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# Synthesis of novel chiral tellurium complexes by redox reaction of planar chiral cyclomercurated ferrocenylienes with tellurium powder and X-ray crystal structure of [TeCl{C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=N-C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>}]

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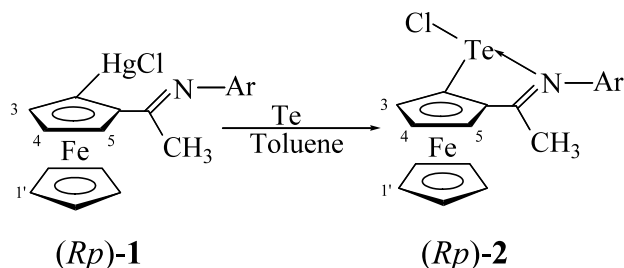
**Abstract**—The redox reaction of planar chiral cyclomercurated ferrocenylienes (*R*)-(+)-[HgCl{C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=NAr}] (Ar=substituted phenyl) with tellurium powder was carried out in refluxing toluene to give optically active cyclotellurated ferrocenylienes (*R*)-(+)-[TeCl{C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=NAr}], which were characterized by elemental analysis, IR and <sup>1</sup>H NMR spectra. The redox reaction proceeded with retention of the planar chirality in the ferrocene moiety, which was confirmed by CD spectra. The crystal structure of [TeCl{C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=N-C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>}] showed that the Te–N distance of 2.28 Å is shorter than the sum of the van der Waals radii of Te and N (3.70 Å), indicating the presence of N→Te intramolecular coordination. © 2003 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The growth of the organic chemistry of tellurium is well documented in several review articles and books.<sup>1</sup> The reason for this is their potential application in a wide range of areas such as material sciences,<sup>2</sup> organic synthesis,<sup>3</sup> organic catalysis,<sup>4</sup> pharmaceutical sciences,<sup>5</sup> and coordination chemistry.<sup>6</sup> Molecules having an intramolecular N→Te interaction have attracted considerable attention.<sup>7</sup> These molecules are remarkably versatile as they afford (a) stable tellurenyl halides,<sup>7b</sup> (b) monomeric volatile tellurolates,<sup>8</sup> and (c) hybrid multi-dentate ligands containing ‘hard’ nitrogen or oxygen in addition to the ‘soft’ tellurium.<sup>9</sup> Whereas a number of Te<sup>IV</sup> or Te<sup>II</sup> compounds bearing carbonyl,<sup>10</sup> azobenzene,<sup>11</sup> azomethines,<sup>12</sup> and pyridines<sup>13</sup> are known, to the best of our knowledge, there are no reports about the preparation of optically active intramolecularly coordinated organotellurium compounds.

Organomercurials have been used extensively in organic synthesis and synthesis of other organometallics due to their ability to accommodate practically all important organic functional groups and their ease in undergoing

transmetalation for forming other organometallics which are useful in organic synthesis.<sup>14</sup> Optically active 1,2-disubstituted ferrocenes have proved to be of particular interest for their applications in material sciences, asymmetric synthesis and asymmetric catalysis.<sup>15</sup> Recently, we reported that the reaction of chiral cyclometallated (Pd, Hg) ferrocenylienes with tin powder proceeded with retention of the planar chirality.<sup>16</sup> This paper reports the synthesis of planar chiral 1,2-disubstituted cyclotellurated ferrocenylienes by the redox reaction of optically active cyclomercurated ferrocenylienes with tellurium powder (Scheme 1) and the X-ray structural analysis of the racemic cyclotellurated ferrocenyliene.



**Scheme 1.** Ar = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (a), *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> (b), *p*-ClC<sub>6</sub>H<sub>4</sub> (c), *p*-BrC<sub>6</sub>H<sub>4</sub> (d), C<sub>6</sub>H<sub>5</sub> (e).

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On the basis of the numerous reports of the utility of organotellurium compounds in carbon–carbon bond formation,<sup>17</sup> functional group interconversion,<sup>18</sup> and preparation of other organometallic compounds,<sup>19</sup> and uses of their antioxidant and biological activity,<sup>20</sup> we believe that these new non-racemic organotellurium compounds could add significantly to the utility of organotellurium compounds, especially in the synthesis of other optically active complexes.

## 2. Results and discussion

### 2.1. Redox reaction

The transmetallation reaction refers to the reaction in general, by which a certain organometallic compound is converted into another one, including the reactive organometallic intermediate.<sup>21</sup> However, the mechanism of this reaction is still not clear at all. We have reported that a series of asymmetric diaryltellurium dichlorides were synthesized by the transmetallation reaction of Schiff-base-type arylmercury compounds with 4-ethoxyphenyltellurium trichloride, in which both the valence states of Hg and Te were unchanged.<sup>22</sup> In the case of the reaction mentioned in this article and reactions of metallic powder with certain organometallic compounds,<sup>14b,c</sup> these reactions should be categorized clearly and unambiguously into redox reaction rather than transmetallations. As shown in Scheme 1, the redox reaction of compounds (*Rp*)-**1** with powdered metallic tellurium in dry toluene at reflux for 8–10 h is a convenient and successful method for synthesizing optically active organotellurium compounds. The chiral cyclotellurated ferrocenylimines (*R*)-(+)-[TeCl{C<sub>5</sub>H<sub>5</sub>-FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=NAr}] obtained are red crystalline compounds, which are stereochemically and air stable. The reaction proceeded with retention of the planar chirality of the ferrocene moiety. The absolute configuration of the products was confirmed by CD spectra. The influence of different substituents in *N*-phenyl ring on the yields of the reaction was not significant.

### 2.2. Spectral properties of the redox products

The IR spectral features of (*Rp*)-**2** are similar to those described in our previous reports.<sup>16b,23a</sup> As shown in Table 1, the C=N absorptions of (*Rp*)-**2** were shifted to lower frequency by 42–45 cm<sup>-1</sup> in comparison with those of the corresponding cyclomercurated ferrocenylimines, indicating that nitrogen is coordinated to Te through its lone pair electrons. By comparison of the C=N absorptions of (*Rp*)-**2** with those of **1**, the corresponding cyclopalladated complexes [PdCl{C<sub>5</sub>H<sub>5</sub>-FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=NAr}]PPh<sub>3</sub> **3** and cyclostannated compounds [SnCl<sub>2</sub>{C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=NAr}]<sub>2</sub> **4**, it can be concluded that the intramolecular N→Te coordination in (*Rp*)-**2** was stronger than the intramolecular N→Hg coordination in **1**, N→Sn in **4** and similar to the intramolecular N→Pd coordination in **3**. Thus there is a sequence of the strength of intramolecular coordination: N→Pd ~ N→Te > N→Sn ~ N→Hg.

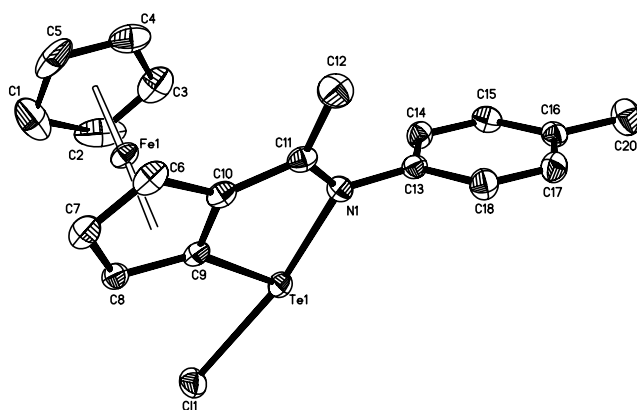
**Table 1.** The C=N stretching frequencies (cm<sup>-1</sup>) for compounds **1–4**

Compounds	a	b	c	d	e
<b>1</b> <sup>23a</sup>	1615	1613	1615	1614	1610
( <i>Rp</i> )- <b>2</b>	1572	1570	1570	1572	1566
<b>3</b> <sup>23b</sup>	1569	1566	1570	1570	1574
<b>4</b> <sup>16b</sup>	1614	1614	1611		

The <sup>1</sup>H NMR spectra of (*Rp*)-**2** were completely consistent with a homoannular 1,2-disubstituted structure and gave the same indications of a strong N→Te interaction. The chemical shifts for all protons (except for those of the unsubstituted Cp ring) in complexes (*Rp*)-**2** appeared considerably downfield, compared with those of the corresponding cyclomercurated ferrocenylimines **1**, especially for H-3. For example, the <sup>1</sup>H NMR spectrum of (*Rp*)-**2a** exhibited signals at δ 5.27, δ 4.59 and δ 4.88 integrating for H-3, H-4 and H-5, respectively. The other signals included two doublets at δ 6.96 and δ 7.25 for protons on the phenyl ring, three signals at δ 2.36, δ 2.41 and δ 4.20 for the protons of C(CH<sub>3</sub>)=N, Ar-CH<sub>3</sub> and unsubstituted Cp ring, respectively. However, the signals for H-3, H-4 and H-5 in complexes **1a** appeared at δ 4.45, δ 4.46 and δ 4.83, respectively. This result also indicates that the N→Te coordination is stronger than N→Hg coordination.

### 2.3. Molecular and crystal structure of compound **2**

An X-ray crystal structure determination of racemic compound **2a** was carried out, since it was difficult to obtain the single crystal of non-racemic tellurium complex. An ORTEP view of racemic compound **2a** is shown in Figure 1. The Te–N(1) distance of 2.28 Å is



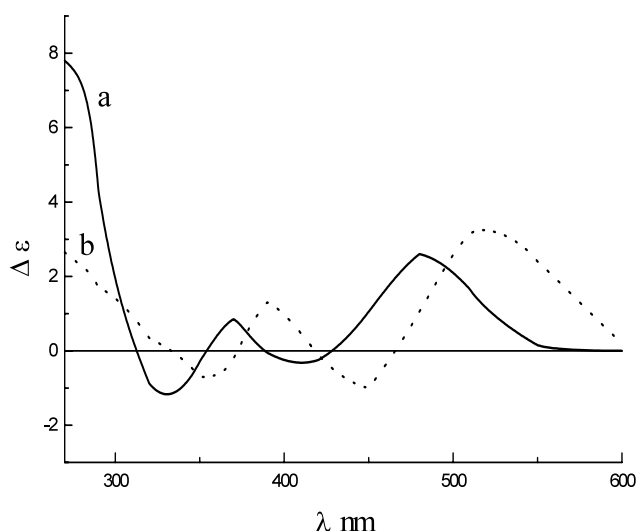
**Figure 1.** Molecular structure of racemic **2a** with atom numbering scheme. Selected bond lengths (Å) and angles (°): Te(1)–Cl(1) 2.55(2), Te(1)–N(1) 2.28(4), Te(1)–C(9) 2.08(3), N(1)–C(11) 1.29(8), C(9)–C(10) 1.44(3), C(10)–C(11) 1.45(1), Cl(1)–Te(1)–C(9) 89.6(2), Cl(1)–Te(1)–N(1) 164.9(8), N(1)–Te(1)–C(9) 75.5(4), C(9)–C(10)–C(11) 118.3(2), C(10)–C(11)–N(1) 114.7(2), Te(1)–N(1)–C(11) 115.9(0), Te(1)–C(9)–C(8) 136.6(2), C(6)–C(10)–C(11) 133.9(3).

much shorter than the sum of the van der Waals radii of Te and N (which amounts to 3.70 Å),<sup>24</sup> indicating intramolecular coordination between Te and N(1) and ensuring the stability of this compound.<sup>12c</sup> The Te–Cl bond (2.552 Å) is quite long compared with the sum of the atomic covalent radii (2.36 Å). The approximate alignment of the Te–Cl bond and the corresponding nitrogen (angle N(1)–Te–Cl 164.97(6)°) may allow an effective orbital interaction between the nitrogen lone pair and the  $\sigma^*$  orbital of the Te–Cl bond, and it may lead to elongation of the Te–Cl bond.

The two Cp rings are almost parallel (dihedral angle 2.4°). The chelate cycle Te–C(9)–C(10)–C(11)–N(1) is nearly planar and the dihedral angle between the substituted Cp ring and this chelate cycle is 2.75°.

#### 2.4. Electronic and circular dichroism spectra

The CD spectrum of (*Rp*)-**2a** is shown together with that of (*Rp*)-**1a** in Figure 2. The sign of the Cotton effects of the complex (*Rp*)-**2a** was similar to that of (*Rp*)-**1a**. This result indicated that (*Rp*)-**2a** and (*Rp*)-**1a** should have the same absolute configuration in the ferrocene moiety,<sup>16a</sup> confirming that the redox reaction proceeded with retention of the planar chirality.



**Figure 2.** CD spectra in dichloromethane of compounds (*Rp*)-**1a** (a) and (*Rp*)-**2a** (b).

### 3. Experimental

#### 3.1. Materials and instruments

Melting points were measured on a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1160 Elemental analyzer. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX 400 spectrometer, using CDCl<sub>3</sub> as solvent and TMS as an internal reference standard; all *J* values were measured in Hertz. IR spectra were recorded on a Perkin–Elmer FTIR 1750 spectrophotometer. Prepara-

tive TLC was performed on dry silica gel plates developed with dichloromethane. Optical rotations were determined at 5890 Å on a Perkin–Elmer 341 polarimeter at 20°C. The CD spectra were recorded on a JASCO J-20C automatic recording spectropolarimeter at 20°C.

All solvents were dried according to the standard methods. Tellurium powder was purified according to the literature.<sup>25</sup> The optically active cyclomercurated ferrocenylimines (*Rp*)-(+)-**1** were prepared according to the literature procedure.<sup>16a</sup>

#### 3.2. General procedure for the synthesis of complexes (*Rp*)-(+)-**2**

(*Rp*)-(+)-**1** (0.1 mmol) and Te powder were refluxed in dry toluene (20 ml) for 8–10 h. After removing the metallic mercury and surplus Te powder by filtration, the solvents were evaporated in vacuo. The purification of the residue was easily achieved by chromatography on silica gel plates developed with dichloromethane. The red TLC band was (*Rp*)-(+)-**2** and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether. The compounds obtained were characterized as follows.

**3.2.1. (*R*)-(+)-[TeCl(C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=N-C<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>)] **2a.** Red crystal. Yield 27.6%. Mp 192–194°C. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +3190.0 (*c* 0.01, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr pellet): 1572, 1505, 1466, 1106, 1001 cm<sup>-1</sup>. <sup>1</sup>H NMR (ppm):  $\delta$  2.36 (s, 3H, C(CH<sub>3</sub>)=N), 2.41 (s, 3H, CH<sub>3</sub>), 4.20 (s, 5H, H-1'), 4.59 (t, 1H, *J* = 2.6 Hz, H-4), 4.88 (d, 1H, *J* = 1.6 Hz, H-5), 5.27 (d, 1H, *J* = 1.6 Hz, H-3), 6.96 (d, 2H, *J* = 8.0 Hz, N-Ar-H), 7.25 (d, 2H, *J* = 8.0 Hz, N-Ar-H). Anal. found: C, 47.99; H, 3.96; N, 2.90. Calcd for C<sub>19</sub>H<sub>18</sub>NCIFeTe: C, 47.61; H, 3.79; N, 2.92%.**

**3.2.2. (*R*)-(+)-[TeCl(C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=N-C<sub>6</sub>H<sub>4</sub>-4-OCH<sub>3</sub>)] **2b.** Red crystal. Yield 36.7%. Mp 200°C (dec.). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +2707.0 (*c* 0.0098, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr pellet): 1570, 1505, 1465, 1106, 1001 cm<sup>-1</sup>. <sup>1</sup>H NMR (ppm):  $\delta$  2.37 (s, 3H, C(CH<sub>3</sub>)=N), 3.86 (s, 3H, OCH<sub>3</sub>), 4.21 (s, 5H, H-1'), 4.59 (t, 1H, *J* = 1.6 Hz, H-4), 4.88 (d, 1H, *J* = 1.6 Hz, H-5), 5.27 (d, 1H, *J* = 1.6 Hz, H-3), 6.97 (dd, 4H, *J* = 8.0 Hz, N-Ar-H). Anal. found: C, 46.10; H, 3.73; N, 2.82. Calcd for C<sub>19</sub>H<sub>18</sub>NOCIFeTe: C, 46.08; H, 3.66; N, 2.83%.**

**3.2.3. (*R*)-(+)-[TeCl(C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=N-C<sub>6</sub>H<sub>4</sub>-4-Cl)] **2c.** Red crystal. Yield 41.3%. Mp 174–176°C. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +3025.6 (*c* 0.0098, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr pellet): 1570, 1486, 1464, 1106, 1002 cm<sup>-1</sup>. <sup>1</sup>H NMR (ppm):  $\delta$  2.36 (s, 3H, CH<sub>3</sub>), 4.21 (s, 5H, H-1'), 4.63 (t, 1H, *J* = 1.6 Hz, H-4), 4.90 (d, 1H, *J* = 1.6 Hz, H-5), 5.28 (d, 1H, *J* = 1.6 Hz, H-3), 7.01 (d, 2H, *J* = 8.4 Hz, N-Ar-H), 7.44 (d, 2H, *J* = 8.4 Hz, N-Ar-H). Anal. found: C, 43.58; H, 3.22; N, 2.83. Calcd for C<sub>18</sub>H<sub>15</sub>NCI<sub>2</sub>FeTe: C, 43.27; H, 3.03; N, 2.80%.**

**3.2.4. (*R*)-(+)-[TeCl(C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=N-C<sub>6</sub>H<sub>4</sub>-4-Br)] **2d.** Red crystal. Yield 22.7%. Mp 166–168°C. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +2141.2 (*c* 0.0085, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr pellet): 1572, 1483, 1466, 1105, 1009 cm<sup>-1</sup>. <sup>1</sup>H NMR (ppm):  $\delta$**

2.36 (s, 3H, CH<sub>3</sub>), 4.21 (s, 5H, H-1'), 4.63 (t, 1H, *J*=2.6 Hz, H-4), 4.90 (d, 1H, *J*=2.4 Hz, H-5), 5.27 (d, 1H, *J*=2.4 Hz, H-3), 6.95 (d, 2H, *J*=8.0 Hz, N-Ar-H), 7.58 (d, 2H, *J*=8.0 Hz, N-Ar-H). Anal. found: C, 39.79; H, 2.91; N, 2.75. Calcd for C<sub>18</sub>H<sub>15</sub>NBrClFeTe: C, 39.73; H, 2.78; N, 2.57%.

**3.2.5. (R)-(+)-[TeCl(C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>3</sub>C(CH<sub>3</sub>)=N-C<sub>6</sub>H<sub>5</sub>)] 2e.** Red crystal. Yield 18.5%. Mp 164–166°C.  $[\alpha]_D^{20} = +3240.0$  (*c* 0.01, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr pellet): 1566, 1467, 1449, 1105, 999 cm<sup>-1</sup>. <sup>1</sup>H NMR (ppm): δ 2.37 (s, 3H, CH<sub>3</sub>), 4.21 (s, 5H, H-1'), 4.61 (t, 1H, *J*=2.4 Hz, H-4), 4.89 (d, 1H, *J*=2.4 Hz, H-5), 5.28 (d, 1H, *J*=2.4 Hz, H-3), 7.06 (d, 2H, N-Ar-H), 7.36 (m, 1H, N-Ar-H), 7.47 (m, 2H, N-Ar-H). Anal. found: C, 46.56; H, 3.50; N, 3.20. Calcd for C<sub>18</sub>H<sub>16</sub>NCIFeTe: C, 46.47; H, 3.47; N, 3.20%.

### 3.3. X-Ray crystal structure determination of racemic 2a

**3.3.1. Crystal data of racemic 2a.** C<sub>19</sub>H<sub>18</sub>ClFeNTe; *Mr*=479.24; space group: monoclinic, *P*2<sub>1</sub>/*c*; *a*=10.372(2), *b*=15.509(3), *c*=12.439(3) Å, α=90, β=113.69(3), γ=90°; *Z*=4, *V*=1840.3(6) Å<sup>3</sup>, *D*<sub>calcd</sub>=1.730 g cm<sup>-3</sup>, *F*(000)=936, μ(Mo Kα)=25.16 cm<sup>-1</sup>.

**3.3.2. Data collection.** All measurements were made on a Rigaku RAXIS-IV area detector with graphite monochromated Mo Kα radiation (λ=0.71073 Å). The data were collected at 18±1°C to a maximum 2θ value of 55.0°. A total of 28 frames of 6.00° oscillation were collected, each being exposed for 17 min. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. A total of 5614 reflections were collected; 3268 reflections were considered as observed with *I*>2.00σ(*I*).

**3.3.3. Structure solution and refinement.** The structure was solved by direct methods<sup>26</sup> and expanded using Fourier techniques. All calculations were performed using the SHELX-93 crystallographic software package.<sup>27</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-square refinement was based on 3268 observed reflections and 209 variable parameters. The final *R* factor was 0.0407 (*R*<sub>w</sub>=0.04652). The maximum and minimum peaks on the final difference Fourier map corresponded to 0.425 and -0.477 e Å<sup>-3</sup>, respectively.

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