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**PHENYLDICYCLOPENTADIENYL TITANIUM(III) AND ITS
COMPLEX WITH NITROGEN
(Preliminary Communication)**

BY

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In contrast to complexes of composition $\text{Cp}_2\text{Ti(IV)R}_2$ (Cp = cyclopentadienyl), very little is known about complexes of the type $\text{Cp}_2\text{Ti(III)R}$, where R is an alkyl or aryl group σ -bonded to the metal¹, although such compounds have been suggested as intermediates in some reaction mixtures^{2,3}. The compound $\text{Cp}_2\text{Ti(III)(C}_2\text{H}_5)$ has been claimed several years ago⁴, but in our opinion this claim most probably is incorrect. Recently, it was found that one of the cyclopentadienyl ligands in the paramagnetic complex tricyclopentadienyltitanium(III) is σ -bonded to the metal⁵; $\text{Cp}_2\text{Ti(III)(C}_5\text{H}_5)$ is, therefore, the first example of the type of compound under discussion that has been isolated*.

We have undertaken a systematic study of compounds of the type $\text{Cp}_2\text{Ti(III)R}$. In the present communication we report the synthesis of $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ and some properties of this compound, particularly its reaction with nitrogen which yields a blue complex of composition $[\text{Cp}_2\text{Ti(C}_6\text{H}_5)\text{N}]_n$.

$\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ was prepared thus:

* In $\text{Cp}_2\text{Ti(III)(C}_3\text{H}_5)$ and homologues the allylic ligands are π -bonded at the metal⁶. Although the structure of the diamagnetic complex $[\text{Cp}_2\text{Ti(C}\equiv\text{CC}_6\text{H}_5)]_2$ is not fully known⁷, the phenylethynyl groups are certainly not simply σ -bonded to the titanium atom.

¹ H. J. de Liefde Meijer and F. Jellinek, *Inorg. Chim. Acta*, in press.

² H. H. Brintzinger, *J. Am. Chem. Soc.* **89**, 6871 (1967).

³ H. Masai, K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Japan* **41**, 750 (1968).

⁴ J. C. W. Chien and C. H. Boss, *J. Am. Chem. Soc.* **83**, 3767 (1961).

⁵ F. W. Siegert and H. J. de Liefde Meijer, *J. Organometal. Chem.* **20**, 141 (1969).

⁶ H. A. Martin and F. Jellinek, *ibid.* **8**, 115 (1967); R. B. Helmholtz, F. Jellinek, H. A. Martin and A. Vos, *Rec. Trav. Chim.* **86**, 1263 (1967).

⁷ J. H. Teuben and H. J. de Liefde Meijer, *J. Organometal. Chem.* **17**, 87 (1969).

After evaporating the solvent in a vacuum the compound was extracted from the reaction mixture with *n*-pentane. The extract was cooled to -78° , $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ separated as green leaflets. The yield was about 50%. All operations were performed in an argon atmosphere at temperatures below -20° .

The compound was characterized by elemental analysis [found: C, 75.45; H, 5.98; Ti, 18.33; calcd. for $\text{C}_{16}\text{H}_{15}\text{Ti}$ (255.18): C, 75.30; H, 5.93; Ti, 18.77%], the infrared spectrum ($\pi\text{-Cp}$ and C_6H_5 absorptions are present) and the magnetic behaviour (μ_{eff} about 1.50 B.M.). In accordance with the proposed composition, $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ in *n*-pentane reacts quantitatively with gaseous HCl thus:

and with bromine thus:

The compound is of low thermal stability. Differential thermal analysis (heating rate $4^{\circ}/\text{min}$) shows that $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ decomposes rapidly at $20\text{--}25^{\circ}$. This thermal decomposition generates 0.9 mole of benzene per mole of $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ (from gaschromatographic analysis), leaving a black residue. (Under the same conditions $\text{Cp}_2\text{Ti(IV)(C}_6\text{H}_5)_2$ decomposed at $110\text{--}120^{\circ}$ yielding 1.8 moles of benzene per mole of the complex.) Both in the solid state and in solution, $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ is extremely sensitive towards oxygen, the reaction resulting in complete destruction of the original structure.

At room temperature, $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ does not react with nitrogen (of atmospheric pressure), but at lower temperature a reaction takes place with formation of a blue complex. This reaction was studied in toluene solution where it is completely reversible; a strong maximum at $616 \text{ m}\mu$ in the absorption spectrum in the visible range indicates the formation of the blue complex (Fig. 1). The maximum at $616 \text{ m}\mu$ disappeared when the solution was warmed, or when the nitrogen atmosphere was replaced by argon; it immediately reappeared when nitrogen gas was again bubbled through the cold solution.

When a toluene solution of $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5)$ (0.56 g in 25 ml of solvent) under nitrogen was cooled at -78° glittering purple crystals separated from the blue solution. The crystals were isolated by filtration and washed with *n*-pentane at about -20° . Yield 0.20 g. The elemental analysis indicated a nitrogen complex of composition $[\text{Cp}_2\text{Ti(C}_6\text{H}_5)\text{N}]_n$ (Found: C, 71.33; H, 5.77; N, 4.6; Ti, 17.69; calcd. for $\text{C}_{16}\text{H}_{15}\text{NTi}$

Fig. 1. Absorption spectrum of a 2×10^{-3} M solution of $\text{Cp}_2\text{Ti(III)(C}_6\text{H}_5\text{)}$ in toluene in a nitrogen atmosphere (1 atm.) at various temperatures (2 mm cell).

(269.2): C, 71.38; H, 5.62; N, 5.20; Ti, 17.79%). The complex appeared to be extremely sensitive towards oxygen and thermally unstable. The complex slowly lost nitrogen in a vacuum or upon standing in a nitrogen or argon atmosphere at temperatures above 0° . Differential thermal analysis (heating rate $4^\circ/\text{min}$) showed a rapid decomposition starting at 60° ; benzene and nitrogen were found in the decomposition products, (gaschromatography). The infrared spectrum of the freshly prepared product in nujol clearly showed the presence of $\pi\text{-Cp}$ and C_6H_5 groups; no absorption in the $2200\text{--}1900\text{ cm}^{-1}$ range indicative of "end-on" coordinated nitrogen⁸ could be observed. Evidence for the presence of the intact Cp_2Ti moiety and the C_6H_5 group σ -bonded to the titanium atom also came from the reaction with HCl in *n*-pentane followed by oxidation, which resulted in the formation of nitrogen and the expected amounts of Cp_2TiCl_2 and C_6H_6 .

Although the experiments described permit of no definite conclusions about the structure of the blue nitrogen complex formed by $\text{Cp}_2\text{Ti(III)}$

⁸ H. Henrici-Olivé and S. Olivé, *Angew. Chem.* **81**, 679 (1969).

(C₆H₅) at low temperatures, they show that the Cp₂Ti moiety is still intact in the nitrogen complex and that the C₆H₅ groups are still bonded to the titanium atoms. The easy regeneration of N₂ by the reaction of the blue complex with HCl or upon heating it in the solid state, as well as the reversible reaction of N₂ with Cp₂Ti(III)(C₆H₅) in toluene solution indicate that the N₂ moiety is still intact in the molecule of the nitrogen complex. Therefore, the complex will not be a monomer, but probably a dimer [(Cp₂TiC₆H₅)₂N₂].

[Cp₂Ti(C₆H₅)N]_n is the first nitrogen complex of titanium that has been isolated. Nitrogen complexes of titanium have been postulated in nitrogen-fixation reactions of the Volpin-Shur and related types⁸; in these reactions nitrogen is recovered in the form of ammonia when the reaction products are solvolized. Solvolysis of [Cp₂Ti(C₆H₅)N]_n, however, did not yield ammonia, nor did reaction of the complex with hydrogen gas; in both cases nitrogen was liberated as N₂.

Other compounds of the type Cp₂Ti(III)R with σ-bonded groups R have also been prepared and their reactions with nitrogen are being studied. These results will be reported elsewhere.

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