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AMINE FORMATION IN THE THERMODECOMPOSITION OF DIARYLTITANOCENES IN THE PRESENCE OF DINITROGEN

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Summary

The reaction of dinitrogen with diaryltitanocenes, Cp_2TiAr_2 (Ar = C_6H_5, *p*-, *m*- and *o*-$CH_3C_6H_4$), has been studied. The heating of Cp_2TiPh_2 with N_2 results in aniline formation. Under similar conditions ditolyltitanocenes yield mixtures of isomeric toluidines. The mechanism of the amine formation is discussed.

Introduction

A number of dinitrogen reactions leading to the formation of amines is known to date. Such transformations were observed in the reactions of N_2 with aryllithiums in the presence of various titanium compounds [1] as well as directly from aromatic hydrocarbons and dinitrogen [2]. It is assumed that these reactions proceed via insertion of the N_2 molecule into the Ti—Ar σ-bond*.

Here we wish to report some new results obtained during of investigation of dinitrogen reactions with individual σ-aryl transition metal compounds.

Results and discussion

We have found that on heating diphenyltitanocene (Cp_2TiPh_2) with N_2 (80—100 atm) the products of dinitrogen fixation (after hydrolysis) contain some aniline (yield 1—2 mol. %) [6] together with ammonia (yield 10—12 mol. %) [7]. The reactions were carried out in benzene or diethyl ether at

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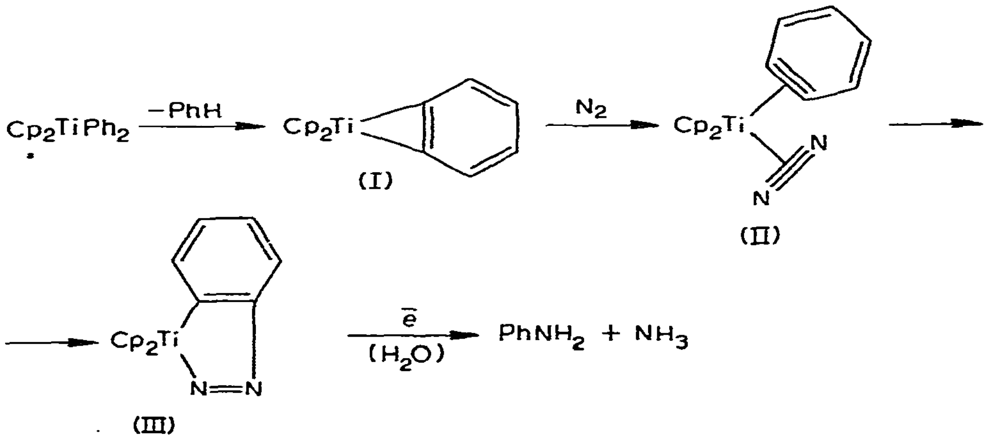
* Concerning the synthesis of amines from ketones (or aldehydes) and nitrides being formed in dinitrogen reduction by the systems Cp_2TiCl_2 + Mg, Cp_2TiCl_2 + $C_{10}H_8^{\cdot -}Na^+$, etc., see ref. [3, 4]. Recently Shiina reported the preparation of $[(CH_3)_3Si]_3N$ by reaction of N_2 with $(CH_3)_3SiCl$ and Li, in the presence of transition metal compounds [5].

80—130°, i.e., under conditions favouring the thermal decomposition of Cp_2TiPh_2 [8]. The replacement of ether by THF results in decreasing yields of both aniline and ammonia.

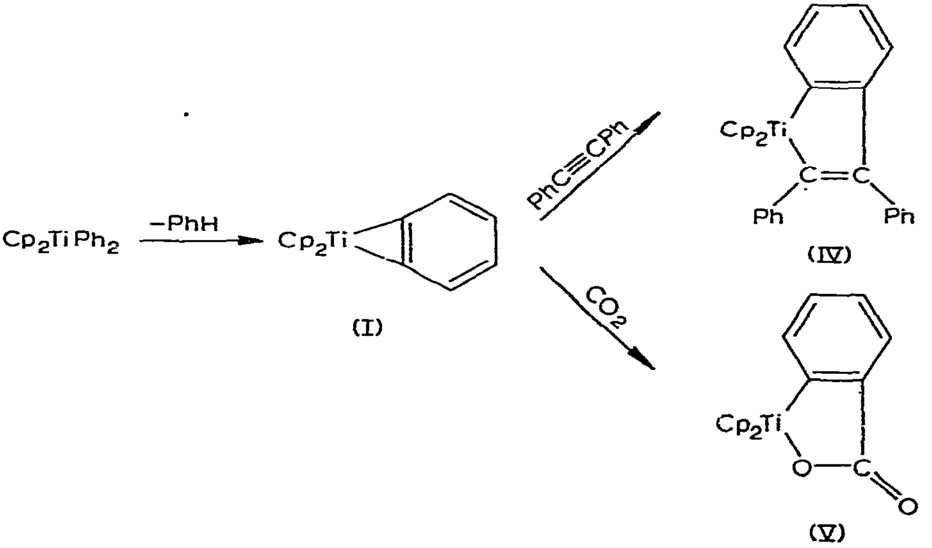
Aniline was identified by TLC and GLC as well as by diazotization and subsequent coupling of the diazonium salt with alkaline solutions of α- and β-naphthols. When Cp_2TiPh_2 was decomposed under helium (instead of N_2) neither aniline nor ammonia were detected upon hydrolysis.

The aniline formation in this reaction may proceed either by dinitrogen insertion into the Ti—Ph σ-bond followed by reductive splitting of an intermediate $Ti{-}N{=}N{-}C_6H_5$ derivative* or via N_2 reaction with the benzyne complex of titanocene (I) according to eqn. 1.



(1)

The formation of the benzyne complex I in the thermodecomposition of Cp_2TiPh_2 has been shown by Dvorak et al. [11]. It is assumed that I is an intermediate in the reaction of Cp_2TiPh_2 with tolane [12, 11] and CO_2 [13], giving rise to complexes IV and V respectively, as shown in eqn. 2.



(2)

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* The reducing agent in this and following reactions may be titanocene (in its hydride [9] or metastable [10] forms), which was reported to be the final product of the thermodecomposition of Cp_2TiPh_2 [8].

To elucidate the mechanism of aniline formation we investigated the reactions of N_2 with various ditolyltitanocenes:

$Cp_2Ti(p\text{-}CH_3C_6H_4)_2$, $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ and $Cp_2Ti(o\text{-}CH_3C_6H_4)_2$.

The thermolysis of these compounds (eqns. 3—5) should yield the corresponding dehydrotoluene complexes: VI from $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$, VII from $Cp_2Ti(o\text{-}CH_3C_6H_4)_2$. In the case of $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ one could expect the formation of a nearly equimolecular mixture of both adducts (VI and VII) provided the elimination of hydrogen atoms from *ortho-* and *para-*positions with respect to the CH_3 group, is equally effective.

Dinitrogen insertion in reactions with VI and VII may occur into either Ti—C bond of the dehydrotoluene adduct. As a result mixtures of isomeric toluidines must be formed: *p-* and *m-*toluidines (in ratio 1/1) from $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$, *o-* and *m-*toluidines (1/1) from $Cp_2Ti(o\text{-}CH_3C_6H_4)_2$ and all three toluidines ($p/m/o$ = 1/2/1) from $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$. More exactly, if polarization of the benzyne ring system under the effect of the electron-donating CH_3 group is taken into account, the ratios of isomeric toluidines in the case of the "benzyne" mechanism of amine formation should differ somewhat from those given above. Thus, if the dinitrogen molecule in the intermediate complexes of type II (which probably precede the cycles III, VIII—XI) bears some negative charge (cf. [14—16]), a tendency to increase the *m-*isomer content is to be expected in all cases.

The reactions of dinitrogen with ditolyltitanocenes were studied in benzene and ether at 100° ($P(N_2)$ 100 atm.). The initial $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ and $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ were prepared from Cp_2TiCl_2 and the corresponding organolithium compound by Summers' method [17] and were characterized by ^{13}C NMR spectra (Table 1).

Di-*o*-tolyltitanocene failed to be isolated by Summers et al. [17] apparently due to the instability of this compound as a result of steric hindrances caused by *o*-CH_3 groups. So we studied the reaction of N_2 with $Cp_2Ti(o\text{-}CH_3C_6H_4)_2$ at the moment of its supposed formation from Cp_2TiCl_2 and $o\text{-}CH_3C_6H_4Li$ (in ratio 1/2).

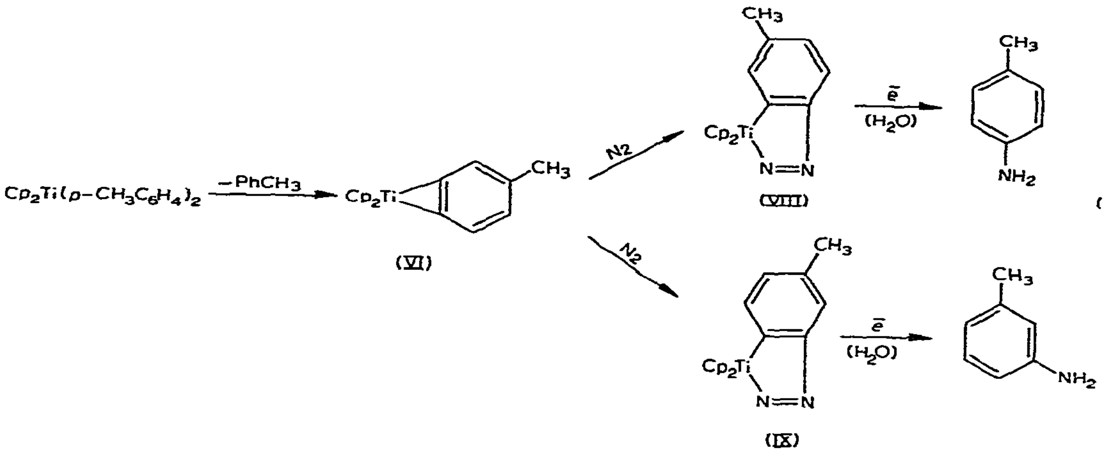
Our experimental data on dinitrogen reactions with ditolyltitanocenes are

TABLE 1

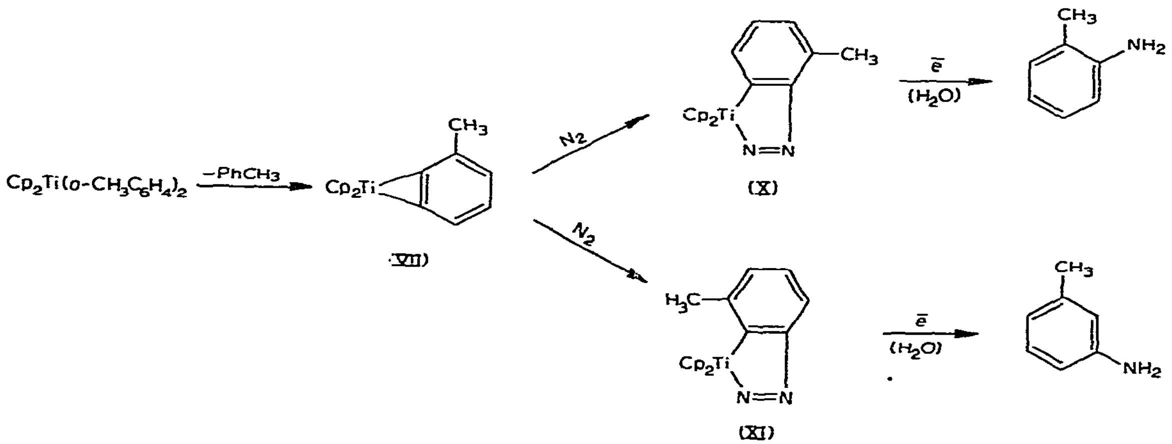
^{13}C NMR CHEMICAL SHIFTS OF DITOLYLTITANOCENES (IN $CHCl_3$)[a]

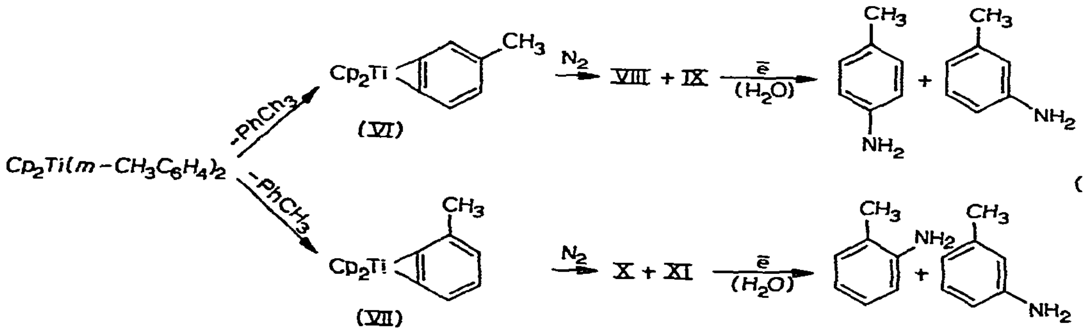
Titanium compound	Chemical shifts (ppm)		
	$\delta(Cp)$	$\delta(CH_3)$	$\delta(C_6H_4)$
$Cp_2Ti(p\text{-}CH_3C_6H_4)_2$	+115.5	+21.1	+187.5; +134.8; +127.0; +132.7;
$Cp_2Ti(m\text{-}CH_3C_6H_4)_2$	+15.5	+21.9	+191.2; +135.2; +131.7; +125.9; +124.2

[a] The spectra were recorded on Brucker HX-90 spectrometer (internal standard $CHCl_3$, values of chemical shifts are relative to TMS).


$Cp_2Ti(p-CH_3C_6H_4)_2$
$-PhCH_3$
Cp_2Ti
CH_3
(VI)
N_2
N_2
Cp_2Ti
N=N
(VIII)
(IX)
ē
(H_2O)
NH_2

(3)


$Cp_2Ti(o-CH_3C_6H_4)_2$
$-PhCH_3$
Cp_2Ti
CH_3
H_3C
(VII)
N_2
N_2
N=N
(X)
(XI)
ē
(H_2O)
NH_2


$Cp_2Ti(m-CH_3C_6H_4)_2$
$-PhCH_3$
$-PhCH_3$
Cp_2Ti
CH_3
(VI)
(VII)
N_2
VIII + IX
X + XI
ē
(H_2O)
NH_2
+

(5)

TABLE 2

THE ISOMERIC COMPOSITION OF TOLUIDINES IN REACTIONS OF N_2 WITH DITOLYLTITANOCENES[a]

Titanium compound	Solvent	Toluidine ratio (%)[b]		
		para	*meta*	*ortho*
$Cp_2Ti(p\text{-}CH_3C_6H_4)_2$	ether	36	64	
	benzene	43	57	
$Cp_2Ti(o\text{-}CH_3C_6H_4)_2$	ether	—	54	46
$Cp_2Ti(m\text{-}CH_3C_6H_4)_2$	ether	33	67	—
	benzene	36	64	—

[a] Reaction time 7 h. [b] From GLC analysis.

given in Table 2. It is seen that these reactions really lead to mixtures of isomeric amines. Thus, on heating N_2 with $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ *p*- and *m*-toluidines are formed. Under similar conditions the reaction of N_2 with $Cp_2Ti(o\text{-}CH_3C_6H_4)_2$ yields a mixture of *o*- and *m*-toluidines. The ratio of toluidines is only slightly dependent on the character of the solvent employed: in all cases *m*-toluidine is produced in greater quantity than the other isomer. All these data are in good agreement with the "benzyne" mechanism of amine formation.

The reaction of N_2 with $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ is more complicated. As mentioned above, in this case all three isomeric toluidines (*p*/*m*/*o* ~ 1/2/1) should be obtained provided the formation of adducts VI and VII is equally probable. However we have found that only *p*- and *m*-toluidines are produced by the reaction. It is essential that their ratio is very close to that of *p*- and *m*-toluidines obtained by the reaction of N_2 with $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$. This fact may indicate that thermolysis of $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ yields only one dehydrotoluene complex (VI). The formation of another complex (VII) seems to be prevented by the steric hindrances caused by the *o*-CH_3 group.

Strictly speaking, all these results could be explained another way by assuming that it is not dinitrogen itself that reacts with coordinated benzyne (or dehydrotoluene) but the nitride titanium derivatives, which are also formed in these reactions and give rise to ammonia upon hydrolysis [7]. Special experiments were carried out to check such a possibility. Diphenyltitanocene was introduced in the reaction with N_2 under conditions producing aniline and nitrides (100°, 7 h, $P(N_2)$ 100 atm., benzene). Dinitrogen was then removed. $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ was added and the mixture was heated for 7 h at 100° under helium pressure. In such conditions the dehydrotoluene—titanium complex could not react with N_2 but might be involved in the reaction with the nitride compound preliminarily formed. It appeared, however, that in the reaction products (upon hydrolysis) only aniline was present. Toluidines were not detected, even in trace amounts*.

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* In a blank experiment Cp_2TiPh_2 was decomposed under helium, $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ was added and the mixture was heated at 100° under N_2 pressure. The reaction products contained *p*- and *m*-toluidines in nearly the same quantities and ratio as in the standard procedure.

Thus, the nitride titanium derivatives formed in these systems are incapable of addition to benzyne; therefore it is unlikely that such compounds were responsible for amine formation in these reactions..

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