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# Synthesis and characterization of some ferrocene-containing telluroether ligands: crystal structure of 1,1'-bis(phenyltelluro)ferrocene

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## Abstract

A series of five monodentate ferrocene tellurium ligands of the type $Fe(C_5H_5)(C_5H_4TeR)$ and five bidentate 1,1'-disubstituted ferrocene tellurium ligands of the type $Fe(C_5H_4TeR)_2$ (R = Me, $^n$Bu, $C_6H_5$, $p$-$MeOC_6H_4$, $p$-$EtOC_6H_4$) has been prepared by the reaction of 1,1'-dilithioferrocene with the appropriate ditellurides $R_2Te_2$. The ligands have been characterized by their elemental analyses, $^1H$ and $^{13}C$ NMR spectra, mass spectra and cyclic voltammetry studies. The structure of $Fe(C_5H_4TeC_6H_5)_2$ has been determined by single-crystal X-ray diffraction study.

*Key words:* Ferrocene; Telluroether; Crystal structure

## 1. Introduction

The ligand chemistry of tellurium has been the subject of considerable interest [1]. Symmetrical bidentate, hybrid bidentate and polydentate tellurium ligands have been studied [2-5]. We recently reported some novel hybrid ligands that contain both "hard" and "soft" donor atoms [6].

Despite the recently developing interest in the ligand chemistry of tellurium, ligands capable of forming potentially binuclear complexes are rare. The 1,1'-disubstituted ferrocene chelates are particularly attractive ligands since the Ni and Pd complexes of 1,1'-bis(diphenyphosphino)ferrocene (dppf) exhibit high catalytic activity for selective cross-coupling reactions [7]. The analogous Rh complexes of the ligand are reported to be highly selective hydroformylation catalysts [8]. These ligands also provide redox-active centres that would be sensitive to the presence of (i) the Lewis acids and (ii) the donor atom. The S [9] and Se [10] analogues of dppf have been reported, and the dynamic structural properties of the metal complexes have been extensively studied in recent years [11]. Although Herberhold and coworkers [12] have reported the synthesis of several tellurium-containing ferrocene derivatives, 1,1'-disubstituted organometallic ligands of the type $Fe(C_5H_4TeR)_2$ are unknown.

We describe below the preparation and characterization of a series of mono- and disubstituted ferrocene tellurium ligands. The crystal structure determination of $Fe(C_5H_4TePh)_2$ is described, and compared with those of other related species.

## 2. Experimental details

### 2.1. General comments

Reactions were carried out by use of standard Schlenk techniques under argon. Solvents were dried, freshly distilled from the drying agent and finally deoxygenated by bubbling a stream of argon through them for at least 15 min before use. The starting

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materials were prepared by the published methods: dimethylditelluride [13], dibutylditelluride [14], diphenylditelluride [15], bis(methoxyphenyl)ditelluride [16] and bis(ethoxyphenyl)ditelluride [16]. Ferrocene, TMEDA and $^{n}$BuLi of reagent-grade quality (E. Merck) were used in the synthesis.

All melting points were determined on a Ketan melting-point apparatus and are uncorrected. Elemental analysis was performed on a Carlo Erba model 1106 elemental analyser. $^{1}$H and $^{13}$C NMR data were recorded on a Varian 300 MHz instrument in $CDCl_3$ with chemical shifts reported in parts per million from tetramethylsilane as internal standard. Mass spectra were determined with a Kratos MS-30 mass spectrometer.

For cyclic voltammetry experiments a Bio-Analytical Systems (BAS) model CV-1B electrochemical analyser was used in a standard three-electrode configuration (a platinum bead working electrode, a platinum wire counterelectrode and an Ag/AgCl reference electrode). All measurements were made with 0.1 M $^{n}Bu_4N^+ClO_4^-$ in $CH_2Cl_2$ as supporting electrolyte and the compound concentration was $5 \times 10^{-4}$ M in $CH_2Cl_2$.

### 2.2. Synthesis

All the compounds were prepared in the same general way and a representative example is outlined below.

### 2.3. Synthesis of 1,1′-bis(phenyltelluro)ferrocene (8) and phenyltelluroferrocene (3)

Ferrocene (0.114 g, 0.61 mmol) was added at room temperature to a solution of 1.6 M $^{n}$BuLi in hexane (0.76 ml, 1.22 mmol) and TMEDA (0.18 mL, 1.22 mmol) in deoxygenated hexane (80 ml). The mixture was stirred for 3 h. The resulting bright orange solution was cooled to −10°C, and a solution of diphenyl ditelluride (0.5 g, 1.22 mmol) in benzene (20 ml) was added dropwise. The mixture was stirred overnight, it was then filtered, and the filtrate was evaporated to dryness. The residue was dissolved in a small amount of $CH_2Cl_2$ and the solution transferred to the top of a silica gel column. Elution with petroleum ether (boiling point, 60–80°C) gave unchanged ferrocene and diphenylditelluride. Further elution with a petroleum ether–ethylacetate mixture (90:10) followed by elution with petroleum ether–ethylacetate mixture (90:20) afforded the compounds **8** and **3** respectively. The crude products were recrystallized from the same solvent mixtures as were used for elution.

### 2.4. Crystal structure determination

An orange prismatic crystal of **8** having approximate dimensions 0.30 mm × 0.15 mm × 0.45 mm was mounted on a glass fibre. Reflections were measured on a Rigaku AFC 6 S diffractometer with graphite-monochromated Mo Kα radiation and a 12 kW rotating-anode generator. The crystal data and numerical details of the data collection and refinement are given in Table 1. The final positional parameters are given in Table 2.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 21 carefully centered reflections in the range $36.5° < 2\theta < 39.3°$, corresponded to a monoclinic cell. Of the 3923 reflections collected, 3791 were unique ($R_{int} = 0.109$). The intensities of three representative reflections measured after every 150 reflections remained constant throughout data collection, indicating crystal stability.

The structure was solved by direct methods [17]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2137 observed reflections ($I > 3.00\sigma(I)$) and 299 variable parameters and converged (the largest parameter shift was 0.20 times its estimated standard deviation) with unweighted and weighted agreement factors of $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.036$ and $R_w = [\Sigma(w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2} = 0.042$ respectively.

Neutral atom scattering factors were taken from Cromer and Waber [18]. Anomalous dispersion effects were included in $F_c$ [19]; the values for $f'$ and $f''$ were those of Cromer [20]. All calculations were performed using the TEXSAN [21] crystallographic software package of molecular structure corporation, PLUTO [22] and ORTEP [23] packages.

## 3. Results and discussion

Herberhold and Leitner [12a] reported the first ferrocenyl compound containing a C–Te bond. The key step in the synthesis was the insertion of tellurium into ferrocenyllithium to give $Fe(C_5H_5)(C_5H_4TeLi)$, which upon air oxidation gave diferrocenyl ditelluride. In the present study, the monosubstituted and disubstituted ferrocene tellurium derivatives were prepared by a procedure similar to that used for the synthesis of S [9] and Se [10] analogues. 1,1′-Dilithioferrocene is obtained in over 90% yield by the reaction ferrocene with stoichiometric quantities of $^{n}$BuLi and TMEDA, and its reaction with suitable reagents usually leads to the isolation of 1,1′-disubstituted ferrocene derivatives.

However, in our hands the reaction of the dilithiated ferrocene with two molar properties of diorganyl ditellurides $R_2Te_2$ (R = Me, $^{n}$Bu, $C_6H_5$, $p$-MeO-$C_6H_4$ and $p$-Et$OC_6H_4$), gave a mixture of monosubstituted ferrocenyltellurides (**1**–**5**) and 1,1′-disubstituted tellurium derivatives (**6**–**10**) (Scheme 1 and Table 3).

TABLE 1. Experimental details

| | |
|---|---|
| *Crystal data* | |
| Empirical formula | $C_{22}H_{18}FeTe_2$ |
| Formula weight | 593.43 |
| Crystal color; habit | Orange, prism |
| Crystal dimensions | 0.30 mm × 0.15 mm × 0.45 mm |
| Crystal system | Monoclinic |
| Number of reflections used for unit-cell determination; $2\theta$ range | 21; 36.5–39.3° |
| $\omega$ scan peak width at half-height | 0.27 |
| Lattice parameters | |
| $a$ | 17.455(2) Å |
| $b$ | 6.135(1) Å |
| $c$ | 18.425(4) Å |
| $\beta$ | 97.51(1)° |
| $V$ | 1956(1) Å$^3$ |
| Space group | $P2_1/a$ (non-standard setting 14) |
| $Z$ value | 4 |
| $D_{calc}$ | 2.015 g cm$^{-3}$ |
| $F_{000}$ | 1120 |
| $\mu$(Mo K$\alpha$) | 37.05 cm$^{-1}$ |
| *Intensity measurements* | |
| Diffractometer | Rigaku AFC6S |
| Radiation | Mo K$\alpha$ ($\lambda$ = 0.71069 Å) |
| Temperature | 23°C |
| Take-off angle | 6.0° |
| Detector aperture | 6.0 mm horizontal, 6.0 mm vertical |
| Crystal-to-detector distance | 40 cm |
| Scan type | $\omega-2\theta$ |
| Scan rate | 8.0° min$^{-1}$ (in $\omega$) (2 rescans) |
| Scan width | $(1.26 + 0.30 \tan\theta)$° |
| $2\theta_{max}$ | 50.0° |
| Number of reflections measured | |
| Total | 3923 |
| Unique | 3791 ($R_{int}$ = 0.109) |
| Corrections | Lorentz polarization<br>Absorption (transmission factors, 0.68–1.00)<br>Secondary extinction (coefficient, 0.23508E × 10$^{-7}$) |
| *Structure solution and refinement* | |
| Structure solution | Direct methods |
| Refinement | Full-matrix least-squares method |
| Function minimized | $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ |
| Least-squares weights | $4F_o^2/\sigma^2(F_o^2)$ |
| $p$ factor | 0.03 |
| Anomalous dispersion | All non-hydrogen atoms |
| Number of observations ($I > 3.00\sigma(I)$) | 2137 |
| Number of variables | 299 |
| Reflection-to-parameter Ratio | 7.15 |
| Residuals | |
| $R$ | 0.036 |
| $R_w$ | 0.042 |
| Goodness-of-fit indicator | 1.40 |
| Maximum shift/error in final cycle | 0.20 |
| Maximum peak in final difference map | 0.69 e$^-$ Å$^{-3}$ |
| Minimum peak in final difference map | −0.53 e$^-$ Å$^{-3}$ |

Recently Butler *et al.* [24] reported that reaction of 1,1′-dilithioferrocene with an excess of 2,2′-bipyridine gives monosubstituted compounds together with the 1,1′-disubstituted derivatives. The ferrocenyltellurides **2** and **4** were made previously by a different route [12a].

The compounds are brightly colored crystalline solids except for **1**, **2**, **6** and **7**, which are viscous liquids. They are soluble in common organic solvents and are air stable in solution and the solid state.

The $^1$H NMR data for the ferrocenyl telluride derivatives are listed in Table 4. The spectra of the 1,1′-disubstituted derivatives consist of a two-"virtual-triplet" ($[AB]_2)_2$ spin system [12b], for the cyclopentadiene ring protons. The low field "virtual triplet" is assigned to the protons in the 3- and 4-positions of the ring, whereas the high field "virtual triplet" is assigned to the ring protons in the 2- and 5-positions. Compounds **1**–**5**, however, exhibit a singlet for the unsubstituted cyclopentadiyl protons in addition to the two "virtual triplets" for the substituted ring.

The $^{13}$C NMR data are listed in Table 5 together with tentative assignments made by reference to relevant previous reports [12,25,26].

In the EI mass spectra of **3**, **4**, **8** and **9** the molecular ion (**3**, $m/e$ 392 (M$^+$, 100%); **4** $m/e$ 422 (M$^+$, 100%);

TABLE 2. Positional parameters and $B_{eq}$ for bis(Phenyl-$n$-cyclopentadienyl-tellurium)iron

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Te(1) | 0.18511(3) | 0.6689(1) | 0.29808(3) | 3.60(3) |
| Te(2) | −0.19414(3) | 0.2662(1) | 0.22036(4) | 3.99(3) |
| Fe | −0.00016(6) | 0.4368(2) | 0.25150(6) | 2.68(5) |
| C(1A) | −0.1020(4) | 0.438(1) | 0.1835(4) | 2.8(3) |
| C(1B) | 0.0983(4) | 0.457(1) | 0.3233(4) | 3.0(4) |
| C(2A) | −0.0435(5) | 0.343(2) | 0.1483(5) | 3.7(4) |
| C(2B) | 0.0337(5) | 0.517(2) | 0.3584(4) | 3.4(4) |
| C(3B) | −0.0176(5) | 0.334(2) | 0.3534(5) | 3.7(4) |
| C(3A) | 0.0148(6) | 0.499(2) | 0.1448(5) | 4.3(5) |
| C(4B) | 0.0160(6) | 0.167(2) | 0.3185(6) | 4.6(5) |
| C(4A) | −0.0064(5) | 0.689(2) | 0.1796(5) | 3.9(4) |
| C(5A) | −0.0788(5) | 0.655(1) | 0.2028(5) | 3.5(4) |
| C(5B) | 0.0872(5) | 0.242(1) | 0.2973(5) | 3.6(4) |
| C(11A) | −0.2740(4) | 0.293(1) | 0.1238(4) | 3.2(4) |
| C(11B) | 0.2725(4) | 0.586(1) | 0.3861(4) | 2.9(4) |
| C(12A) | −0.3193(5) | 0.472(2) | 0.1110(5) | 4.6(5) |
| C(12B) | 0.2728(5) | 0.391(1) | 0.4216(5) | 3.5(4) |
| C(13A) | −0.3728(7) | 0.483(3) | 0.0481(7) | 6.8(7) |
| C(13B) | 0.3299(6) | 0.352(2) | 0.4788(5) | 4.3(5) |
| C(14B) | 0.3858(6) | 0.501(2) | 0.4982(5) | 4.5(5) |
| C(14A) | −0.3823(7) | 0.320(2) | −0.0018(6) | 6.4(6) |
| C(15B) | 0.3856(6) | 0.695(2) | 0.4629(6) | 4.8(5) |
| C(15A) | −0.3370(7) | 0.147(2) | 0.0109(7) | 6.3(6) |
| C(16A) | −0.2824(5) | 0.122(2) | 0.0743(5) | 4.6(5) |
| C(16B) | 0.3288(6) | 0.737(2) | 0.4054(5) | 4.2(4) |

TABLE 3. Yields, colors, melting points and analyses of compounds **1**–**10**

| Compound | Yield (%) | Color | Melting point (°C) | Analysis: found (calculated) (%) | |
|---|---|---|---|---|---|
| | | | | C | H |
| **1** | 30 | Red oil | – | – | – |
| **2** | 40 | Red oil | – | – | – |
| **3** | 26 | Reddish-orange solid | 109–111 | 49.0 (49.2) | 3.5 (3.6) |
| **4** | 33 | Orange solid | 82– 83 | 49.1 (48.6) | 4.1 (3.8) |
| **5** | 24 | Orange solid | 142–143 | 48.8 (49.8) | 4.1 (4.1) |
| **6** | 30 | Red oil | – | – | – |
| **7** | 40 | Red oil | – | – | – |
| **8** | 48 | Red–orange solid | 105–106 | 44.3 (44.4) | 3.0 (3.0) |
| **9** | 58 | Yellow solid | 139–140 | 44.0 (44.0) | 3.4 (3.3) |
| **10** | 42 | Orange solid | 138–139 | 45.9 (45.7) | 3.8 (3.8) |

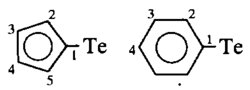
TABLE 4. $^1$H NMR data

| Compound | δ (ppm relative to tetramethylsilane, recorded in $CDCl_3$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ferrocenyl protons | | | Aryl protons | | | Alkyl protons | | | | |
| | $H_{3,4}$ | $H_{2,5}$ | $C_5H_5$ | $C_6H_4$ | $C_6H_5$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_3$ | $OCH_3$ | $OCH_2$ |
| Ferrocene | | | 4.12 (s) | | | | | | | | |
| **1** | 4.36 (vt) | 4.2 (vt) | 4.15 (s) | – | – | – | – | – | 1.97 (s) | | |
| **2** | 4.32 (vt) | 4.2 (vt) | 4.14 (s) | – | – | 2.6 (t) | 1.6 (m) | 1.3 (m) | 0.85 (t) | – | – |
| **3** | 4.45 (vt) | 4.3 (vt) | 4.2 (s) | – | 7.15–7.5 (m) | – | – | – | – | – | – |
| **4** | 4.42 (vt) | 4.25 (vt) | 4.19 (s) | 7.4 (d), 7.7 (d) | | – | – | | | 3.7 (s) | |
| **5** | 4.4 (vt) | 4.25 (vt) | 4.2 (s) | 6.6 (d), 7.6 (d) | | – | – | | 1.4 (t) | – | 3.8 (q) |
| **6** | 4.37 (vt) | 4.21 (vt) | | | | | | | 1.97 (s) | | |
| **7** | 4.37 (vt) | 4.24 (vt) | – | – | – | 2.6 (t) | 1.6 (m) | 1.3 (m) | 0.84 (t) | | |
| **8** | 4.48 (vt) | 4.32 (vt) | – | – | 7.4–7.1 (m) | | | | | | |
| **9** | 4.41 (vt) | 4.25 (vt) | – | 6.7 (d) | 7.5 (d) | | | | | 3.7 (s) | |
| **10** | 4.41 (vt) | 4.25 (vt) | – | 6.7 (d) | 7.5 (d) | – | – | – | 1.3 (t) | | 3.9 (q) |

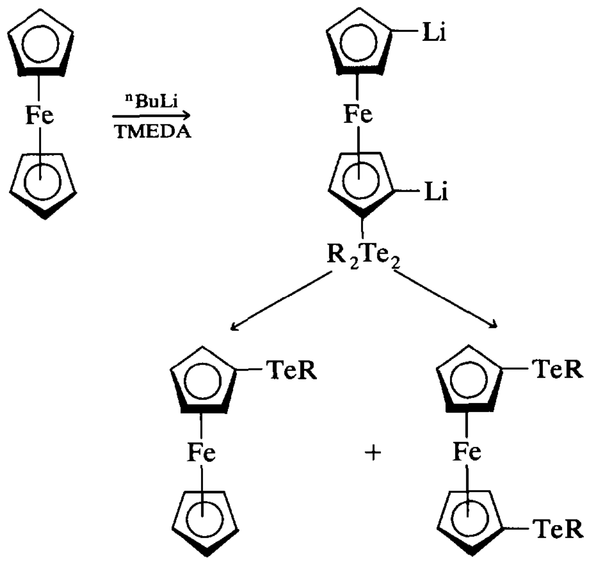
TABLE 5. $^{13}$C nuclear magnetic resonance data

| Compound | δ (ppm) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ferrocenyl carbons [a] | | | | Aryl carbons [a] | | | | Alkyl carbons | | | |
| | $C_1$ | $C_{2,5}$ | $C_{3,4}$ | $C_5H_5$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $CH_2$ | $CH_2$ | $CH_2$ | $CH_3$ [b] |
| Ferrocene | | | | 67.8 | | | | | | | | |
| **1** | 44.3 | 70.7 | 78.3 | 69.2 | | | | | | | | NO |
| **2** | 44.5 | 72.3 | 80.3 | 69.1 | | | | | 34.0 | 24.8 | 13.3 | 8.6 |
| **3** | 47.8 | 71.7 | 79.6 | 69.3 | 117.3 | 134.8 | 129.1 | 126.7 | | | | |
| **6** | 45.3 | 72.1 | 79.3 | | | | | | | | | NO |
| **7** | 44.4 | 72.1 | 80.3 | | | | | | 33.8 | 24.6 | 13.1 | 8.4 |
| **8** | 47.5 | 72.9 | 80.7 | | 116.8 | 135.3 | 129.0 | 126.9 | | | | |
| **9** | 48.5 | 72.7 | 80.2 | | 105.5 | 138.1 | 115.0 | 159.1 | | | | 55.1 |
| **10** | 48.4 | 72.6 | 80.2 | | 105.2 | 138.1 | 115.6 | 158.6 | 63.2 | | | 14.7 |

[a]



[b] NO, not observed in the range 0–200 ppm.



**1**: R = Me **6**: R = Me
**2**: R = $^n$Bu **7**: R = $^n$Bu
**3**: R = $C_6H_5$ **8**: R = $C_6H_5$
**4**: R = $p$-MeO$C_6H_4$ **9**: R = $p$-MeO$C_6H_4$
**5**: R = $p$-EtO$C_6H_4$ **10**: R = $p$-OEt$C_6H_4$

Scheme 1.

**8**, *m/e* 594 ($M^+$, 100%); **9**, *m/e* 656 ($M^+$, 100%) was observed in the expected isotope pattern. The major fragments arise from the loss of $R_2Te$, RTe and R

TABLE 6. Cyclic voltammetry data

| Compound | $E_{1/2}^{(1)}$ (eV) | $E_{1/2}^{(2)}$ (eV) |
|---|---|---|
| Ferrocene | 0.51 | |
| **1** | 0.57 | 0.80 |
| **3** | 0.58 | 0.89 |
| **4** | 0.56 | 0.99 |
| **6** | 0.53 | |
| **8** | 0.74 | |
| **9** | 0.72 | |
| **10** | 0.73 | |

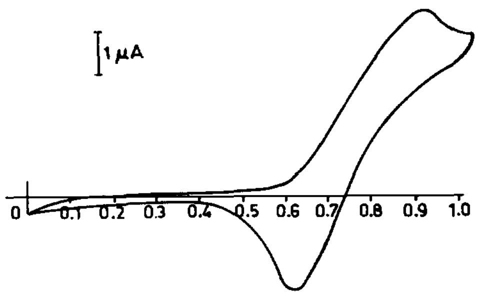


Fig. 1. Cyclic voltammogram of **8** in $CH_2Cl_2$ solution (scan rate 50 mV $s^{-1}$).

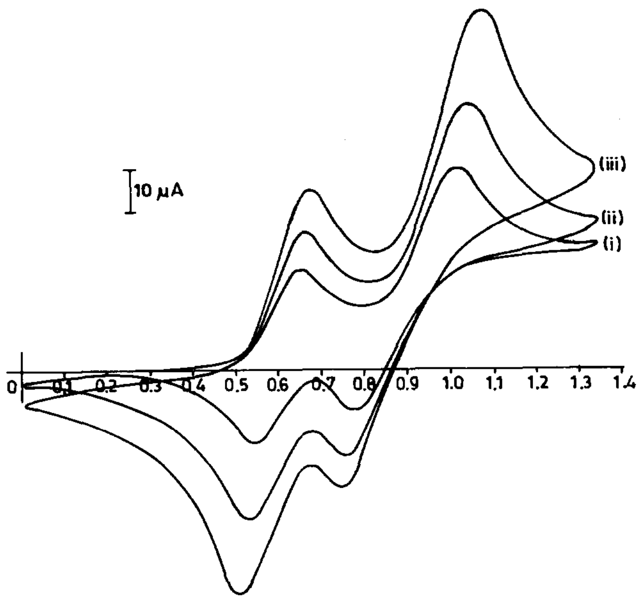


Fig. 2. Cyclic voltammograms of **3** in $CH_2Cl_2$ solution for scan rates of 50 mV $s^{-1}$ (curve (i)) 100 mV $s^{-1}$ (curve (ii)) and 200 mV $s^{-1}$ (curve (iii)).

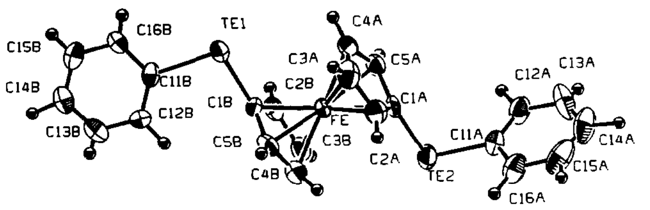


Fig. 3. Molecular structure of **8**.

TABLE 7. Intramolecular distances (Å) (estimated standard deviations in the least significant figure are given in parentheses)

| | | | |
|---|---|---|---|
| Te(1)–C(1B) | 2.093(8) | C(2A)–C(3A) | 1.40(1) |
| Te(1)–C(11B) | 2.138(8) | C(2B)–C(3B) | 1.43(1) |
| Te(2)–C(1A) | 2.108(8) | C(3B)–C(4B) | 1.38(1) |
| Te(2)–C(11A) | 2.119(8) | C(3A)–C(4A) | 1.40(1) |
| Fe–C(1A) | 2.037(7) | C(4B)–C(5B) | 1.43(1) |
| Fe–C(1B) | 2.032(8) | C(4A)–C(5A) | 1.40(1) |
| Fe–C(2A) | 2.035(9) | C(11A)–C(12A) | 1.36(1) |
| Fe–C(2B) | 2.042(9) | C(11A)–C(16A) | 1.38(1) |
| Fe–C(3B) | 2.041(9) | C(11B)–C(12B) | 1.36(1) |
| Fe–C(3A) | 2.054(9) | C(11B)–C(16B) | 1.36(1) |
| Fe–C(4B) | 2.06(1) | C(12A)–C(13A) | 1.39(1) |
| Fe–C(4A) | 2.031(9) | C(12B)–C(13B) | 1.37(1) |
| Fe–C(5A) | 2.041(8) | C(13A)–C(14A) | 1.35(2) |
| Fe–C(5B) | 2.032(9) | C(13B)–C(14B) | 1.35(1) |
| C(1A)–C(2A) | 1.40(1) | C(14B)–C(15B) | 1.36(1) |
| C(1A)–C(5A) | 1.43(1) | C(14A)–C(15A) | 1.33(2) |
| C(1B)–C(2B) | 1.42(1) | C(15B)–C(16B) | 1.38(1) |
| C(1B)–C(5B) | 1.41(1) | C(15A)–C(16A) | 1.42(2) |

TABLE 8. Intramolecular bond angles (°) (estimated standard deviations in the least significant figure are given in parentheses)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(2A)-C(1A)-C(5A) | 107.5(8) | Fe-C(5A)-C(4A) | 69.5(5) | C(1B)-Te(1)-C(11B) | 98.6(3) | C(2B)-Fe-C(3B) | 41.1(4) |
| Te(1)-C(1B)-Fe | 118.0(4) | C(1A)-C(5A)-C(4A) | 107.5(8) | C(1A)-Te(2)-C(11A) | 97.9(3) | C(2B)-Fe-C(3A) | 145.3(4) |
| Te(1)-C(1B)-C(2B) | 125.5(6) | Fe-C(5B)-C(1B) | 69.7(5) | C(1A)-Fe-C(1B) | 175.4(3) | C(2B)-Fe-C(4B) | 67.5(4) |
| Te(1)-C(1B)-C(5B) | 125.2(6) | Fe-C(5B)-C(4B) | 70.8(5) | C(1A)-Fe-C(2A) | 40.4(3) | C(2B)-Fe-C(4A) | 115.4(4) |
| Fe-C(1B)-C(2B) | 70.0(5) | C(1B)-C(5B)-C(4B) | 107.3(8) | C(1A)-Fe-C(2B) | 135.4(3) | C(2B)-Fe-C(5A) | 111.0(4) |
| Fe-C(1B)-C(5B) | 69.7(5) | Te(2)-C(11A)-C(12A) | 120.9(6) | C(1A)-Fe-C(3B) | 110.1(3) | C(2B)-Fe-C(5B) | 68.6(4) |
| C(2B)-C(1B)-C(5B) | 108.4(8) | Te(2)-C(11A)-C(16A) | 119.8(7) | C(1A)-Fe-C(3A) | 67.7(3) | C(3B)-Fe-C(3A) | 172.6(4) |
| Fe-C(2A)-C(1A) | 69.9(5) | C(12A)-C(11A)-C(16A) | 119.3(8) | C(1A)-Fe-C(4B) | 114.3(4) | C(3B)-Fe-C(4B) | 39.4(4) |
| Fe-C(2A)-C(3A) | 70.6(5) | Te(1)-C(11B)-C(12B) | 122.1(6) | C(1A)-Fe-C(4A) | 68.1(4) | C(3B)-Fe-C(4A) | 146.4(4) |
| C(1A)-C(2A)-C(3A) | 108.4(9) | Te(1)-C(11B)-C(16B) | 117.1(7) | C(1A)-Fe-C(5A) | 40.9(3) | C(3B)-Fe-C(5A) | 115.7(4) |
| Fe-C(2B)-C(1B) | 69.2(5) | C(12B)-C(11B)-C(16B) | 120.8(8) | C(1A)-Fe-C(5B) | 143.6(4) | C(3B)-Fe-C(5B) | 68.4(4) |
| Fe-C(2B)-C(3B) | 69.4(5) | C(11A)-C(12A)-C(13A) | 120(1) | C(1B)-Fe-C(2A) | 143.7(4) | C(3A)-Fe-C(4B) | 134.2(5) |
| C(1B)-C(2B)-C(3B) | 107.2(8) | C(11B)-C(12B)-C(13B) | 118.6(9) | C(1B)-Fe-C(2B) | 40.8(3) | C(3A)-Fe-C(4A) | 40.2(4) |
| Fe-C(3B)-C(2B) | 69.5(5) | C(12A)-C(13A)-C(14A) | 123(1) | C(1B)-Fe-C(3B) | 68.6(3) | C(3A)-Fe-C(5A) | 67.6(4) |
| Fe-C(3B)-C(4B) | 71.2(6) | C(12B)-C(13B)-C(14B) | 121(1) | C(1B)-Fe-C(3A) | 114.2(4) | C(3A)-Fe-C(5B) | 109.0(4) |
| C(2B)-C(3B)-C(4B) | 108.2(8) | C(13B)-C(14B)-C(15B) | 120.7(9) | C(1B)-Fe-C(4B) | 67.8(4) | C(4B)-Fe-C(4A) | 173.6(4) |
| Fe-C(3A)-C(2A) | 69.2(5) | C(13A)-C(14A)-C(15A) | 117(1) | C(1B)-Fe-C(4A) | 110.3(4) | C(4B)-Fe-C(5A) | 145.3(4) |
| Fe-C(3A)-C(4A) | 69.0(5) | C(14B)-C(15B)-C(16B) | 119(1) | C(1B)-Fe-C(5A) | 135.1(3) | C(4B)-Fe-C(5B) | 40.8(4) |
| C(2A)-C(3A)-C(4A) | 107.9(8) | C(14A)-C(15A)-C(16A) | 123(1) | C(1B)-Fe-C(5B) | 40.6(3) | C(4A)-Fe-C(5A) | 40.2(4) |
| Fe-C(4B)-C(3B) | 69.4(6) | C(11A)-C(16A)-C(15A) | 118(1) | C(2A)-Fe-C(2B) | 174.3(4) | C(4A)-Fe-C(5B) | 133.8(4) |
| Fe-C(4B)-C(5B) | 68.4(5) | C(11B)-C(16B)-C(15B) | 119.8(9) | C(2A)-Fe-C(3B) | 133.7(4) | C(5A)-Fe-C(5B) | 173.7(4) |
| C(3B)-C(4B)-C(5B) | 108.8(9) | | | C(2A)-Fe-C(3A) | 40.1(4) | Te(2)-C(1A)-Fe | 116.2(4) |
| Fe-C(4A)-C(3A) | 70.8(6) | | | C(2A)-Fe-C(4B) | 109.8(4) | Te(2)-C(1A)-C(2A) | 125.0(7) |
| Fe-C(4A)-C(5A) | 70.3(5) | | | C(2A)-Fe-C(4A) | 67.9(4) | Te(2)-C(1A)-C(5A) | 126.3(6) |
| C(3A)-C(4A)-C(5A) | 108.6(9) | | | C(2A)-Fe-C(5A) | 68.1(4) | Fe-C(1A)-C(2A) | 69.8(5) |
| Fe-C(5A)-C(1A) | 69.4(4) | | | C(2A)-Fe-C(5B) | 113.0(4) | Fe-C(1A)-C(5A) | 69.7(5) |

fragments from the molecular ion, to give the ion $Fe(C_{10}H_8)^+$ ($m/e = 184$).

Cyclic voltammetry data in $CH_2Cl_2$ for some of the compounds are listed in Table 6. A well-defined quasi-reversible single-electron redox wave was obtained for the oxidation of the disubstituted derivatives (**6** and **8**–**10**) (Fig. 1), and two reversible single-electron waves in the case of the monosubstituted derivatives (**1**, **3** and **4**) (Fig. 2). The difference $E_{p_a} - E_{p_c}$) between the oxidative and reductive peak potentials is somewhat higher than the theoretical limit of 60 mV for a reversible one-electron process [27]. The introduction of the organoltelluro groups in ferrocene increases the redox potential from +0.51 to +0.73 V, a feature similar to that observed for the corresponding P [28] and S [9] derivatives.

### *3.1. Structure*

The molecular structure of **8** is shown in Fig. 3, and the bond lengths and angles are listed in Tables 7 and 8 respectively. The molecular structure is quite similar to that of the phosphine analogue, *i.e.* 1,1′-bis(diphenylphosphino)ferrocene, which is centrosymmetric with the inversion centre at the Fe atom, and the asymmetric unit is represented by a half-molecule [29]. However, molecule **8** is pseudocentrosymmetric and the asymmetric unit consists of the complete molecule. The two cyclopentadienyl rings are nearly parallel and staggered with a *trans* arrangement of Te–$C_6H_5$ substituents. Upon chelation a conformational change to *cis* arrangement is forced upon the ligand. The *trans* bond angles, *i.e.* the C–Fe–C′ angles, are close to 180°. The two cyclopentadienyl rings are slightly tilted with respect to each other, with a dihedral angle of 0.95°. The planes containing the cyclopentadienyl rings are almost orthogonal to the planes containing the phenyl groups. The cyclopentadienyl and the phenyl rings are planar, and the bond distances and angles are normal.

The iron–carbon distances range from 2.031(9) to 2.06(1) Å which agree well with those in other ferrocene derivatives. The carbon–carbon distances in the cyclopentadienyl rings range from 1.40(1) to 1.43(1) Å, and the C–C–C bond angles within the ring range from 107.2(8) to 108.8(9)°. The ferrocene-C–Te bond distances (Te(1)–C(1B), 2.093(8) Å; Te(2)–C(1A), 2.108(8) Å) are in excellent agreement with the sum of the Pauling [30] single bond covalent radii for a Te–C ($sp^2$) single bond (2.11 Å) and with the only other recently reported ferrocene-C–Te bond distances, those in 1,2,3-tritellura[3]ferrocenophane [31]. The Te–C(phenyl) distances (Te(1)–C(11B), 2.138(8) Å; Te(2)–C(11A), 2.119(8) Å) are slightly longer than the sum of the covalent radii but are in good agreement with those for corresponding bonds $Te^{II}$, Te–C(aryl) bonds in $PhTe(tu)_2Cl_2$ [32], PhTe(tmsh)Cl, $RTe(p\text{-}C_6H_4OEt)$ (R ≡ 2-(2-pyridyl)-phenyl) [33].

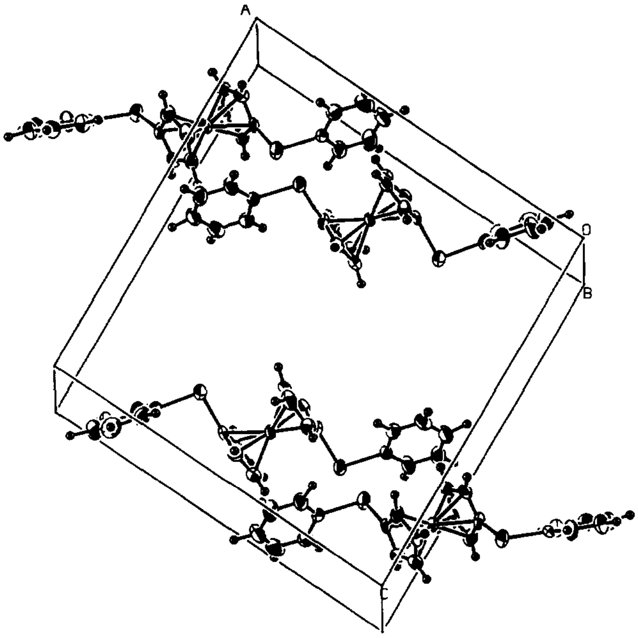


Fig. 4. Packing diagram.

The packing diagram is shown in Fig. 4. The title compound is essentially monomeric, but it is linked to other neighboring molecules by weak Te ··· Te intermolecular interactions to give loose dimers. Examination of the intermolecular distances shows that the shortest distance between the Te(1) ··· $Te(2)^i$ ($i = \frac{1}{2} + x, \frac{1}{2} - y, z$) is 3.795(7) Å and Te(1) ··· $Te(2)^i$ ($i = \frac{1}{2} + x, \frac{3}{2} - y, z$ and 4.392(3) Å. These distances are close to the van der Waals distance of 4.40 Å. Supplementary data are available from the authors.

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