REACTION OF TITANOCENE ALKYLS WITH PYRIDINES; A NOVEL TYPE OF CYCLOMETALLATION REACTION

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Summary

Reaction of Cp₂TiR (R = alkyl) with 2-substituted-pyridines and with quinolines leads to α-metallation of these ligands with formation of triangular titanocycles containing TiIII. Proof of the metallation at the α-position comes from reactions of the complexes formed with I₂ and D₂O/DCI which yield the corresponding iodo- and deuteropyridine and -quinoline derivatives. Reaction of Cp₂TiR with the structurally related ligand benzalaniline leads to a side-on coordinated benzalaniline complex of titanocene. Reactions of this diamagnetic complex with I₂, CO₂ and H₂ are described.

Introduction

The coordinatively unsaturated, thermally unstable compounds Cp₂TiR (R = alkyl) [1,2] show interesting reactivity towards a variety of organic substrates. Reagents such as isocyanides, isocyanates and carbon dioxide insert in the Ti-R bond. Pinacol-type dimerisation reactions take place with ketones [2] and disproportionation to Cp₂TiR₂ and Cp₂TiCS₂ is observed with carbon disulfide [1]. In this paper we describe reactions of Cp₂TiR (R = CH₃, C₂H₅, n-C₅H₁₁) with ligands formally containing the imine fragment –CH=N– e.g. 2-substituted pyridines, quinolines and benzalaniline. The properties of the complexes formed and some characterisation reactions are described. A preliminary report on part of this study has appeared previously [3].

Results and discussion

Reactions with 2-substituted pyridines and quinolines

Reaction of Cp₂TiR (R = CH₃, n-C₅H₁₁) with the 2-substituted pyridines 2-methylpyridine, 2-phenylpyridine and 2-vinylpyridine and with quinoline and
8-methylquinoline yields, in a novel type of cyclometallation, the α-metallated products I-V, according to Scheme 1.

SCHEME 1

Addition of these heterocyclic bases to green (R = CH₃) or brown (R = n-C₄H₉) solutions of Cp₂TiR at -80°C results in a colour change to dark green or blue, indicating formation of the adduct Cp₂TiR · L. On warming to room temperature a pronounced colour change to brown-purple is observed accompanied by evolution of RH, indicating metallation. The rate of metallation depends on the nitrogen base used. Under the conditions employed (∼10⁻¹ M in ether) α-metallation starts at about -40°C for all ligands except for 2-vinylpyridine, for which it sets in at about 0°C. The products (I-V, Scheme 1) are purple crystalline solids, and are obtained in 10-60% yields. They were characterized by elemental analyses (Table 1), IR and molecular weight determination (monomeric, Table 1).

As shown in Fig. 1, the IR spectra of the complexes I-V show the characteristic η²-C₆H₅ absorptions around 1010 cm⁻¹ and 790 cm⁻¹ and specific C-H out of plane deformation modes for the ligands.

The compounds are paramagnetic (EPR, Table 1) with 1 unpaired electron.

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**TABLE 1**

ANALYTICAL AND PHYSICAL DATA FOR THE COMPOUNDS I-V

(for numbering see Scheme 1)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>Melting point (°C)</th>
<th>Dec. Temp. °C</th>
<th>Mol. weight (g) ± 0.03 (calcld.)</th>
<th>Analysis (found (calcd.) (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>I</td>
<td>40</td>
<td>120</td>
<td>133</td>
<td></td>
<td>71.04(71.12)</td>
</tr>
<tr>
<td>II</td>
<td>35</td>
<td>114</td>
<td>124</td>
<td></td>
<td>75.42(75.91)</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>129</td>
<td>148</td>
<td>250 (283)</td>
<td>73.51(74.52)</td>
</tr>
<tr>
<td>IV</td>
<td>40</td>
<td>118</td>
<td>122</td>
<td></td>
<td>74.80(75.00)</td>
</tr>
<tr>
<td>V</td>
<td>60</td>
<td>118</td>
<td>137</td>
<td>288 (320)</td>
<td>74.80(75.00)</td>
</tr>
</tbody>
</table>

*a From DTA measurements. *b Cryoscopically in benzene. *c EPR (ether, 30°C, DPPH); g = 1.990(s). 
*d μeff = 1.67 B.M. (spin only-value expected for Ti(III) 1.73 B.M).
per Ti atom (Table 1), as expected for Ti$^{III}$ compounds. They are thermally stable up to about 130° C (Table 1), which indicates the presence of a coordinative Ti-N bond since coordinatively unsaturated compounds Cp$_2$TiR (R = aryl)
have a far lower thermal stability [4]. Internal coordination is also indicated by the fact that the complexes do not react with \( \text{N}_2 \) even at very low temperatures, in contrast to the complexes \( \text{Cp}_2\text{TiR} \) which form \( \text{(Cp}_2\text{TiR})_2\text{N}_2 \) [5]. The formulation of the complexes (I-V) as triangular titanocycles in which the ligand is \( \eta^2 \)-coordinated to Ti corresponds to the structure of other titanocene complexes such as \( \text{Cp}_2\text{Ti-acyl} \) [6] and \( \text{Cp}_2\text{Ti-iminoacyl} \) [7] complexes in which the ligands are also \( \eta^2 \)-coordinated to Ti; it is consistent with the preference of early transition metals to form small metallocycles. The observed \( \alpha \)-metallation is quite unusual, since normally metallation of this type of ligand gives five-membered metallocyclic rings with structures such as A, B and C [8-12].

![Diagrams](image)

(A) (B) (C)

The existence of a Ti-C bond at the 6-position in the pyridine complexes (I, II) and at the 2-position in the quinoline derivatives (IV, V) is demonstrated by reactions with \( \text{I}_2 \) or with \( \text{D}_2\text{O/DCI} \), which yield the expected iodo- and deuterio-pyridines and -quinolines according to Scheme 2. \( \text{Cp}_2\text{TiI}_2 \) and \( \text{Cp}_2\text{Ti-Cl}_2 \) were obtained almost quantitatively (80-95%), and were identified by IR, UV-vis and mass spectrometry. The pyridine and quinoline ligands formed (85-95%) were identified by IR, \(^1\text{H NMR} \) (Table 2) and mass spectrometry.
TABLE 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>M⁺(m/e)</th>
<th>δ(H₃)</th>
<th>¹J(H₄, H₂,δ)</th>
<th>δ(H₃, H₄)</th>
<th>δ(R⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>219</td>
<td>7.50(dd)</td>
<td>2.8 and 5.8</td>
<td>7.03-7.31(m)</td>
<td>δ(CH₃) 2.53(s)</td>
</tr>
<tr>
<td>Ib</td>
<td>94</td>
<td>7.47(t)</td>
<td>7.6 and 7.6</td>
<td>6.85-7.13(m)</td>
<td>δ(CH₃) 2.53(s)</td>
</tr>
<tr>
<td>Ib</td>
<td>156</td>
<td>7.95(dd)</td>
<td>3.0 and 8.0</td>
<td>c</td>
<td>δ(CH₃) 7.05-7.75(m)</td>
</tr>
<tr>
<td>IVa</td>
<td>255</td>
<td>7.97(d, br)</td>
<td>8.6</td>
<td>7.26-7.81(m)</td>
<td>d</td>
</tr>
<tr>
<td>IVb</td>
<td>130</td>
<td>8.07(d)</td>
<td>8.2</td>
<td>7.15-7.85(m)</td>
<td>d</td>
</tr>
<tr>
<td>Va</td>
<td>269</td>
<td>7.68(s, br)</td>
<td>—</td>
<td>7.60-7.72(m)</td>
<td>δ(CH₃) 2.75(d)</td>
</tr>
<tr>
<td>Vb</td>
<td>144</td>
<td>8.02(d)</td>
<td>8.0</td>
<td>7.08-7.72(m)</td>
<td>δ(CH₃) 2.73(s)</td>
</tr>
</tbody>
</table>

a CDCl₃, TMS, 35°C. b 100°C. c Coinciding with the phenyl absorptions. d δ(H₄) coinciding with δ(H₁, H₅, H₆, H₇).

(Table 2). As an example, Fig. 2 shows the ¹H NMR spectra of 2-methylpyridine and 2-methyl-6-deuteriopyridine (Ib). It can easily be seen that the characteristic H₆ signal in 2-methylpyridine disappears on deuteration, as, of course, does the coupling ¹J(H₄, H₃) (about 2 Hz in 2-methylpyridine).

It is remarkable that the α-metallation seems to be limited to ligands in which only one α-hydrogen is present. If two α-hydrogen atoms are present e.g. in pyridine itself or in 3- or 4-methylpyridine α-metallation does not take place. A plausible explanation could be that the presence of an α-substituent sterically forces the pyridine (or quinoline) ligand in the adduct stage in the yz plane of the molecule, in such a way that α-metallation with formation of RH is the favoured process (Fig. 3). In the absence of an α-substituent the ligand can rotate around the Ti-N bond out of the yz plane to a position where interaction of the π-electron system on the ligand with “in plane” (the yz plane) orbitals on Ti [13] leads to a stabilisation. In this situation the α-hydrogen is shifted into a position un favourable for RH formation and consequently α-metallation is unlikely.

Reactions with benzalaniline

In order to examine the scope of the α-metallation described above we treated Cp₂TiR (R = CH₃, C₂H₅) with another ligand containing the imine fragment –N=CH– viz. benzalaniline, a ligand which is known to be easily ortho-metallated [14]. This reaction gave a side-on coordinated benzalaniline com-
plex of titanocene, with formation of methane for R = CH₃ and a mixture of ethene and ethane (ratio 3 : 7) for R = C₂H₅, as shown in Scheme 3.

SCHEME 3

\[
\text{Cp}_2\text{TiR} + \text{N} = \text{C}_6\text{H}_5 \xrightarrow{\text{H}_2\text{C}_6\text{H}_5} \text{Cp}_2\text{Ti} \left(\begin{array}{c} H \\ N \\ \text{C}_6\text{H}_5 \end{array}\right) \rightarrow \text{CH}_4 (R = \text{CH}_3) \quad \text{or} \quad \text{C}_2\text{H}_4 \quad \text{and} \quad \text{C}_2\text{H}_5 (R = \text{C}_2\text{H}_5)
\]
Fig. 3. Schematic view of the adduct system Cp₂TiR • L (left) and of the corresponding yz plane for Cp₂TiR • 2-substituted pyridine (right).

Fig. 4. IR spectrum of Cp₂Ti • C₅H₅N=CHC₆H₅ (KBr, Nujol).

Fig. 5. ¹H NMR spectrum of Cp₂Ti • C₅H₅N=CHC₆H₅ (ether-d₄, TMS, 35°C; solvent peaks are omitted).
The green complex formed was isolated in 45\% yield. It is diamagnetic, thermally stable up to 130° C and monomeric. It was characterised by elemental analysis, IR (Fig. 4), ¹H NMR (Fig. 5) and ¹³C NMR.

As can be seen in Fig. 4, the IR spectrum of the compound shows the characteristic υ(C–H) and phenyl absorptions, and a band at 1312 cm⁻¹ which is tentatively assigned to υ(CN) (in benzalaniline υ(CN) is found at 1627 cm⁻¹; in secondary aromatic amines in the range 1260-1340 cm⁻¹). The ¹H NMR spectrum (Fig. 5) consists of two singlets for the Cp ligands at δ6.28 ppm and δ6.40 ppm, a singlet for the imine hydrogen at δ5.68 ppm (in the free ligand δ8.38 ppm) and a multiplet at δ6.50-7.40 due to the phenyl groups. The ¹³C NMR spectrum ether-d₁₀; 35° C) shows the Cp carbon atoms at δ120.5 ppm and δ118.7 ppm, the imine carbon atom at δ162.9 ppm (free ligand δ162.3 ppm) and the phenyl carbons in the range δ117.0-131.6 ppm. Both the IR and NMR data suggest a side-on coordination of the benzalaniline ligand to Ti and not an end-on coordination via the nitrogen lone pair, since this would not result in such a drastic lowering of υ(CN) in the IR spectrum or such a large upfield shift in the ¹H NMR spectrum of the imine hydrogen resonance (Δ 2.70 ppm) compared to the free ligand [15,16].

Concerning the mechanism of the reaction as shown in Scheme 3, it must be noted that in the reaction with R = C₂H₅ a substantial amount of ethene is formed. This suggests a benzalaniline-induced homolysis of the Ti-R bond with formation of the complex described and alkyl radicals, which can abstract hydrogen atoms from the medium or disproportionate. This reaction resembles to some extent the reaction of Cp₂TiR (R = CH₃) with CS₂ to yield Cp₂TiCS₂ and Cp₂TiR₂ [1], but in the present case formation of Cp₂TiR₂ is not observed. Furthermore, it is evident that in contrast to the reactions with pyridines and quinolines, no α-metallation takes place. This difference in reactivity is probably related to the fact that benzalaniline has the anti-conformation [17]. Upon coordination to Cp₂TiR the adduct shown in Fig. 6 will first be formed. In this adduct the imine hydrogen is in an unfavourable position with respect to the Ti-R bond, in contrast to the adducts formed by 2-substituted pyridines (Fig. 3). Therefore, in the case of benzalaniline α-metallation does not take place for steric reasons. Due to the high reactivity of the Ti-R bond the adduct is not stable and decomposes via cleavage of the Ti-R bond to give the products described.

The question arises whether the complex Cp₂Ti·C₆H₅N=CHC₆H₅ should preferably be regarded as a formally Ti⁺⁺ complex (with essentially sp² hybridised C and N and π-interaction between Ti and the ligand) or as a Ti⁺⁺ complex (a σ-bonded triangular metallacycle with sp³ C and N). The related azobenzene complex Cp₂Ti·C₆H₅N=NC₆H₅ was tentatively formulated as a Ti⁺⁺ complex mainly because hydrolysis yielded hydrazobenzene [18]. In order to get more insight in the bonding in our benzalaniline complex we carried out reactions with I₂, CO₂ and H₂, as shown in Scheme 4. In the reaction with I₂ Cp₂TiI₂ (81\%) and free benzalaniline is formed (85\%). Reaction with CO₂ gives the carbonato complex [(Cp₂Ti)(CO₂)]₂ (76\%) [19], CO and benzalaniline (90\%); this reaction can be regarded as a two-electron disproportionation of CO₂:

\[ 2 \text{CO}_2 + 2 e^- \rightarrow \text{CO}_3^{2-} + \text{CO} \]
Fig. 6. Schematic view of the adduct system $\text{Cp}_2\text{Ti} \cdot \text{benzalaniline}$ in the $yz$ plane of the molecule. The Cp ligands are omitted (see also Fig. 1).

**SCHEME 4**

\[
\begin{align*}
\text{Cp}_2\text{Ti} \xrightarrow{\text{I}_2} & \quad \text{Cp}_2\text{TiI}_2 + \text{C}_6\text{H}_5\text{N} = \text{CHC}_6\text{H}_5 \\
\text{Cp}_2\text{Ti} \xrightarrow{\text{CO}_2} & \quad \frac{1}{4} \left[ \text{Cp}_2\text{Ti}(\text{CO}_3)_2 \right]_2 + \frac{1}{2} \text{CO} + \text{C}_6\text{H}_5\text{N} = \text{CHC}_6\text{H}_5 \\
\text{Cp}_2\text{Ti} \xrightarrow{\text{H}_2} & \quad [\text{Ti}] + \text{C}_6\text{H}_5\text{CH}_2\text{NHCO}_2\text{H}_5
\end{align*}
\]

A similar disproportionation was reported by Floriani et al. for $\text{Cp}_2\text{Ti(CO)}_2$ [19]:

$$
\text{Cp}_2\text{Ti(CO)}_2 + ^{13}\text{CO}_2 \rightarrow \frac{1}{4} [(\text{Cp}_2\text{Ti})_2(^{13}\text{CO}_3)_2] + 2 \text{CO} + \frac{1}{2} ^{13}\text{CO}
$$

Reaction of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N} = \text{C} = \text{CHC}_6\text{H}_5$ with $\text{H}_2$ (and subsequent reaction with $\text{HCl}$ and $\text{NaOH}$) gives benzyl(phenyl)amine (92%).

The results of these three reactions do not enable us to distinguish definitely between the limiting formulations of the complex as a formally $\text{Ti}^{III}$ or $\text{Ti}^{IV}$ complex. The results of the reactions with $\text{I}_2$ and $\text{CO}_2$ seem to favour a description as a divalent titanium complex, but the reaction with $\text{H}_2$ suggests a tetravalent $\text{Ti}$ compound. The spectroscopic data as described above (IR, NMR) also do not allow a definite distinction to be made between the two limiting situations, although as mentioned before, the early transition metals seem to prefer to form small metallocycles.

**Experimental**

All experiments were carried out under argon. Solvents were distilled from benzophenoneketyltsodium under nitrogen. Compounds $\text{Cp}_2\text{TiR}$ were prepared from $\text{Cp}_2\text{TiCl}$ and $\text{RLi}$ at 80° C according to ref. 2. The pyridines and quinolines were distilled before use and stored under nitrogen; commercially available benzalaniline was used without further purification. $\text{CO}_2$ and $\text{H}_2$ were pur-
chased from Gardner Cryogenics. Elemental analyses were performed in the Microanalytical Department of this University under the supervision of Mr. A.F. Hamminga. IR spectra were measured on a JASCO IRA-2 spectrophotometer (KBr/Nujol), 1H NMR spectra were recorded on a Perkin-Elmer R-24B spectrometer and on a Varian XL-100 spectrometer. The EPR spectra were recorded on a Varian E3 X-band EPR spectrometer. Melting points and decomposition temperatures of solids were determined by differential thermal analysis (heating rate 1.5° C/min). Mass spectra were recorded by Mr. A. Kiewiet on an AEI-902 spectrometer at an ionizing voltage of 70 eV. GC experiments were performed on a Hewlett-Packard 428 GC apparatus on a Porapak Q column at 100° C.

**Preparation of** 
\[ \text{Cp}_5\text{Ti} \rightarrow \begin{array}{c} \text{CH}_3 \\ \text{Cp}_5\text{Ti} \end{array} (V, \text{Scheme 1}) \]

To a solution of 4.00 mmol of Cp₅TiCH₃ in 30 ml of ether at -78° C 5.00 mmol of 8-methylquinoline were added. The dark green mixture was slowly warmed to room temperature (two hours) during which the colour changed to brown-purple and methane was evolved (from about -40° C; GC). After being stirred at room temperature for 15 hours, the mixture was evaporated to dryness and extracted with 30 ml of n-pentane. On cooling the n-pentane extract to -78° C purple crystals of the title compound separated (2.40 mmol; 60%). The product is very air-sensitive and readily soluble in the common organic solvents. The other α-metallated compounds (I-IV) were prepared in the same way.

**Reaction of V with I₂**

To a solution of 0.30 mmol of the α-metallated product V in 5 ml of n-hexane at -78° C 0.45 mmol of I₂ was added. After warming to room temperature (two hours) a black precipitate of Cp₅TiI₂ (0.26 mmol; 87%) and a light yellow n-hexane solution had formed. Evaporation of this solution gave 2-iodo-8-methylquinoline (Va; 0.27 mmol; 90%). The reactions of the other α-metallated products (I-IV) with I₂ were carried out in the same way.

**Reaction of V with D₂O/DCI**

To a solution of 0.30 mmol of the α-metallated product V in 20 ml of ether at -78° C an eightfold excess of DCI in D₂O was added. After warming to room temperature (two hours) a red suspension (Cp₅TiCl₂) had formed. After addition of an excess of NaOH in 5 ml of D₂O and stirring for one hour a white aqueous layer and a light yellow ether layer had formed. Evaporation of the ether layer gave 2-deuterio-8-methylquinoline (Vb; 0.25 mmol; 83%). The reactions of the other α-metallated products (I-IV) with D₂O/DCI were carried out in the same way.

**Preparation of Cp₅Ti · C₅H₅N=CHC₄H₅**

To a solution of 4.00 mmol of Cp₅TiCH₃ in 30 ml of ether at -78° C 4.00 mmol of benzalaniline were added. The brown-green mixture was slowly warmed to room temperature (two hours) during which the colour changed to
green and methane was evolved (GC). After stirring at room temperature for two hours the mixture was evaporated to dryness and washed several times with 30 ml of n-pentane. The green product was recrystallized from 30 ml of ether to give green crystals of \( \text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\equiv \text{CHC}_6\text{H}_5 \) (1.80 mmol; 45%). The product is very air-sensitive and readily soluble in common organic solvents. Elemental analysis: C, 75.92; H, 6.25; Ti, 13.64. \( \text{C}_{25}\text{H}_{21}\text{NTi} \) calcd.: C, 77.09; H, 5.63; Ti, 13.37%. Molecular weight (cryoscopically in benzene): found 354 (calcd. 359). Decomposition temperature (DTA): 129\(^\circ\) C.

**Reaction of \( \text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\equiv \text{CHC}_6\text{H}_5 \) with \( \text{I}_2 \)**

To a solution of 1.00 mmol of \( \text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\equiv \text{CHC}_6\text{H}_5 \) in 20 ml of ether at -78\(^\circ\) C 1.00 mmol of \( \text{I}_2 \) was added. After warming to room temperature (two hours) a black precipitate of \( \text{Cp}_2\text{TiI}_2 \) (0.81 mmol; 81%; IR; mass spectrometry) and a light yellow ether solution had formed. Evaporation of this solution gave benzalaniline (0.85 mmol; 85%; IR; \(^1\)H NMR).

**Reaction of \( \text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\equiv \text{CHC}_6\text{H}_5 \) with \( \text{CO}_2 \)**

A solution of 0.50 mmol of \( \text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\equiv \text{CHC}_6\text{H}_5 \) in 30 ml of n-pentane was connected to a gas burette filled with \( \text{CO}_2 \). The reaction started immediately with formation of a green precipitate of \( [\text{Cp}_2\text{Ti}(\text{CO}_3)]_2 \) (0.38 mmol; 76%; IR) and CO (GC), and was complete after 30 minutes. Evaporation of the light-yellow n-pentane solution gave benzalaniline (0.45 mmol; 90%; IR; \(^1\)H NMR).

**Reaction of \( \text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\equiv \text{CHC}_6\text{H}_5 \) with \( \text{H}_2 \)**

A solution of 4.00 mmol of \( \text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\equiv \text{CHC}_6\text{H}_5 \) in 30 ml of ether was connected to a gas burette filled with \( \text{H}_2 \). The reaction started immediately with formation of a brown-purple solution and was complete after 30 minutes. The solution was cooled to -78\(^\circ\) C and an eightfold excess of \( \text{HCl} \) in \( \text{H}_2\text{O} \) was added, and the solution turned green (\( \text{Cp}_2\text{TiCl} \)). After addition of an excess of \( \text{NaOH} \) in 5 ml of \( \text{H}_2\text{O} \) and stirring for one hour with warming to room temperature, a white aqueous layer and a light yellow ether layer had formed. Evaporation of the ether layer gave benzyl(phenyl)amine (3.68 mmol; 92%; IR; \(^1\)H NMR; mass spectrometry).

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