233

1,3-Ditellura[3]ferrocenophanes, Fe(C₅H₄Te)₂E (E = S, Se, Te, or CH₂)

1,3-Ditellura[3]ferrocenophanes, $Fe(C_5H_4Te)_2E$ (E = S, Se, Te, or CH_2)

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Abstract

Dilithium 1,1′-ferroceneditellurolate, $Fe(C_5H_4TeLi)_2$, has been used to prepare a series of 1,3-ditellura[3]ferrocenophanes, $Fe(C_5H_4Te)_2E$ (E = S, Se, Te, CH_2), which have been characterized by ^1H NMR and mass spectroscopy.

Introduction

Following the initial report on 1,2,3-trithia[3]ferrocenophane, $Fe(C_5H_4)_2S_3$, by Davison and Smart [1] in 1969, several papers on trichalcogena[3]ferrocenophanes of the types **1** and **2** have appeared. In particular, 1,2,3-trithia[3]ferrocenophane (**1a**) [1–6] and 1,2,3-triselena[3]ferrocenophane (**2b**) [5–9] have been thoroughly investigated. However, 1,2,3-tritellura[3]ferrocenophane (**3c**) [10] was only recently synthesized and structurally characterized. Other tellura[3]ferrocenophanes of type **3**, containing tellurium directly bound to the cyclopentadienyl rings, have also been unknown up to now. This is due to the fact that dilithium 1,1′-ferroceneditellurolate, $Fe(C_5H_4TeLi)_2$ (**4**), was not available for syntheses so far, although the corresponding dilithio derivatives of 1,1′-ferrocene dithiol and diselenol, $Fe(C_5H_4ELi)_2 \cdot 2THF$ (E = S, Se), are available in the form of their solid THF adducts [9] and can be easily handled under an inert gas.
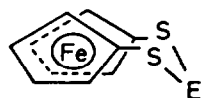
Fe(C₅H₄S)₂E (**1**)
1a: E = S   [1–6,11]
1b: E = Se   [5–9]
1c: E = Te   [5–8]
1d: E = CH₂ [9,11,12]
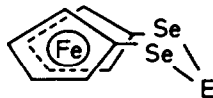
Fe(C₅H₄Se)₂E (**2**)
2a: E = S   [5–8]
2b: E = Se   [5–9]
2c: E = Te   [5,6,8]
2d: E = CH₂ [6,9,13]

Fe(C₅H₄Te)₂E (**3**)
3a: E = S
3b: E = Se
3c: E = Te   [10]
3d: E = CH₂

The present paper describes the preparation and characterization of the new 1,3-ditellura[3]ferrocenophanes **3a–d**. The accompanying paper summarizes the results of dynamic NMR studies which were carried out with **3a–c** at the University of Exeter in order to determine the barriers of the trichalcogena bridge reversal motion [14].

Results and discussion

The dilithium 1,1′-ferroceneditellurolate $Fe(C_5H_4TeLi)_2$ (**4**) is generated when a cooled THF solution of dilithioferrocene, "$Fe(C_5H_4Li)_2 \cdot (TMEDA)$" * [2], is allowed to warm slowly to room temperature in the presence of the stoichiometric amount of tellurium powder [10,15]. The dark-red solution of **4** can be used directly for further reactions at room temperature.
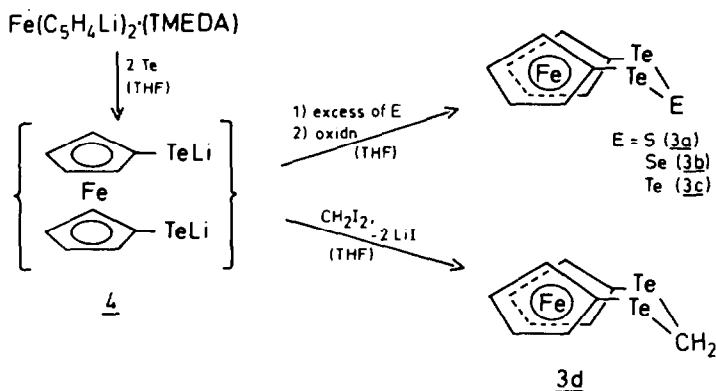
The 1,3-ditellura[3]ferrocenophanes **3a–c** were obtained by stirring THF solutions of **4** in air in the presence of an excess of the chalcogen E (= S, Se, Te). In line with observations reported by Köllemann et al. [16], it can be assumed that the additional chalcogen E is initially inserted into the Te–Li bonds. Reaction of intermediate **4** with diiodomethane gave 1,3-ditellura[3]ferrocenophane (**3d**), in addition to **3c**.

The [3]ferrocenophanes **3a–c** are only sparingly soluble in common organic solvents such as toluene, diethyl ether, tetrahydrofuran, dichloromethane and chloroform; the saturated solutions (ca 10^{-3} molar) are intensely coloured. The compounds are air-stable in the solid state; **3c** forms thin needles with a metallic lustre [10].

The ^1H NMR spectra of **3a–c** are temperature dependent owing to the restricted trichalcogena bridge inversion process, which is slowed down at low temperatures [14]. Below $-30°C$ the limiting low-temperature spectrum is observed and this corresponds to the static structure with four different protons ($[ABCD]_2$ spin system); the cyclopentadienyl rings are eclipsed as in the solid state structure (cf.

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* Abbreviations: Cp = cyclopentadienyl, η^5-C_5H_5; Fc = ferrocenyl, η^1 = $CpFe(C_5H_4)$-; ^nBu = n-butyl, $^nC_4H_9$; TMEDA = tetramethylethylenediamine.

Table 1

^{1}H NMR spectra of Fe(C$_5$H$_4$Te)$_2$E (3a–d) [a]

Compound	Low temperature (−50°C) [b]				High temperature (+50°C) [c]	
	H^2	H^3	H^4	H^5	H^2/H^5	H^3/H^4
3a (E = S)	4.52	4.38	4.56	3.90	4.22	4.42
3b (E = Se)	4.49	4.36	4.50	3.89	4.20	4.40
3c (E = Te)	4.41	4.33	4.41	3.97	4.20	4.33
3d (E = CH$_2$) [d]					4.15 [e]	4.37 [e]

[a] CDCl$_3$ Solutions, δ values (ppm). [b] Broadened signals (Bruker AC 300). [c] Virtual triplets with coupling constants $\sum(^3J(H, H) + ^4J(H, H)) = 3.5$ Hz. [d] Measured at 0°C, δ(CH$_2$) = 3.71(s) ppm. [e] Coupling constants, $\sum(^3J(H, H) + ^4H(H, H)) = 3.6$ Hz.

ref. 10). Table 1 lists the chemical shifts measured at −50 and +50°C, with the assignments made on the basis of the ^{1}H NMR study [14]. The high-temperature limiting spectrum at 50°C consists of two pseudo-triplets ([[AB]$_2$]$_2$ spin system), indicating a rapid bridge inversion process. In the case of the methylene complex, Fe(C$_5$H$_4$Te)$_2$(CH$_2$) (3d), the high-temperature limiting situation is reached even at −60°C.
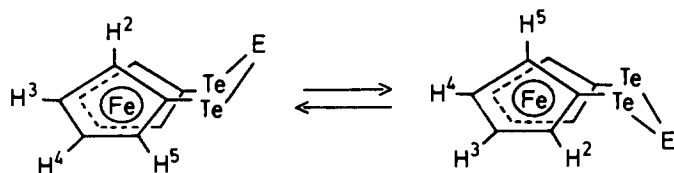
From the dynamic ^{1}H NMR studies [14], the free activation energies, $\delta G^\ddagger$(298 K), were found to decrease in the order 3a (56.3 kJ mol^{-1}) > 3b (55.4 kJ mol^{-1}) > 3c (51.8 kJ mol^{-1}). The corresponding barrier for 3d must be much smaller. The same trend had been observed for the free activation energies for the series 1a > 1b > 1c and 2a > 2b > 2c [5], and the barrier for the methylene derivative 1d is smaller than that for the 1,3-dithia-2-chalcogena[3]ferrocenophanes 1a–c [12]. The mechanism of the bridge inversion process is shown to involve a transition state with staggered cyclopentadienyl rings [14].

Table 2

^{13}C NMR spectra [a] of 1,3-dichalcogena[3]ferrocenophanes (1d–3d) and bis(ferrocenylchalcogeno)-methanes [17]
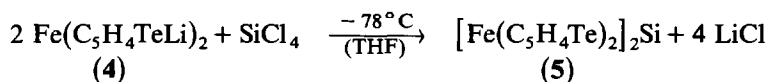
Compound	C^1	C^2/C^3	C^3/C^4	CH$_2$	Cp
Fe(C$_5$H$_4$S)$_2$(CH$_2$) (1d) [b]	82.4	73.3	70.6	52.7	
Fe(C$_5$H$_4$Se)$_2$(CH$_2$) (2d) [b]	70.7	74.5	70.4	33.8	
Fe(C$_5$H$_4$Te)$_2$(CH$_2$) (3d)	59.9	78.3	71.1	−25.2	
FcS(CH$_2$)SFc [17]	78.6	73.8	69.1	46.3	69.3
FcSe(CH$_2$)SeFc [17]	71.3	75.1	69.7	24.0	69.2
FcTe(CH$_2$)TeFc [17]	47.2	79.2	71.3	−35.1	68.9

[a] CDCl$_3$ Solutions, δ values (ppm). [b] The data agree well with the literature values given for 1d [18] and 2d [13].

Table 2 summarizes the ^{13}C NMR data for the 1,3-dichalcogena[3]ferrocenophanes **1d–3d** that contain a methylene group between the chalcogen atoms and are more soluble than **3a–c**. As in earlier studies [15,17], the heavy metal effect can be used to assign the three signals of the ferrocenylene unit unequivocally to C^1, C^2/C^5 and C^3/C^4. The shielding of the methylene carbon (CH_2) increases markedly if the two adjacent chalcogen atoms are changed from sulfur to selenium to tellurium. The same effect is observed in bis(ferrocenylchalcogeno)methanes, $FcE(CH_2)EFc$ (E = S, Se, Te) [17].

In the electron-impact mass spectra of **3a–c** the molecular ion is observed with the expected isotope pattern. Stepwise loss of three chalcogens leads to the ferrocenylene ion $Fe(C_{10}H_8)^+$ (m/e 184). In the case of the 2-thia[3]ferrocenophanes **2a** and **3a**, the molecular ion of **1a** is also observed, together with the corresponding fragments. Apparently the stable and more volatile 1,2,3-trithia[3]ferrocenophane (**1a**) is formed in the ion source of the mass spectrometer.

The stepwise loss of tellurium is similarly observed for the EI fragmentation of the spiro compound **5**, which is obtained from silicon tetrachloride:

$$2\,Fe(C_5H_4TeLi)_2 + SiCl_4 \xrightarrow[\text{(THF)}]{-78\,^\circ C} [Fe(C_5H_4Te)_2]_2Si + 4\,LiCl$$
$$\text{(4)} \qquad\qquad\qquad\qquad\qquad \text{(5)}$$

The mass spectrum of **5** showed the molecular ion with the expected tellurium-deficient fragments, and also indicated the formation of both $Fe(C_5H_4Te)_2Te$ (**3c**) and $[Fe(C_5H_4)_2]_2Si$ [19,20].

Experimental

All reactions were carried out under N_2 in dry, N_2-saturated solvents. The TMEDA-stabilised 1,1'-dilithioferrocene, "$Fe(C_5H_4Li)_2 \cdot (TMEDA)$", was obtained by the standard method [2]. The stoichiometric insertion of tellurium into the carbon–lithium bonds to give $Fe(C_5H_4TeLi)_2$ (**4**) was conducted at low temperatures (-50 to $25\,^\circ C$) in THF as solvent, as described before [10,15]. It is possible to use the filtered THF solution of **4** directly. Solvent-free **4** was obtained by removing the THF under vacuum, washing the THF-containing initial product repeatedly with diethyl ether and toluene, and finally freeze-drying the toluene solutions. It is a red-brown, pyrophoric powder (yield ca 90%).

1,3-Ditellura-2-chalcogena[3]ferrocenophanes, $Fe(C_5H_4Te)_2E$ (3a–c)

An excess of the chalcogen E (= S, Se, Te; ca 2–3 mmol) was added to a dark-red solution containing 0.30 g (0.66 mmol) $Fe(C_5H_4TeLi)_2$ (**4**) in 200 ml THF. The mixture was stirred for 0.5 h under N_2, then for 1 h under air. The solvent was removed and the residue extracted several times with toluene. The combined toluene solutions were concentrated and cooled to $-25\,^\circ C$ to allow crystallization.

$Fe(C_5H_4Te)_2S$ (3a): Red-brown crystals, m.p. 186–188$\,^\circ C$ (dec.). Yield 0.18 g (57%). Anal. Found: C, 26.30; H, 1.86; S, 6.63; Te, 50.6; mol. mass 476 by mass spectrometry, ref. to ^{130}Te. $C_{10}H_8FeSTe_2$ (471.27) calc.: C, 25.48; H, 1.71; S, 6.80; Te, 54.15%.

$Fe(C_5H_4Te)_2Se$ (3b): Dark-brown needles, m.p. 190–192$\,^\circ C$ (dec.). Yield 0.23 g (66%). Anal. Found: C, 22.63; H, 1.64; Fe, 10.33; Te, 47.3; mol. mass 524 by mass

spectrometry, ref. to ^{80}Se and ^{130}Te. $C_{10}H_8FeSeTe_2$ (578.7) calc.: C, 23.18; H, 1.56; Fe, 10.58; Te, 49.25%.

Fe(C$_5$H$_4$Te)$_2$Te (3c) [10]: Lustrous needles, dec. > 140 °C. Yield 0.05 g (13.2%). Anal. Found: C, 21.66; H, 1,51; Te, 65.4, mol. mass 574 by mass spectrometry, ref. to ^{130}Te. $C_{10}H_8FeTe_3$ (566.81) calc.: C, 21.19, H, 1.42; Te, 67.54%.

1,3-Ditellura[3]ferrocenophane, Fe(C$_5$H$_4$Te)$_2$(CH$_2$) (3d)

A THF solution (200 ml) containing 0.30 g (0.66 mmol) 4 was slowly treated with 0.053 ml (0.66 mmol) CH_2I_2 at −78 °C. The solution was brought to room temperature, the solvent THF removed under vacuum, and the residue taken up in toluene. Crystallization gave 0.04 g (13%) golden-yellow needles of **3d**, m.p. 128–130 °C (dec.). Anal. Found: mol. mass 458 by mass spectrometry, ref. to ^{130}Te. $C_{11}H_{10}FeTe_2$ (453.24).

Instrumentation

NMR spectra: Jeol FX 90Q (^{1}H NMR) and Bruker AC 300 (^{13}C and ^{1}H at −50 °C). Mass spectra: Varian MAT CH7 (ionization energy 70 eV). Elemental analyses: Mikroanalytisches Labor Pascher, Remagen.

Acknowledgement

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