Synthesis and characterization of some new titanocene and zirconocene derivatives of functionalised less hindered phenols

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Titanocene and zirconocene derivatives of the type \( \text{Cp}_2\text{MCl}_{2-x} (\text{OAr})_x \) \( \text{Ia}: \text{M} = \text{Ti}, X = 1, \text{Ar} = 3, 5\text{-dimethylphenyl(Ar')} \); \( \text{Ib}: \text{M} = \text{Ti}, X = 2, \text{Ar} = 3, 5\text{-dimethylphenyl(Ar')} \); \( \text{IIa}: \text{M} = \text{Zr}, X = 1, \text{Ar} = 3, 5\text{-dimethylphenyl(Ar')} \); \( \text{IIb}: \text{M} = \text{Zr}, X = 2, \text{Ar} = 3, 5\text{-dimethylphenyl(Ar')} \); \( \text{IIIa}: \text{M} = \text{Zr}, X = 1, \text{Ar} = 2, 5\text{-dimethylphenyl(Ar''')} \) and \( \text{IIIb}: \text{M} = \text{Zr}, \text{Ar} = 2, 5\text{-dimethylphenyl(Ar''')} \) have been prepared and characterized by elemental analyses, IR, PMR and molecular weight measurements.

The titanocene and zirconocene alkoxides of the type \( \text{Cp}_2\text{M}(\text{OR})_2 \) \( \text{Ia}: \text{M} = \text{Ti or Zr, R = alkyl group} \) are well known. In contrast, titanocene and zirconocene aryloxides, which are less studied, are reported to be prepared by the reaction of metallocene dichloride with an appropriate simple or substituted phenol, usually in the presence of a base or alternatively with its alkali metal salt. However, the course of a particular reaction is often not predictable, as the stoichiometry and yields of the products frequently depend markedly on the reaction conditions and reagents employed. For example, the reaction of titanocene dichloride with sodium phenoxide is claimed to yield titanocene diphenoxide, whereas, a related reaction involving excess of \( \text{NaOC}_{6}\text{F}_{5} \) gave only \( \text{Cp}_2\text{TiCl} (\text{OC}_{6}\text{F}_{5}) \). Recently Lappert and coworkers have described the synthesis and characterization of a large number of titanocene and zirconocene aryloxides using isopropyl or \( t \)-butyl substituted phenols. They have also reported that interaction of titanocene dichloride with two equivalent of \( [\text{Li(OC}_{6}\text{H}_{3}\text{Bu}^{1-2,6}) \text{(OEt)}] \) and a catalytic amount of \( \text{N,N,N',N'}\text{-tetramethylethylenediamine (TMEDA)} \) yields deep purple crystals of \( \text{Cp}_2\text{Ti(OR)} \), wherein Ti(IV) is reduced to Ti(III).

In view of the above, we describe herein the synthesis and characterization of some new titanocene and zirconocene aryloxides derived from less hindered phenols.

Materials and Methods

All experiments were carried out under anhydrous conditions. Prior to use all the glass apparatus were carefully washed, rinsed with ethyl alcohol and oven-dried at 130-140°C for ~2 hr and cooled either in a desiccator or in a dry environment after protecting them with guard tubes filled with anhydrous calcium chloride.

The \( \text{Cp}_2\text{M(OR)}_2 \) \( \text{(M = Ti or Zr, R = alkyl group)} \) was purified by recrystallization from CHCl, Solvents(s) were made anhydrous by published procedures prior to use. Phenols were purified by recrystallization from n-hexane, followed by distillation under reduced pressure. Titanium and zirconium were estimated as their oxides, while chloride was estimated by Vohlard's method.

Infrared (4000-200 cm\(^{-1}\)) and PMR spectra were recorded on a Perkin-Elmer model 557 and 90 MHz JEOL FX 90 instruments respectively. Molecular weights were measured ebullioscopically (Gallenkamp) in benzene.

Synthesis of complexes

The following preparative methods are typical of each type of titanocene and zirconocene aryloxides.

(a) \( \text{Synthesis of} \ \text{Cp}_2\text{TiCl} (\text{OAr'}) (\text{Ia}) \)

To a suspension of \( \text{Cp}_2\text{TiCl}_2(2.31 g; 9.3 \text{ mmol}) \) in THF (~30 ml) was added a solution of \( \text{KOAr'} \). To the mixture was added a solution of \( \text{Li(OC}_{6}\text{H}_{3}\text{Bu}^{1-2,6}) \text{(OEt)} \) and a catalytic amount of \( \text{N,N,N',N'}\text{-tetramethylethylenediamine (TMEDA)} \) yields deep purple crystals of \( \text{Cp}_2\text{Ti(OR)} \), wherein Ti(IV) is reduced to Ti(III).

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The \( \text{Cp}_2\text{MCl}_2(M = \text{Ti or Zr} \) (Aldrich) was purified by recrystallization from CHCl. Solvents(s) were made anhydrous by published procedures prior to use. Phenols were purified by recrystallization from n-hexane, followed by distillation under reduced pressure. Titanium and zirconium were estimated as their oxides, while chloride was estimated by Vohlard's method.

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To a suspension of \( \text{Cp}_2\text{TiCl}_2(2.31 g; 9.3 \text{ mmol}) \) in THF (~30 ml) was added a solution of \( \text{KOAr'} \) [prepared by refluxing potassium (0.36 g; 9.2 mmol) and 3,5-dimethylphenol (1.13 g; 9.3 mmol) in THF (~60 ml)] and the reaction mixture stirred for ~12 hr at room temperature. The precipitated KCl(0.70 g; ~94%) was removed by filtration. Removal of volatiles from the filtrate afforded (2.92 g; ~94%) as brown red solid. The product was purified by recrystallization from THF-n-hexane mixture.

(b) \( \text{Synthesis of} \ \text{Cp}_2\text{ZrCl}(\text{OAr'})_2 (\text{IIb}) \)

Freshly prepared solution of \( \text{KOAr'} \) [prepared by refluxing potassium (0.51 g; 13.0 mmol) and 2,5-dimethylphenol (1.60 g; 13.1 mmol) in THF (~60 ml)] was added at room temperature to a suspension
of \( \text{Cp}_2\text{ZrCl}_2 \) (1.91g; 6.5 mmol) in THF (~20 ml). The resulting reaction mixture was stirred at room temperature for ~18 hr, the precipitated KCl (1.05g; 14.0 mmol) filtered off, volatiles and solvent removed from the filtrate and the dirty-green solid (2.06g; ~70%) obtained, was recrystallized from THF-n-hexane, to afford pure IIIb.

Results and Discussion

The reactions of metallocene dichloride (\( \text{Cp}_2\text{MCl}_2 \)) with potassium aryloxide in 1:1 and 1:2 molar ratios in THF at room temperature result in the formation of mono- and di-aryloxide derivatives respectively (Eq.1) (Table 1).

\[
\text{Cp}_2\text{MCl}_2 + x \text{KOAr} \rightarrow \text{Cp}_2\text{MCl}_{(2-x)} (\text{OAr})_x + x \text{KCl} \quad (1)
\]

Ia: \( M = \text{Ti}, \ x = 1, \text{Ar} = 3,5\text{-dimethylphenyl(}\text{Ar'}\text{)} \)
Ib: \( M = \text{Ti}, \ x = 2, \text{Ar} = \text{Ar'} \)
IIa: \( M = \text{Zr}, \ x = 1, \text{Ar} = \text{Ar'} \)
IIb: \( M = \text{Zr}, \ x = 2, \text{Ar} = \text{Ar'} \)
IIIa: \( M = \text{Zr}, \ x = 1, \text{Ar} = 2,5\text{-dimethylphenyl(}\text{Ar}''\text{)} \)
IIIb: \( M = \text{Zr}, \ x = 2, \text{Ar} = \text{Ar}'' \)

These derivatives I-III appear to be less moisture-sensitive in comparison with the corresponding alkoxide derivatives. In order to examine the relative reactivity of Zr-Cl and Zr-OAr bonds, the reaction of \( \text{Cp}_2\text{ZrCl} (\text{OAr'}) \) with water in 2:1 molar ratio in THF has been carried out; formation of the product, IV (\( \text{Cp}_2\text{ZrCl}_2\text{O} \)) (Eq.2), indicates a greater reactivity Zr-OAr bond compared to the Zr-Cl bond.

\[
2\text{Cp}_2\text{ZrCl} (\text{OAr'}) + \text{H}_2\text{O} \rightarrow (\text{Cp}_2\text{ZrCl})_2\text{O} + 2\text{Ar'}\text{OH} \quad (2)
\]

All these complexes are coloured (dirty-green, light-yellow or brown-red) solids. Except (\( \text{Cp}_2\text{ZrCl}_2\text{O} \)) all these derivatives are soluble in common organic solvents such as THF, benzene, toluene, and are monomeric (ebullioscopically) in benzene.

Infrared spectra in Nujol mull of these derivatives exhibit structurally important absorptions: 470-540 \( \text{v(M-O)} \) (M = Ti or Zr) and ~1200 \( \text{v(C-O)} \) cm\(^{-1}\), the shift of \( \text{v(C-O)} \) to lower wavenumber by \( \Delta \text{v} \sim 30 \text{ cm}^{-1} \) from those observed in free phenols (\( \sim 1230 \text{ cm}^{-1} \)) is an evidence of the attachment of aryloxide moiety to metal through oxygen. The absorptions due to bonded cyclopentadienyl groups are observed at 810 ± 10 \( \text{v(C-H) deformation out-of-plane,} \) 1020 ± 10 \( \text{v(C-H) deformation in-plane,} \) 1120 \( \text{v(ring breathing mode)} \), and 1430± 15 cm\(^{-1}\) (vC=C), while vC-H modes appear to merge into the nujol peaks. The absorptions due to aromatic ring have been

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Reactants (g; mmole)</th>
<th>Product yield (g, %) and nature</th>
<th>Found (Calc.) %</th>
<th>mp. (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Cp}_2\text{TiCl}_2 ) (2.31; 9.3) + KOAr'</td>
<td>{K(0.36;9.2) + Ar'OH(1.13; 9.3)}</td>
<td>\text{Cp}_2\text{TiCl(OAr') (Ia),} (2.92; ~94), brown-red solid</td>
<td>14.16(14.30) 10.45(10.60) 107</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Cp}_2\text{TiCl}_2 ) (1.96; 7.8) + 2KOAr'</td>
<td>{K(0.62;15.7) + Ar'OH(1.92;15.7)}</td>
<td>\text{Cp}_2\text{Ti(OAr')}_2 (Ib) (3.20; ~97), brown-red solid</td>
<td>11.28(11.40) — 88</td>
</tr>
<tr>
<td>3</td>
<td>( \text{Cp}_2\text{ZrCl}_2 ) (2.00;6.9) + KOAr'</td>
<td>{K(0.27;5.8) + Ar'OH(0.84;6.8)}</td>
<td>\text{Cp}_2\text{ZrCl(OAr') (IIa),} (2.18; ~91), light yellow solid</td>
<td>23.66(24.00) 9.50(9.30) 102</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Cp}_2\text{ZrCl}_2 ) (2.15;7.4) + 2KOAr'</td>
<td>{K(0.58;14.7) + Ar'OH(1.80;14.7)}</td>
<td>\text{Cp}_2\text{Zr(OAr')}_2 (IIb), (3.37; ~98), light brown solid</td>
<td>19.70(19.69) — 97</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Cp}_2\text{ZrCl}_2 ) (2.09;7.1) + KOAr'</td>
<td>{K(0.28;7.1) + Ar'OH(0.87;7.1)}</td>
<td>\text{Cp}_2\text{ZrCl(OAr') (IIIa),} (2.51; ~93), light green solid</td>
<td>23.50(24.00) 9.46(9.30) 100</td>
</tr>
<tr>
<td>6</td>
<td>( \text{Cp}_2\text{ZrCl}_2 ) (1.91;6.5) + 2KOAr'</td>
<td>{K(0.51;13.0) + Ar'OH(1.60;13.1)}</td>
<td>\text{Cp}_2\text{Zr(OAr')}_2 (IV), (2.06; ~70), dirty-green solid</td>
<td>20.04(19.89) — 86</td>
</tr>
<tr>
<td>7</td>
<td>( \text{Cp}_2\text{ZrCl(OAr')} + ) H(_2)O (0.03;1.5)</td>
<td></td>
<td>34.50(34.46) 13.38(13.41) —</td>
<td></td>
</tr>
</tbody>
</table>

* Melts with decomposition
observed in the range: 1150-1160 (ν = C-H deformation in-plane), 945 ± 5, 750-760 (ν = C-H deformation out-of-plane) and 1560-1640 (νC = C) cm⁻¹. In the chloro derivatives Ia, IIA and IIla, ν(M-Cl) modes are observed at 345 ± 5 cm⁻¹. All these assignments have been made on the basis of published data on aryloxide derivatives.

The PMR spectrum of Ia in CDCl₃ exhibits singlets at δ 2.19 and 6.32 due to methyl and Cp-protons respectively, whereas aromatic protons are observed as complex multiplets in the range of δ 6.52-5.98 due to overlapping of signals due to α- and p-protons. In the PMR spectrum of Ib, methyl and cyclopentadienyl protons are observed as singlets at δ 2.33 and 6.26 respectively. The aryloxide ring p-proton is observed as a triplet (J = 4.3 Hz) centred at δ 6.48, while a doublet (J = 4.3 Hz) centred at δ 6.34 is due to o-protons. The PMR spectrum of IIa exhibits two singlets at δ 2.31 and 6.39 for methyl and cyclopentadienyl protons respectively, whereas signals due to aryloxide ring protons appear as complex multiplets in the range of 6.11-6.65 ppm. The spectrum of IIb displays methyl and Cp-protons as singlets at δ 2.21 and 6.27 respectively, while signals due to resonating aromatic ring protons appear as a triplet (J = 4.3 Hz) at δ 6.43 (p-protons) and as a doublet (J = 4.3 Hz) centred at δ 6.34 (α-protons).

The PMR spectrum of IIIa, exhibits α-, m-methyl and Cp-protons as singlets at δ 2.17, 2.39 and 6.33 respectively. The m-aromatic proton appears as a doublet (J = 8.6 Hz) centred at δ 6.95, while the p-aromatic proton appears as a triplet centred at δ 6.61 arising from two overlapping doublets. The α-aromatic proton signal appears as a doublet (J = 4.3 Hz) centred at 6.43 one peak of which merges into the Cp-protons signal.

The PMR spectrum of IIIb displays singlets at δ 2.12, 2.26 and 6.29 for α, m-methyl and Cp-protons respectively, whereas m- and o-aromatic protons appear as doublets at 6.99 (J = 8.6 Hz) and 6.36 (J = 4.3 Hz) respectively. The p-aromatic protons appear as a triplet centred at δ 6.58 due to the overlapping of double doublets.

A characteristic feature of the PMR data is that the signal due to Cp-protons in all these new derivatives has been found to shift to higher field compared to that in the parent metallocene dichlorides (Cp₂MCl₂). This may be due to enhancement of electron density on the central metal atom by replacement of a chloride with an aryloxide ligand. Such an enhancement of electron density on the metal centres, would favour donation of electron density from the metal to the Cp rings, consequently enhancing the shielding effect for ring protons.

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References