Bis(cyclopentadienyl)titanium(IV)/zirconium(IV) derivatives of Schiff bases derived from thiophene-2-aldehyde

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Summary
The reactions of Schiff bases, derived by the condensation of thiophene-2-aldehyde with ethylenediamine, o-phenylenediamine or 4-methyl-o-phenylenediamine with bis-(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride have been studied in refluxing THF in the presence and absence of base. Two types of derivatives [Cp2MCl2·L] and [(Cp2MCl)2L]Cl2 have been isolated and characterized by elemental analyses, electrical conductance, magnetic moment and spectral (electronic, i.r., 1H n.m.r. and 13C n.m.r.) studies. 1H and 13C n.m.r. spectra reveal rapid rotation of the cyclopentadienyl ring around the metal-ring axis (n.m.r. time scale) at 25°C. Probable structures for the complexes are proposed.

Introduction
Many Schiff base transition metal complexes have been synthesized and characterized recently (1-12). Schiff bases generally form stable complexes with metal ions, especially if the amine and/or the carbonyl group contain a second functional group sufficiently near the coordination site. In view of the diverse synthetic and structural aspects of these complexes, interest in them continues to increase. This paper describes the synthesis and structural features of (cyclopentadienyl)titanium/zirconium(IV) derivatives with Schiff bases derived from thiophene-2-aldehyde (1).

Experimental
All operations were carried out under strictly anhydrous conditions. THF (J. T. Baker, b.p. 65.66°C) was dried and stored over Na wire and then boiled under reflux, until it gave the characteristic blue with benzophenone. It was finally dried by distilling from LiAIH4.

Bis(cyclopentadienyl) titanium/zirconium dichloride was prepared by reacting the appropriate MC14 with NaCp in C6H6. The ligands were prepared from thiophene-2-aldehyde and (CH2NH2)2, o-phenylenediamine or 4-methyl-o-phenylenediamine, following the method of Ho and Livingstone (13).

The analytical method and physical measurement details were described earlier (12).

Preparation of complexes
[Cp2MCl2·L]
Bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride (10mmol) and appropriate Schiff base (10mmol) were dissolved in anhydrous THF (50cm3) and the reaction mixture was boiled under reflux for 10-28 h. The solution was filtered and the vol reduced to ca. 15cm3. Dry petroleum ether (60-80°C, 15cm3) was added and the mixture was kept aside overnight. The coloured product, thus obtained, was filtered and dried in vacuo.

[(Cp2MCl)2L]Cl2
A mixture of bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride (20mmol) and the appropriate Schiff base (10mmol) was dissolved in dry THF (60cm3) and dry n-BuNH2 (40mmol) was added. The mixture was stirred for 45-50h at room temperature, and the resulting complex, which precipitated, was removed by filtration, washed thoroughly with THF and dried in vacuo.

Reaction of bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride with different Schiff bases are summarized in Table 1.

Results and discussion
A systematic study of the reactions of bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride with Schiff bases (L), derived by condensing thiophene-2-aldehyde with ethylenediamine, o-phenylenediamine or 4-methyl-o-phenylenediamine in anhydrous THF in the absence and presence of base (n-butyllamine) is represented by the following equations:

Cp2MCl2 + L THF reflux 10-28h

[(Cp2MCl)2L]Cl2

(M = Ti or Zr, L = SB1, SB2 or SB3)

The physical properties and analytical data for the complexes are given in Table 1. Complexes of the [Cp2MCl2·L] type are soluble in THF, CH3Cl2, PhNO2, DMF and DMSO, while the [(Cp2MCl)2L]Cl2 complexes are only soluble in DMF and DMSO. All are air-stable. The [(Cp2MCl)2L]Cl2 complexes are also unaffected by boiling H2O; however, the [Cp2MCl2·L] complexes are not.
complexes slowly hydrolyze upon contact with water, and change colour. Similar behaviour has been reported for certain other Schiff base transition metal complexes; the following reaction has been proposed:

\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH}_2
\end{align*}
\]

Electrical conductance measurements in DMF reveal the non-electrolytic nature of the \([\text{Cp}_2\text{MCl}_2\text{L}]\) complexes, whereas the \([\text{Cp}_2\text{MCl}_2\text{L}][\text{Cl}_2]\) complexes exhibit 1:2 electrolytic behaviour. Magnetic susceptibility measurements show that the complexes are diamagnetic.

### Electronic spectra

The electronic spectra of the complexes, recorded in DMF, exhibit a single band in the 23000–24500 cm\(^{-1}\) region, assigned to a charge-transfer band, in accord with their (n–1)d\(^n\)s electronic configuration. The ligands also exhibit bands at ca. 30000 and 33000 cm\(^{-1}\), which are assigned to the azomethine linkage and aromatic ring π – π* transitions. Upon complexation, these bands move to slightly lower energy.

### I.r. spectra

The i.r. spectra of the complexes show bands at ca. 3100 cm\(^{-1}\) for v(C–H), ca. 1430 cm\(^{-1}\) for v(C–C), and ca. 1020 cm\(^{-1}\) for δ(C–H) commensurate with the cyclopentadienyl ring. All bands are similar to those reported for the \((\eta^5\text{-C}_5\text{H}_5)\text{MC}l_2\) group in bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride. The v(M–C\(_5\text{H}_5\)) vibration band appears at ca. 400–380 cm\(^{-1}\).

The i.r. spectra of the ligands exhibit a v(C=N) band at ca. 1630 cm\(^{-1}\), which shifts by 420 cm\(^{-1}\) in the far i.r. spectra.

The spectra of the ligands, thiophene ring (161 bands) occur at ca. 3500 cm\(^{-1}\) and at ca. 1570 cm\(^{-1}\), and remain at the same position in the \([\text{Cp}_2\text{MCl}_2\text{L}][\text{Cl}_2]\) complexes. However, in the \([\text{Cp}_2\text{MCl}_2\text{L}][\text{Cl}_2]\) complexes these bands are shifted by ca. 20 cm\(^{-1}\) to higher frequencies suggesting that the heterocyclic ring sulphur participates in coordination. The v(C=N) splitting suggests that only one nitrogen atom is involved in coordination. This feature is further supported by the appearance of a v(C=N) band at ca. 420 cm\(^{-1}\) in the far i.r. spectra.

### Table 1. Reactions of \([\text{Cp}_2\text{MCl}_2\text{L}]\) with Schiff bases in THF

<table>
<thead>
<tr>
<th>Reactants (Molar ratio)</th>
<th>Reflux stirring time(h)</th>
<th>Product Colour (OHm(^{-1}) cm(^2) Mol(^{-1}))</th>
<th>Yield (%)</th>
<th>Found (Calcd.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti + SB(_1) (1:1)</td>
<td>25</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_1]) yellow brown, (82)</td>
<td>0.52</td>
<td>53.0 4.3 12.7 9.6 14.3</td>
</tr>
<tr>
<td>Ti + SB(_2) (1:1)</td>
<td>28</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_2]) brown, (48)</td>
<td>0.65</td>
<td>(53.1) (4.5) (12.9) (9.6) (14.3)</td>
</tr>
<tr>
<td>Ti + SB(_3) (1:1)</td>
<td>28</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_3]) brown, (52)</td>
<td>0.80</td>
<td>(57.2) (4.0) (11.8) (8.8) (13.0)</td>
</tr>
<tr>
<td>Ti + SB(_4) (1:1)</td>
<td>50</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_4]) Cl(_2) yellow, (58)</td>
<td>0.65</td>
<td>(57.8) 4.2 11.5 8.5 12.6</td>
</tr>
<tr>
<td>Ti + SB(_5) (1:1)</td>
<td>50</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_5]) Cl(_2) brown, (48)</td>
<td>0.80</td>
<td>(58.0) (4.3) (11.5) (8.6) (12.7)</td>
</tr>
<tr>
<td>Ti + SB(_6) (1:1)</td>
<td>50</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_6]) Cl(_2) brown, (48)</td>
<td>0.80</td>
<td>(55.0) (4.2) (17.9) (11.8) (17.5)</td>
</tr>
<tr>
<td>Ti + SB(_7) (1:1)</td>
<td>10</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_7]) light yellow, (62)</td>
<td>0.72</td>
<td>48.7 4.1 11.8 16.5 13.0</td>
</tr>
<tr>
<td>Ti + SB(_8) (1:1)</td>
<td>10</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_8]) brown, (58)</td>
<td>0.80</td>
<td>(53.0) (4.8) (10.9) (15.5) (12.0)</td>
</tr>
<tr>
<td>Ti + SB(_9) (1:1)</td>
<td>10</td>
<td>([\text{Cp}_2\text{TiCl}_2\text{SB}_9]) brown, (58)</td>
<td>0.78</td>
<td>(53.0) (4.0) (10.5) (15.0) (11.5)</td>
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<tr>
<td>Ti + SB(_{10}) (1:1)</td>
<td>45</td>
<td>([\text{Cp}_2\text{TiCl}<em>2\text{SB}</em>{10}]) Cl(_2) red yellow, (60)</td>
<td>0.72</td>
<td>46.1 3.7 7.5 21.8 17.0</td>
</tr>
<tr>
<td>Ti + SB(_{11}) (1:1)</td>
<td>45</td>
<td>([\text{Cp}_2\text{TiCl}<em>2\text{SB}</em>{11}]) Cl(_2) brown, (48)</td>
<td>0.80</td>
<td>(46.1) (3.9) (7.7) (21.9) (17.0)</td>
</tr>
<tr>
<td>Ti + SB(_{12}) (1:1)</td>
<td>45</td>
<td>([\text{Cp}_2\text{TiCl}<em>2\text{SB}</em>{12}]) Cl(_2) brown, (48)</td>
<td>0.80</td>
<td>(49.6) (3.7) 7.1 20.3 15.7</td>
</tr>
</tbody>
</table>