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Teuben, J.H.; Liefde Meijer, H.J. de

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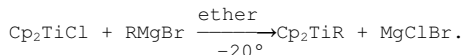
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NITROGEN COMPLEXES OF DICYCLOPENTADIENYL-
TITANIUM(III) COMPOUNDS.

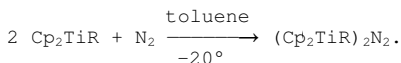
J.H. Teuben, H.J. de Liefde Meijer.

Laboratorium voor Anorganische Chemie,
Rijksuniversiteit, Bloemsingel 10, Groningen.
The Netherlands.

In nitrogen-fixation systems based on Cp_2TiCl_2 , viz.:
 $\text{Cp}_2\text{TiCl}_2/\text{Na-naphthalide}$ or $\text{Cp}_2\text{TiCl}_2/\text{RMgBr}$, R=alkyl, the
exact nature of the active species is still unknown. It
has been suggested that Cp_2TiCl_2 is first converted to
low-valent titanium compounds. The latter compounds then
form complexes with nitrogen, whereupon nitrogen is reduced.
So far, nitrogen complexes of titanium have not been
isolated. We felt that a study of compounds of the type
 $\text{Cp}_2\text{Ti}^{\text{III}}\text{R}$ may be of importance in connection with the
above mentioned nitrogen-fixation reactions. The compounds
 Cp_2TiR were synthesized according to:

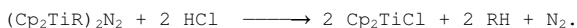


Complexes with R=phenyl, 2-methylphenyl, 3-methylphenyl,
4-methylphenyl, 2,6-dimethylphenyl, pentafluorophenyl and
benzyl were isolated and characterized. With the exception
of $\text{Cp}_2\text{Ti}(2,6\text{-dimethylphenyl})$ the compounds reacted at low
temperatures with molecular nitrogen:

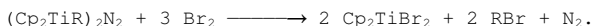


The nitrogen complexes were isolated as deep-blue crystalline
compounds and characterized by elemental analysis, physical
and chemical properties. The thermal stabilities of the
complexes appeared to be strongly dependent on the nature of
the group R, in the opposite sense as the stabilities of the
nitrogen-free complexes.

The nitrogen complexes in which the phenyl group bears no ortho-substituents and the benzyl compound decomposed at about 70°; the other complexes were found to be thermally less stable. Thermal decomposition quantitatively yielded N₂ together with RH and a dark Ti-containing residue in which the Cp₂Ti-group was no longer present. With HCl the nitrogen complexes reacted according to:



With bromine the reaction was as follows:



The complexes dissolved in toluene showed an intense absorption at 590 - 600 mμ ($\epsilon \sim 4 \cdot 10^4$ l/mol.cm). The IR spectra (recorded in nujol) showed that the Cp₂Ti-moiety and Ti-R bonds are present. No absorption in the 2200 - 1800 cm⁻¹ range contributable to end-on coordinated nitrogen was observed. ESR and magnetic-susceptibility measurements indicated the complexes to be diamagnetic. In accordance with the analysis and properties described we formulate the complexes as (Cp₂TiR)₂N₂; the N₂ group probably is coordinated to both Ti-atoms. (Cp₂TiC₆H₅)₂N₂ reacted with Na-naphthalide in THF. After addition of HCl to the reaction mixture, N₂H₄ and NH₃ were found to be present among the reaction products; their yield depended on the ratio (Cp₂TiC₆H₅)₂N₂ : Na-naphthalide.

The reaction of Cp₂TiCl with RMgBr (R=alkyl) did not result in the isolation of the corresponding alkyl complexes Cp₂TiR and (Cp₂TiR)₂N₂ so far. However in the reaction of Cp₂TiCl and C₂H₅MgBr the formation of a deep-blue nitrogen complex was observed at low temperatures. After addition of HCl to this reaction mixture NH₃ was found.