

Chelated Titanium(IV) Derivatives of 1,1-Diphenylethanol & Phenolphthalein†

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The substitution of isopropoxy groups in bis-chelated titanium(IV) diisopropoxides by 1,1-diphenylethanol or phenolphthalein affords the chelated titanium(IV) derivatives. The monobasic bidentate chelating ligands used are salicylaldehyde, 8-hydroxyquinoline, β -diketones, ketonic phenols etc. The products have been found to be monomeric and appear to have a hexacoordinated octahedral geometry around titanium similar to the parent bis-chelated titanium diisopropoxides.

In our continuing interest in the chemistry of hexacoordinated bis-chelated titanium(IV) complexes¹⁻⁴, in this note we report the preparation and characterisation of some new bis-chelated titanium complexes of 1,1-diphenylethanol and phenolphthalein.

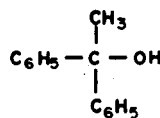
Reactions were carried out under dry nitrogen using anhydrous solvents.

Bis-salicylaldehyde-di-(diphenylethoxy)titanium(IV):

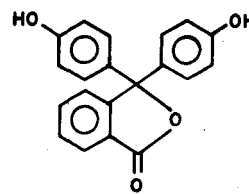
Isopropyl titanate (1.42 g; 5 mmol) and salicylaldehyde (1.22 g; 10 mmol) were mixed in benzene (50 ml) and isopropanol formed in the reaction was removed azeotropically (2 hr). Without isolating the diisopropoxide derivative, it was further reacted with 1,1-diphenylethanol (1.98 g; 10 mmol) in benzene (25 ml), again removing isopropanol formed azeotropically (3 hr). After the reaction, the contents were filtered or centrifuged and the clear solution concentrated under reduced pressure to get yellow crystals of the desired product which were washed with hexane and kept *in vacuo*, yield 70% (2.4 g) [Found: Ti, 7.02; C, 73.93; H, 5.04. $(C_7H_5O_2)_2Ti(C_{14}H_{13}O)_2$ requires Ti, 7.01; C, 73.68; H, 5.26%].

Other chelated titanium derivatives of diphenylethanol and those of phenolphthalein were prepared similarly; with the latter 1:1 molar ratio was used.

Vigorous reaction took place when solutions of titanium tetrachloride and 1,1-diphenylethanol (I) in inert solvent were mixed in the cold giving rise to a mixture of chlorotitanium derivatives and HCl gas.

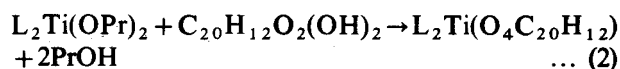
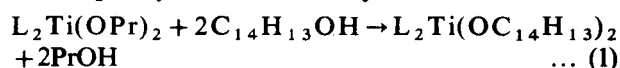


I



II

Phenolphthalein (II) also behaved similarly and gave chlorotitanium compounds of indefinite composition. However, the reaction between bis-chelated titanium diisopropoxide and 1,1-diphenylethanol in 1:2 molar proportion or phenolphthalein in 1:1 molar proportion proceeded smoothly in boiling benzene (Eqs 1 and 2). The liberated isopropanol was removed azeotropically and estimated by GLC.



No sign of any ligand exchange was noticed. The pure compounds were isolated from the solution by concentration and addition of a small amount of hexane if necessary. The diphenylethanol derivatives were more soluble in common organic solvents than those of phenolphthalein. Molecular weight determinations of diphenylethanol complexes (vapour pressure osmometry in toluene) indicated them to be monomeric. However, the phenolphthalein complexes were found to be polymeric.

The IR spectrum (ν_{max} in cm^{-1}) of 1,1-diphenylethanol exhibited $\nu(OH)$ at 3250(s) which disappeared in the spectra of bis-chelated di-(diphenylethoxy)titanium(IV) chelates. The $\nu(C=O)$ modes in the ligand, viz., salicylaldehyde, 2-hydroxyacetophenone and 2-hydroxy-4-methoxybenzophenone were seen at 1660, 1630 and 1620 respectively. In the titanium complexes of the above ligands with diphenylethanol, the $\nu(C=O)$ modes were shifted to lower wavenumbers and appeared at 1600, 1590 and 1580, respectively indicating coordination through carbonyl oxygen. In the chelate with acetoacetanilide, the $\nu(C=O)$ (ketonic) which appeared at 1680 was shifted to 1530 on coordination. The single peak at 1587 for $\nu(C=N)$ in 8-hydroxyquinoline appeared as split bands at 1570 and 1600 in its titanium complex containing diphenylethanol indicating coordination through nitrogen. In N-benzoyl-N-phenylhydroxylamine the $\nu(N-O)$

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Table 1—Products Obtained in the Reaction of Bis-chelated Diisopropoxytitanium $[L_2Ti(OPr)_2]$ with 1,1-Diphenylethanol and Phenolphthalein in 1:2 and 1:1 Molar Ratios respectively.

| LH | Product* (colour) | m.p. (°C) |
|-------------------------------------|---|--------------|
| Salicylaldehyde | $(C_7H_5O_2)_2Ti(C_{14}H_{13}O)_2$ (yellow) | † |
| 8-Hydroxyquinoline | $(C_9H_6NO)_2Ti(C_{14}H_{13}O)_2$ (yellow) | 65 |
| 2-Hydroxyacetophenone | $(C_8H_7O_2)_2Ti(C_{14}H_{13}O)_2$ (yellow) | † |
| 2-Hydroxy-4-methoxy benzophenone | $(C_{14}H_{11}O_3)_2Ti(C_{14}H_{13}O)_2$ (yellow) | 45 |
| Benzoylphenyl hydroxylamine | $(C_{13}H_{10}O_2N)_2Ti(C_{14}H_{13}O)_2$ (yellow) | 87 |
| Acetoacetanilide | $(C_{10}H_{10}O_2N)_2Ti(C_{14}H_{13}O)_2$ (yellow) | † |
| Salicylaldehyde | $(C_7H_5O_2)_2Ti(C_{20}H_{12}O_4)$ (brown) | 228 |
| 8-Hydroxyquinoline | $(C_9H_6NO)_2Ti(C_{20}H_{12}O_4)$ (grey) | 215 |
| Methyl salicylate | $(C_8H_7O_3)_2Ti(C_{20}H_{12}O_4)$ (yellow) | 248 |
| Acetylacetone | $(C_5H_7O_2)_2Ti(C_{20}H_{12}O_4)$ (brown) | 259 |
| Benzoylacetone | $(C_{10}H_9O_2)_2Ti(C_{20}H_{12}O_4)$ (red) | 190 |
| Dibenzoylmethane | $(C_{15}H_{12}O_2)_2Ti(C_{20}H_{12}O_4)$ (red) | 142 |
| Benzoylphenyl hydroxylamine | $(C_{13}H_{10}O_2N)_2Ti(C_{20}H_{12}O_4)$ (yellow) | 255 |
| Cyclopentadiene | $(C_5H_5)_2Ti(C_{20}H_{12}O_4)$ (orange) | 158 |

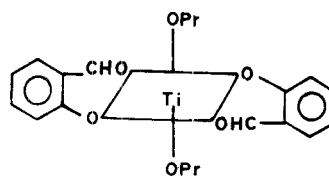
* Composition confirmed by elemental analysis.

† Low melting solids.

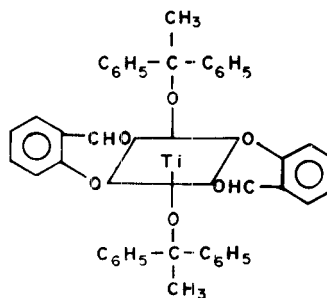
appeared at 920 in the ligand. This was shifted to 945 in the titanium complex indicating coordination of the ligand to the metal ion.

The spectra of phenolphthalein complexes were similar to those of 1,1-diphenylethanol derivatives but complicated. The broad bands due to both phenolic hydroxyl groups of phenolphthalein around 3200-3000 were absent in the spectra of the chelated titanium compounds. Coordination of the chelating ligands with titanium in the phenolphthalein derivatives were similar to that of diphenylethanol.

The PMR spectra of diphenylethanol in CCl_4 displayed hydroxyl proton as a singlet at δ 2.13. This signal was absent in its chelated titanium derivatives. Methyl protons of diphenylethanol appeared as a



III



IV

singlet at δ 1.86 and aromatic protons resonated as a multiplet at δ 7.0-7.4. The methyl protons absorbed downfield whereas aromatic protons shifted upfield and appeared in the region δ 6.5-7.4 in the complexes. The aldehydic proton of salicylaldehyde, the acetyl protons of 2-hydroxyacetophenone, the benzoyl protons of 2-hydroxy-4-methoxybenzophenone and the methine proton of acetoacetanilide—all resonated downfield in their titanium complexes as expected due to deshielding during complex formation. The PMR spectra of phenolphthalein derivatives could not be recorded because of their poor solubility in solvents.

From the IR and PMR spectra, and molecular weight measurements it may be concluded that these new bis-chelated titanium derivatives of 1,1-diphenylethanol and phenolphthalein contain hexacoordinated titanium in an octahedral environment similar to the parent bis-chelated titanium diisopropoxides. For example, bis-salicylaldehyde-titanium diisopropoxide and its condensation product with 1,1-diphenylethanol have similar geometry (see structures III and IV).

References

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