Studies on Hydrazine & Azine Derivatives of Bis(indenyl)-titanium (IV) & -Zirconium (IV)

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Hydrazine and azine derivatives of bis(indenyl)-titanium (IV) and -zirconium (IV) of the types \( M(C_6H_5OCR:NNHR'(C_6H_5)_2)Cl \) and \( M(C_6H_5OCR:NNCR'OC_6H_5(C_6H_5)_2) \), where \( M = \text{Ti or Zr}, \ R = \text{H or CH}_3, \ R' = \text{H or CH}_3, \) have been synthesized by the reaction of bis(indenyl) titanium (IV) or -zirconium (IV) dichloride and appropriate hydrazone or azine in 30 ml tetrahydrofuran. The products have been characterized by chemical analyses, electrical conductance, IR, \(^1\text{H} \) NMR and electronic spectral studies.

The interest in the study of hydrazones has been growing due to their presence in biological systems\(^ 1\) and use in analytical chemistry\(^ 2\). In continuation of our previous work\(^ 3,4\) on organometallic hydrazine and azine complexes, some pentacoordinated hydrazine and azine derivatives of bis(indenyl)-titanium (IV) and -zirconium (IV) are reported in this note.

The reagents used were of AR grade. Bis(indenyl)-titanium (IV)\(^7\) or -zirconium (IV)\(^8\) dichloride, hydrazine and azine ligands\(^5\) were prepared by the methods reported in our earlier communications.

Titanium, zirconium, nitrogen and chlorine were determined by the standard methods\(^9\).

Conductance measurements were made in DMSO on a Systronic digital direct reading conductivity meter type 304. IR spectra were recorded in KBr in the 4000-400 cm\(^{-1}\) region on a Perkin-Elmer 621 grating spectrophotometer. \(^1\text{H} \) NMR spectra were recorded in deuterated chloroform on a JEOL JNM-Fx 200 FT NMR spectrometer. Chemical shifts are expressed relative to TMS as an internal reference (\(1\% \) by volume). The electronic spectra of the complexes were run on a Perkin-Elmer instrument.

**Preparation of the complexes**

To a stirred solution of bis(indenyl)-titanium (IV) or -zirconium (IV) dichloride (8 mmol) in 30 ml tetrahydrofuran, a solution containing 8 mmol of appropriate hydrazine or azine in 30 ml tetrahydrofuran was added slowly and the reaction mixture was refluxed for 10-12 hr. It was then filtered and the volume of the filtrate reduced to \( \approx 20 \) ml by evaporating the solvent under reduced pressure. Crystals of the product were precipitated on adding about 80 ml petroleum ether (60-80°C) to the concentrated filtrate. These were filtered, washed with petroleum ether, dried in vacuo and recrystallized from dichloromethane.

The reactions involved in the preparation of hydrazine and azine derivatives of bis(indenyl)-titanium (IV) and -zirconium (IV) may be represented by equations 1 and 2, respectively,

\[
(C_6H_5)_2MCl_2 + C_6H_4(OH)CR:NNHR'(C_6H_5)_2 + \text{THF} \rightarrow M(C_6H_5OCR:NNHR'(C_6H_5)_2)Cl + \text{HCl} \quad (1)
\]

\[
(C_6H_5)_2MCl_2 + C_6H_4(OH)CR:NNCR'OC_6H_5(C_6H_5)_2 + 2\text{HCl} \rightarrow M(C_6H_5OCR:NNCR'OC_6H_5(C_6H_5)_2) + 2\text{HCl} \quad (2)
\]

where \( M = \text{Ti or Zr}, \ R = \text{H or CH}_3, R' = \text{H or CH}_3, \) and \( R'' = \text{H or CH}_3 \).

The complexes were obtained as yellowish-brown to light brown solids. These are moderately soluble in chloroform, dichloromethane, acetone, THF and DMSO. Electrical conductance measurements in DMSO show these complexes to be nonelectrolytes. Table 1 lists the analytical data and physical characteristics of the complexes. The satisfactory elemental analysis support the stoichiometries assigned to these complexes.

The assignment of characteristic infrared frequencies was made on the basis of published work. The \( \text{C} - \text{H} \) stretching frequency at \( \approx 3090 \) cm\(^{-1}\) in the complexes is indicative of the indenyl group.\(^7\) The perpendicular hydrogen wagging vibration around 830 cm\(^{-1}\), the parallel hydrogen wagging mode at \( \approx 1025 \) cm\(^{-1}\), the bands due to \( \text{C} - \text{C} \) stretching and the ring breathing mode of the \( \pi \)-bond at \( \approx 1440 \) and \( \approx 1160 \) cm\(^{-1}\), respectively further confirm the presence of the indenyl group.\(^10\) Appearance of these indenyl bands in the complexes under investigation indicates that electrons in the indenyl group remain delocalised and \( \pi \)-bonded (\( \eta^2 \)) to the metal.\(^12\) Apart from this, the band at 445 cm\(^{-1}\) may be assigned to metal-ring stretching vibrations.\(^11\)

A strong band is observed at \( \approx 1630 \) cm\(^{-1}\) in the spectra of free hydrazine ligands, which can be
Table 1—Analytical and Physical Data of M(C₆H₄OCR:NNHR,)(C₉H₇)₂Cl and M(C₆H₄OCR:NN:CR'OCl₆H₄)(C₉H₇)₂ Complexes

<table>
<thead>
<tr>
<th>R, R' or R&quot;</th>
<th>Yield (%)</th>
<th>Dec. temp. (°C)</th>
<th>% Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M* N Cl</td>
</tr>
<tr>
<td>1 R = H, R' = H</td>
<td>72</td>
<td>219-222</td>
<td>10.26 6.13 7.74</td>
</tr>
<tr>
<td>2 R = H, R' = C₆H₅</td>
<td>68</td>
<td>164-165</td>
<td>(10.68) (6.24) (7.92)</td>
</tr>
<tr>
<td>3 R = H, R' = C₆H₄(NO₂)₂</td>
<td>64</td>
<td>185-188</td>
<td>(9.13) (5.34) (6.77)</td>
</tr>
<tr>
<td>4 R = CH₃, R' = H</td>
<td>62</td>
<td>180-181</td>
<td>7.42 9.02 5.63</td>
</tr>
<tr>
<td>5 R = CH₃, R' = C₆H₅</td>
<td>68</td>
<td>151-152</td>
<td>(7.80) (9.11) (5.78)</td>
</tr>
<tr>
<td>6 R = CH₃, R' = C₆H₄(NO₂)₂</td>
<td>65</td>
<td>175-178</td>
<td>(9.36) (5.54) (6.55)</td>
</tr>
<tr>
<td>7 R' = H</td>
<td>70</td>
<td>207-208</td>
<td>8.91 5.24 —</td>
</tr>
<tr>
<td>8 R&quot; = CH₃</td>
<td>68</td>
<td>183-185</td>
<td>(9.28) (5.43) —</td>
</tr>
<tr>
<td>9 R = H, R' = H</td>
<td>70</td>
<td>182-185</td>
<td>8.36 5.02 —</td>
</tr>
<tr>
<td>10 R = H, R' = C₆H₅</td>
<td>60</td>
<td>174-176</td>
<td>(8.81) (5.15) —</td>
</tr>
<tr>
<td>11 R = H, R' = C₆H₄(NO₂)₂</td>
<td>60</td>
<td>182-185</td>
<td>(18.15) (5.47) (7.03)</td>
</tr>
<tr>
<td>12 R = CH₃, R' = H</td>
<td>58</td>
<td>186-188</td>
<td>(18.55) (5.69) (7.22)</td>
</tr>
<tr>
<td>13 R = CH₃, R' = C₆H₅</td>
<td>62</td>
<td>137-138</td>
<td>15.84 4.78 6.09</td>
</tr>
<tr>
<td>14 R = CH₃, R' = C₆H₄(NO₂)₂</td>
<td>56</td>
<td>172-174</td>
<td>(16.07) (4.93) (6.25)</td>
</tr>
<tr>
<td>15 R' = H</td>
<td>60</td>
<td>117-120</td>
<td>13.52 8.57 5.56</td>
</tr>
<tr>
<td>16 R&quot; = CH₃</td>
<td>62</td>
<td>165-167</td>
<td>(13.87) (8.51) (5.40)</td>
</tr>
</tbody>
</table>

*M = Ti for S. No. 1-8 and Zr for S. No. 9-16.

assigned to the absorption due to the azomethine ( >C =N − ) group8,12. In the complexes, this band is shifted to lower wave numbers (~ 1606 cm⁻¹) showing the coordination of azomethine nitrogen to the metal13,14. The N − N frequency found at ~940 cm⁻¹ in the free ligands is shifted to higher values (~ 970 cm⁻¹).

A high intensity band at ~1265 cm⁻¹ in the free hydrazone ligands may be assigned to the phenolic C − O stretching8,12. In the complexes this band appears at ~1295 cm⁻¹, indicating bonding of the hydrazone ligand through oxygen. Furthermore, the disappearance of the broad ν(OH) band (present in the ligand in the 3450-3390 cm⁻¹ region) from the spectra of hydrazone complexes also indicates the replacement of the hydroxyl proton with the metal.

The coordination of the azomethine nitrogen and bonding of the phenolic oxygen to the metal are supported by the appearance of two new absorption bands in the spectra of hydrazone derivatives at 530-550 and 435-470 cm⁻¹, which may be assigned to ν(M −N) and ν(M −O) vibrations15, respectively. A band at ~370 cm⁻¹ is characteristic of ν(M −Cl) vibration12.

As expected, the spectra of the azine complexes do not show ν(OH), ν(NH) and ν(M −Cl) vibrations. The splitting and lowering of the ν(C = N) vibration suggest the coordination of one of the methine nitrogens and hence the formation of two dissimilar rings. The ν(C − O) phenolic shifts to higher frequency and ν(M −N) and ν(M −O) vibrations appear as a result of complex formation.

The ¹H NMR spectra of the complexes have been recorded in deuterated chloroform. All the hydrazone compounds give three different resonance signals corresponding to (i) the −CR = N − group proton(s),
appearing at $\delta 8.64$ (R=H) and $\delta 3.00$ (R=CH$_3$),
which show a downfield shift as compared to the
signals in the corresponding free hydrazone ligands at
$\delta 8.40$ (R=H) and $\delta 2.75$ (R=CH$_3$), indicating
deshielding as a result of coordination of the nitrogen
to metal; (ii) the resonance signals due to indenyl
protons overlap with those of aromatic proton signals
of hydrazone ligand and result in a complex multiplet
in the range $\delta 6.70-7.80$; (iii) the $\text{-NH-}$ and $\text{-NH}_2$
protons ($\delta 4.85$ and $\delta 4.30$, respectively) appear at
the same positions as observed for the free hydrazone
ligands.

The $^1\text{H}$ NMR spectra of the azine complexes show
two different resonance signals corresponding to (i)
$\text{CR}^+ = \text{N-}$ group proton(s); and (ii) aromatic
protons and are quite similar to the $^1\text{H}$ NMR spectra of the hydrazone complexes.

The electronic spectra of the complexes in
chloroform exhibit a single band in the region 402-
413 nm in accordance to the electronic configuration $(n-1)d^0, ns^0$ of titanium and zirconium$^{12}$.
Based on analytical data, general behaviour and
physicochemical studies, structures I and II may be
proposed for the present hydrazone and azine
derivatives respectively.

References