C}_6\text{D}_5$ ; internal standard:  $\delta$  ( $\text{C}_6\text{D}_5\text{CD}_2\text{H}$ ) = 2.09.

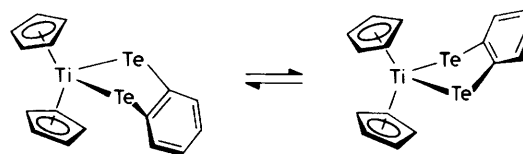


Figure 2. Chelate ring inversion of (1).

(electron impact, 70 eV,  $205^\circ\text{C}$ ): 514 (72%)  $M^+$ , 449 (5)  $M^+$  - cp, 384 (4)  $M^+$  - Te, 319 (7)  $M^+$  - Te - cp, 284 (5)  $\text{Te}_2\text{C}_2^+$ , 254 (15)  $(M^+ - \text{Te}) - \text{Te}$ , 189 (27)  $(M^+ - \text{cp}) - \text{Te}_2$ , and 178 (100%)  $M^+ - \text{Te}_2\text{C}_6\text{H}_4$ ; values given relate to  $^{48}\text{Ti}$ ,  $^{130}\text{Te}$ ; ion genesis was proved by metastable transitions (linked scan) for  $m/z$ : 449, 384, 319, 254, 189, and 178] (1) shows an intense peak due to the molecular ion and, analogous to the corresponding selenium derivative (2)<sup>4,5</sup> reveals a similar fragmentation pattern, the cleavage of the Ti-Te bond being preferred.

The singlet due to the cp protons which appeared in the room temperature  $^1\text{H}$  n.m.r. spectrum of (1) was subject to a coalescence phenomenon at lower temperatures and, below  $-40^\circ\text{C}$ , was split into two signals of equal intensity (Figure 1). From this result, an envelope conformation of the metallocycle folded along the  $\text{Te} \cdots \text{Te}$  axis in solution can be deduced (Figure 2). Whereas at room temperature rapid ring inversion takes place, 'freezing' of the chelate ring in the fixed envelope conformation with different surroundings for the two cp ligands of each molecule appears at low temperature (Figure 2).

The activation parameters of the chelate ring inversion of (1) and the analogous selenium and sulphur compounds (2) and (3) are summarized in Table 1. Surprisingly,  $\Delta G_c^\ddagger$  values virtually do not differ in the series of titanocene dichalcogenolene chelates  $[(\text{cp})_2\text{Ti}(\text{X}_2\text{C}_6\text{H}_4)]$  with X = Te (1), Se (2), and S (3).

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## References

- K. Andrä, *J. Organomet. Chem.*, 1968, **11**, 567.
- H. Köpf and M. Schmidt, *J. Organomet. Chem.*, 1965, **4**, 426.
- H. Köpf and Th. Klapötke, *Z. Naturforsch., Teil B*, 1986, **41**, 667.
- B. Gautheron, G. Tainturier, S. Pouly, F. Théobald, H. Vivier, and A. Laarif, *Organometallics*, 1984, **3**, 1495.
- H. Köpf and Th. Klapötke, *J. Organomet. Chem.*, in the press.
- A. Kutoglu, *Z. Anorg. Allg. Chem.*, 1972, **390**, 195.
- H. Köpf, *Angew. Chem.*, 1971, **83**, 146.
- K. Lerstrup, M. Lee, F. M. Wiygul, T. J. Kistenmacher, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 1983, 294.