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Preliminary communication

INTERACTION OF TITANOCENE GENERATED IN THE SYSTEM Cp_2TiCl_2 + Mg IN THF WITH BENZYNE AND TOLANE. A NOVEL ROUTE TO TITANAINDENE AND TITANACYCLOPENTADIENE COMPLEXES

V.B. SHUR, E.G. BERKOVICH, M.E. VOL'PIN,
Institute of Organo-Element Compounds of the USSR Academy of Sciences, Vavilov St. 28, Moscow 117813 (U.S.S.R.)
B. LORENZ and M. WAHREN
Zentralinstitut für Isotopen- und Strahlenforschung der Akademie der Wissenschaften der DDR, Permoser Str. 15, 705 Leipzig (D.D.R.)

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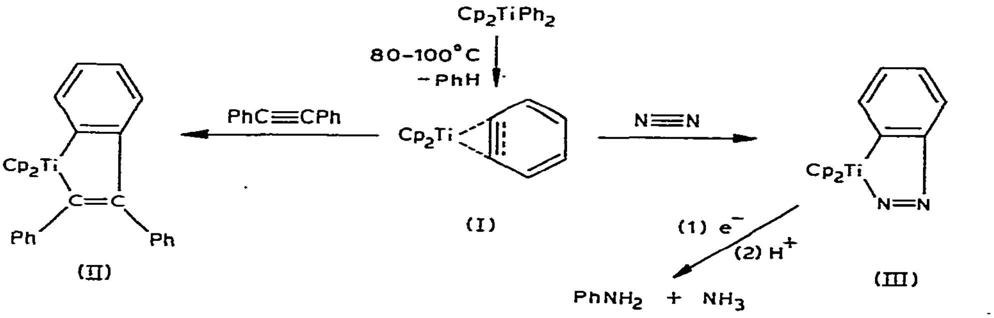
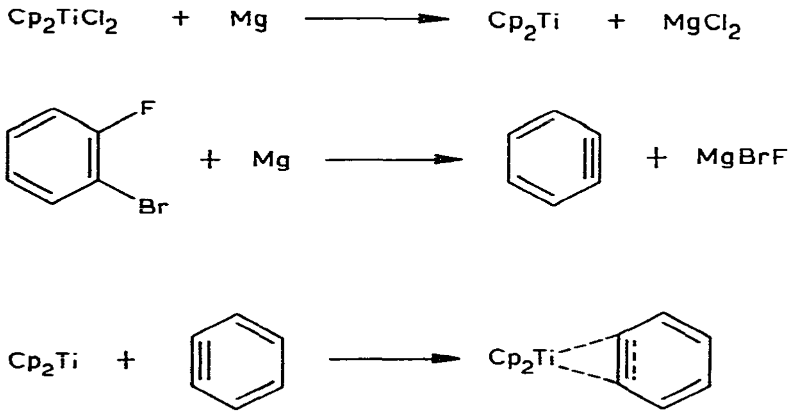
Summary

Direct synthesis of the titanaindene complex $Cp_2\overline{Ti[o\text{-}C_6H_4C(Ph)=C}(Ph)]$ through reaction of tolane with Cp_2Ti and benzyne, generated in the system Cp_2TiCl_2 + Mg + *o*-fluorobromobenzene in THF is described. Under similar conditions, reaction of Cp_2TiCl_2 with Mg in THF, in the presence of tolane only (ratio $Cp_2TiCl_2/Mg/Ph_2C_2 \sim 1/1/2$) yields the titanacyclopentadiene complex $Cp_2\underline{TiC(Ph)=C(Ph)C(Ph)=C}(Ph)$.

Thermal decomposition of Cp_2TiPh_2 proceeds via an intermediate benzyne complex of titanocene (I) [1] which can be trapped with tolane to form a stable titanaindene derivative (II) [2]. In an analogous reaction with dinitrogen, the corresponding metallacycle III was postulated as an intermediate, the products of the reaction, after hydrolysis, being aniline and ammonia [3].

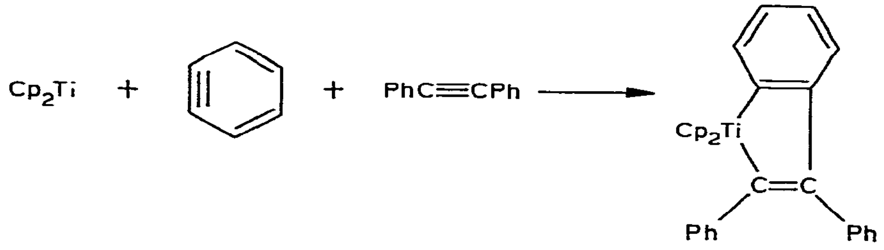


Recently we have found [4] that a similar mechanism of formation of aniline takes place in the interaction of dinitrogen with the system Cp_2TiCl_2 + Mg + *o*-fluorobromobenzene in THF, where the reaction of Cp_2Ti with free benzyne in situ may result in the same benzyne complex (I) as in thermolysis of Cp_2TiPh_2.



(I)

We now describe the isolation of titanaindene (II) from the reaction of tolane with this system, which is the first time that a metallaindene complex is synthesized from free benzyne and acetylene.

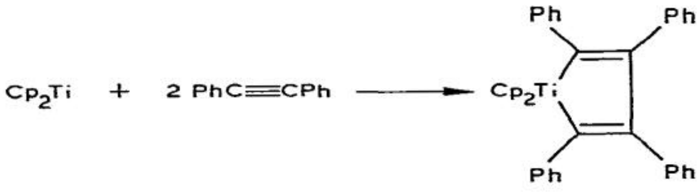


(II)

In a typical experiment, 1 g (4 mmol) of Cp_2TiCl_2, 0.72 g (4 mmol) of tolane, and 0.31 g (12.8 mmol) of Mg in 40 ml of THF were treated under argon with 1.4 g (8 mmol) of *o*-fluorobromobenzene, and the mixture was stirred under argon for 2.5—3 h. The resulting dark brown solution was evaporated to dryness in vacuo, and the residue was chromatographed under argon on a column packed with alumina. Elution of the greenish olive band with benzene, followed by evaporation of the solvent, yielded 1.1 g of a band with benzene, followed by evaporation of the solvent, yielded 1.1 g of a brownish-black resinous product. Its recrystallization from CH_2Cl_2/petroleum ether produced 0.26 g (15%) of dark green crystals of II, m.p. 225—228°C (dec.) under argon (lit. m.p. 227—228°C [2]). The IR and mass spectra of the product were identical to those of an authentic sample of II [2].

It is of interest that if the reaction between Cp_2TiCl_2 and Mg in THF is carried out in the presence of tolane only (ratio $Cp_2TiCl_2/Mg/Ph_2C_2 \sim 1/1/2$), a dark green solution is formed from which a well known titanacyclopentadiene (IV) [5] can be isolated. The reaction proceeds at room temperature with good yield and seems to be the best synthetic route to IV described until now [5—9]. The experimental procedure is given below.

$$Cp_2TiCl_2 + Mg \longrightarrow Cp_2Ti + MgCl_2$$



(IV)

1 g (4 mmol) of Cp_2TiCl_2, 0.1 g (4.1 mmol) of Mg, and 1.43 g (8 mmol) of tolane in 40 ml of THF were stirred at 20°C under argon for 5 h, and the resulting dark green solution was evaporated in vacuo. Chromatography of the residue on alumina under argon with benzene as the eluent gave 1.75 g (ca. 82%) of dark green IV. An analytical sample of IV with m.p. 148—150°C (dec.) under argon was obtained by recrystallization from hexane (lit. m.p. 150°C [5—7]). The ^1H NMR spectrum is identical to that described in the literature [6].

Thus, the titanocene generated in the system Cp_2TiCl_2 + Mg in THF is capable of reacting with benzyne and tolane, to form titanaindene and titanacyclopentadiene complexes. At present, we are studying the mechanisms of these reactions as well as exploring the possibility of using the Cp_2TiCl_2 + Mg system for the synthesis of other similar metallacycles.

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