COMMUNICATION

SYNTHESIS AND RING INVERSION OF THE FIRST HAFNOCENE DITELLUROLENE CHELATE: $[(\eta^5-C_5H_5)_2Hf(1,2-Te_2C_6H_4)]$

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Abstract—[(cp)₂Hf(1,2-Te₂C₆H₄)] (1) (cp = η^5 -C₅H₅) was obtained from [(cp)₂HfCl₂] and equivalent amounts of 1,2-(LiTe)₂C₆H₄ as the first hafnocene ditellurolene metallacycle and the last missing member of the widely investigated subgroup IV metallocene dichalcogenolene chelate complexes of the type [(cp)₂M(1,2-X₂C₆H₄)] (M = Ti, Zr, Hf; X = S, Se, Te). Hafnocene benzene-1,2-ditellurolate (1) was shown by temperature-dependent ¹H NMR spectroscopy to exist in toluene solution in an envelope conformation, the five-membered HfTe₂C₂ chelate ring undergoing rapid inversion at room temperature.

Metallocene heterocycles of subgroup IV with S,S⁻¹⁻⁶ and Se,Se-coordinated⁷⁻⁸ benzene-1,2-dichalcogenolato chelate ligands have been synthesized. Recently there were reports about the preparation of the analogous tellurium derivatives of the titanocene⁹ and zirconocene¹⁰ systems using different reaction routes and that no metallacycle could be obtained analogous to the synthesis of the Zr complex when the metal was Hf.¹⁰ We now report on the synthesis and spectroscopic characterization of hafnocene benzene-1,2-ditellurolate (1), the first example of a Te containing hafnocene metallacycle and the last missing member of the metallocene ditellurolene chelates of subgroup IV.

The reaction in an argon atmosphere and exclusion of air and moisture of hafnocene dichloride $[(cp)_2HfCl_2]^{11}$ (5.14 mmol) with 1,2-(LiTe)₂C₆H₄¹² (5.19 mmol) in 200 cm³ tetrahydrofurane (thf)/ether (1:1) at -78°C afforded the desired hafnocene ditellurolene metallacycle (1) as a deep red solid, sensitive towards air and moisture (Scheme 1). The product was recrystallized from dry toluene and gave 1 in 37% yield with satisfactory elemental analysis and spectroscopic

results in agreement with the expected theoretical values: IR (KBr) \tilde{v} : v (CH, cp) 3105, ω (CC, cp) 1435, δ (CH, cp) 1010, γ (CH, cp) 800, γ (CH, 1,2-C₆H₄) 720 cm⁻¹; ¹H NMR (toluene-d₈): 8.30–6.75 (m, 4H, 1,2-C₆H₄), and 5.74 (s, 10H, cp) ppm; MS (EI, 70 eV, 180°C) *m/z*: 640 (46%) M⁺, 564 (20) M⁺-C₆H₄, 512 (25) M⁺-Te, 436 (19) M⁺-C₆H₄-Te, 384 (60) M⁺-2 Te, 308 (100) M⁺-Te₂C₆H₄, 243 (11) M⁺-Te₂C₆H₄-cp, 178



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Scheme 1. Preparation and reaction behavior of 1, $cp = \eta^{5} - C_{5}H_{5}$.

М	х	δ (cp) (ppm)	<i>T_c</i> (°C)	Δν (Hz)	$\Delta G_c^+ $ (kJ mol ⁻¹)	Ref.
Ti	Te	5.76	- 38	10.0	51	9
Zr	Te	5.96 ^b	- 30	20.9	51	10
Hf	Te	5.74	50	9.4	48	present work
Hf	Se	5.46	-75	_		8
Hf	S	5.46	-64	20.0	45	6

Table 1. ¹H NMR data^{*a*} and activation parameters of $[(cp)_2M(1,2-X_2C_6H_4)]$

^{*a*} Solvent : $CD_3C_6D_5$; ^{*b*} cp = $\eta^{5-t}BuC_5H_4$.

(28) Hf⁺; (values given relate to 178 Hf and 128 Te); Fp: 225°C, decomposition. 1 reacts with halides such as bromine, dissolved in thf, or hydrogen halides as with hydrogen chloride saturated benzene yielding the corresponding hafnocene dihalides (Scheme 1).

In the dynamic ¹H NMR spectrum the singlet due to the ten equivalent cp protons at room temperature was subject to a coalescence phenomenon at a lower temperature and was split into two sharp singlets of equal intensity at temperatures below -50° C (Fig. 1). From this result an envelope conformation of the five-membered chelate ring, folded along the Te---Te axis and undergoing rapid inversion at room temperature, can be derived (Fig. 2). The activation parameters of the chelate ring inversion of 1 and the analogous titanocene and zir-



Fig. 1. Temperature-dependent ¹H NMR spectrum (cp region) of 1 in CD₃C₆D₅, δ in ppm, T in °C.



Fig. 2. Chelate ring inversion of 1.

conocene derivatives as well as those of the S or Se coordinated hafnocene complexes are given in Table 1. With regard to an estimation of the error of these ΔG_c^+ values ($\pm 13\%$) surprisingly there is no significant connection between this activation parameter and the central atom or the coordinating chalcogen atom.

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