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NITROGEN FIXATION BY TRANSITION METAL COMPOUNDS: RESULTS AND PROSPECTS

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All modern processes for production of nitrogen-containing compounds begin with the fixation of atmospheric nitrogen, i.e. with its transformation from the molecular form into compounds with other elements. However, owing to the inertness of dinitrogen the overwhelming majority of its reactions proceed only at high temperatures and pressures, or under the action of electrical discharge.

At the same time it is well known that many microorganisms can fix dinitrogen directly from the atmosphere under ordinary conditions. The enzymic systems of these microorganisms, the active centers of which contain transition metals (iron and molybdenum or sometimes vanadium) catalyse the N_2 reduction to ammonia which is then utilized for synthesis of amino acids and proteins. The evident superiority of the enzymatic process over chemical methods of nitrogen fixation has long been noted by researchers, but all attempts at its imitation in a non-enzymatic way proved vain.

In 1962 we began work on this problem on the basis of the concepts and methods of coordination chemistry and metal complex catalysis. The important part which is played by transition metals in the biological process provided groups for the assumption that perhaps they might be used for non-enzymatic activation of dinitrogen, while, on the other hand, certain similarities between N_2 and the isoelectronic molecule CO suggested the possibility of complexing of dinitrogen by transition metal compounds, which could result in its activation.

In such an approach the key question was whether dinitrogen could in fact form complexes with transition metal compounds. When we began our study and up to the time of our first publications (1964) [1] no such complexes were known, although the possibility of their existence had been discussed in the literature. In 1960 Syrkin advanced arguments in favor of the possibility that N_2 chemisorption on transition metal surfaces could be described in terms of three-center bonds just as in the case of the typical π-complexes of olefins and

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* This review was written jointly with Dr. V.B. Shur, and I request that his name be included in references to this paper.

acetylenes [2]. In the same year Orgel discussed the relative advantages of the "end-on" and "side-on" coordination of N_2 with metals [3]. However, the main question, whether dinitrogen complexes could exist, remained unanswered.

In this respect a first examination of the electronic structure of the N_2 molecule did not give much ground for optimism. The energy of the highest occupied $3\sigma_g$-orbital of dinitrogen, determining its electron-donating capacity, is very low, —15.6 eV, i.e. 1.6 and 4.2 eV below the corresponding CO and acetylene energies. For this reason dinitrogen does not in practice behave as a base, and, consequently, complexes wherein it would exclusively play the role of a σ-donor should be very unstable.

A more promising possibility arose when considering the π-acceptor capacity of dinitrogen, and, particularly, on taking into account possible synergism between the effects of σ- and π-bonding (cf. ref. 3).

According to Mulliken [4] the energy of the lowest vacant $1\pi_g^*$-orbital of N_2 is —7 eV, which is 1 eV below the corresponding value for the CO molecule (—6 eV). However CO is capable of forming very stable complexes with transition metal compounds, despite its similarly weak basic properties. We thus conjectured that if conditions could be established for an effective $d_\pi(M) \rightarrow 1\pi_g^*$-(N≡N) interaction of N_2 with metals (by utilizing for instance, their lower-valent derivatives) the formation of dinitrogen complexes, at least as unstable intermediates, might be possible. Now, when following the pioneer work of Allen and Senoff (1965) [5], hundreds of varied dinitrogen complexes, including highly stable ones, have become known, it is difficult to imagine all the uncertainty which surrounded this question at that time.

On the basis of the reasoning indicated, we first attempted the reduction of dinitrogen to ammonia or to nitride derivatives under conditions in which one could expect the formation of N_2 complexes with transition metal compounds. In the first experiments systems based on transition metal halides ($CrCl_3$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $PdCl_2$, CuCl) and metal hydrides ($NaBH_4$ in MeOH, $LiAlH_4$ in ether) as reducing agents were tested. The reactions were carried out at room temperature and atmospheric pressure. At the end of each run the reaction mixture was hydrolysed and then analysed for ammonia.

The results showed that in the presence of $FeCl_3$, $CoCl_2$, $NiCl_2$, $PdCl_2$ and CuCl no reduction of dinitrogen by $LiAlH_4$ or $NaBH_4$ takes place. In no experiment did the amounts of ammonia exceed its content as impurity in the initial reagents. A different picture was observed in the reaction of N_2 with $LiAlH_4$ in the presence of $CrCl_3$. In that case the amount of ammonia in the hydrolyzate was markedly above the impurity value. Although yields of NH_3 were very low (not more than 0.02 mol per mol of $CrCl_3$) they were well reproducible. Similar results were obtained in the reaction of N_2 with a mixture of $CrCl_3$ and excess C_2H_5MgBr in ether, where small amounts of ammonia were also formed [1].

In the search for ways of raising the efficiency of these reactions, experiments under elevated dinitrogen pressures were carried out. This immediately raised the activity of the systems. An especially marked effect of pressure was observed in the system $CrCl_3 + C_2H_5MgBr$ in ether, where by raising the N_2 pressure to 150 atm the yield of ammonia was increased almost ten-fold ($NH_3/Cr \sim 0.17$) [1]. Under these conditions the chlorides of other elements of Group VIB ($MoCl_5$, WCl_6) and also $TiCl_4$ and $FeCl_3$ proved to be active. The results obtained were confirmed by experiments with labeled dinitrogen $^{15}N_2$ [6]. Further, it was found that in this reaction $LiAlH_4$ and C_2H_5MgBr can be successfully replaced by a number of other reducing agents, namely various organo-lithium, -magnesium and -aluminium compounds [1,7—9], by metallic magnesium [10] etc. Finally, by changing the ligand environment of the transition metal, systems were found such as, for instance, Cp_2TiCl_2 + C_2H_5MgBr in ether [7—9], which could reduce dinitrogen even at atmospheric pressure and room temperature to give close to quantitative yields of ammonia (relative to the amount of transition metal present).

Further development of these studies led to the finding of a large number of multivarious nitrogen-fixing systems capable of transforming N_2 not only into ammonia, but also into hydrazine and amines, and also able to bring about the catalytic fixation of dinitrogen. A next important step was the discovery by Shilov et al. of nitrogen-fixing systems functioning in protic media [11]. On the other hand the synthesis of the first dinitrogen complex by Allen and Senoff [5] had indicated the pathway for a new approach; namely the chemistry of complexes of molecular nitrogen, which has had a profound influence on our understanding of the mechanism of nitrogen fixation.

In the present paper we confine ourselves to consideration of N_2 reactions in aprotic media, since nitrogen fixation in protic media and the chemistry of dinitrogen complexes have been covered in detail in recent reviews [12,13]. Although attention will be given predominantly to our own studies we shall consider also some general aspects of chemical nitrogen fixation.

Stoichiometric reduction of molecular nitrogen under the action of transition metal compounds

At present numerous systems are known which are capable of reducing molecular nitrogen in aprotic media and their study has led to the accumulation of a considerable amount of information. The reactions concerned have been treated in a number of comprehensive reviews [12,14—19]. We shall, therefore, consider here only the basic relationships observed in this area.

Table 1 gives examples of some typical nitrogen-fixing systems. They all consist of two principal components: a transition metal compound for complexing and activating dinitrogen and a sufficiently strong reducing agent, which serves as a source of electrons for reducing the activated dinitrogen molecule. The presence of both components is necessary for manifestation of nitrogen-fixing capacity by the system. The reactions proceed at room temperature in organic solvents such as ethers or hydrocarbons. As a rule the final N_2 reduction products are nitride-like compounds, differing, however, from the simple nitrides formed in the high temperature N_2 reactions with metals. Hydrolysis of the products yields ammonia.

The nitrogen-fixing activity of the systems varies widely depending on the reagents and reaction conditions. A crucial factor here is the metal species in the initial salt or in the complex. The strongest N_2 reducing capacity is displayed by transition metals of Groups IV, V and VI of the Periodic Table namely Ti, V, Cr, Mo and W [17]. Particularly active are titanium compounds. With the first row transition metals, the ammonia yields in general fall from left to right,

TABLE 1

NITROGEN-FIXING SYSTEMS

System	Molar ratio of reagents	Solvent	$P(N_2)$ (atm)	Reaction time (h)	NH_3 yield (mol./g.-at.) of transition metal	Ref.
Cp_2TiCl_2 + EtMgBr	1/9	Et_2O	150	31	0.93	7, 8, 17
Cp_2TiCl_2 + EtMgBr	1/9	Et_2O	1	9	0.67	7, 8, 17
$CpTiCl_3$ + EtMgBr	1/9	Et_2O	100	11	0.23	17
$TiCl_4$ + EtMgBr	1/9	Et_2O	100	11	0.12	1, 17
$CrCl_3$ + EtMgBr	1/9	Et_2O	150	11	0.17	1, 17
$CrCl_3$ + n-PrMgBr	1/9	Et_2O	150	11	0.30	8, 17
$MoCl_5$ + EtMgBr	1/9	Et_2O	150	11	0.08	1, 17
WCl_6 + EtMgBr	1/9	Et_2O	150	11	0.15	1, 17
$FeCl_3$ + EtMgBr	1/9	Et_2O	150	11	0.09	1, 17
$VO(acac)_2$ + EtMgBr	1/9	Et_2O	100	10	0.12	22
Cp_2TiCl_2 + n-BuLi	1/9	n-heptane	100	11	0.50	14, 17
$TiCl_4$ + n-BuLi	1/9	n-heptane	100	11	0.29	14, 17
$VO(acac)_2$ + n-BuLi	1/9	n-heptane	75	10	0.32	22
$MoO_2(acac)_2$ + n-BuLi	1/9	n-heptane	75	10	0.07	22
$CpTiCl_3$ + i-Bu_3Al	1/6	toluene	90	11	0.15	17
$TiCl_4$ + i-Bu_3Al	1/3	n-heptane	150	11	0.25	1
$Ti(OEt)_4$ + i-Bu_3Al	1/6	toluene	30	10	0.33	17, 22
$Cr(acac)_3$ + i-Bu_3Al	1/6	toluene	100	10	0.14	22
$TiCl_4$ + $LiAlH_4$	1/9	Et_2O	150	12	0.25	1
$CrCl_3$ + $LiAlH_4$	1/9	Et_2O	150	12	0.07	1, 17
$MoCl_5$ + $LiAlH_4$	1/9	Et_2O	150	12	0.03	1
Cp_2TiCl_2 + Mg + MgI_2	1/8/3	Et_2O/C_6H_6	80—100	7	0.8—1.0	10, 17, 43
Cp_2TiCl_2 + Mg + MgI_2	1/14/2.5	Et_2O/C_6H_6	1	5	0.25	43
Cp_2TiCl_2 + Mg + $MgBr_2$	1/14/5	Et_2O/C_6H_6	80—100	7	1.3	43
$CpTiCl_3$ + Mg + MgI_2	1/14/2.5	Et_2O/C_6H_6	80—100	7	ca. 1.0	43
$TiCl_4$ + Mg + MgI_2	1/14/5	Et_2O/C_6H_6	80—100	7	1.3	10, 17, 43
$ZrCl_4$ + Mg + MgI_2	1/14/2.5	Et_2O/C_6H_6	80—100	7	0.2	43
Cp_2ZrCl_2 + Mg + MgI_2	1/14/2.5	Et_2O/C_6H_6	80—100	7	0.04	43
$CrCl_3$ + Mg + MgI_2	1/14/5	Et_2O/C_6H_6	80—100	7	0.35	10, 17, 43
$MoCl_5$ + Mg + MgI_2	1/14/5	Et_2O/C_6H_6	80—100	7	0.36	10, 17, 43
WCl_6 + Mg + MgI_2	1/14/5	Et_2O/C_6H_6	80—100	7	0.58	10, 17, 43
$FeCl_3$ + Mg + MgI_2	1/14/2.5	Et_2O/C_6H_6	80—100	7	0.26	43
Cp_2TiCl_2 + Li + LiI	1/10/10	Et_2O	80—100	7	0.3	17, 43
$TiCl_4$ + Li + LiI	1/10/10	Et_2O	80—100	7	0.06	43
$CrCl_3$ + Li + LiI	1/10/10	Et_2O	80—100	7	0.05—0.14	43
$TiCl_3(THF)_3$ + Mg	1/8.5	THF	1	2—3	ca. 1.0	28
Cp_2TiCl_2 + Li	excess Li	THF	1	35	0.75	38
Cp_2TiCl_2 + Na	1/4	THF	1	18	0.56	38
Cp_2TiCl_2 + K	excess K	THF	1	50	0.09	38
Cp_2TiCl_2 + Mg	1/2	THF	1	120	0.46	38
Cp_2TiCl_2 + Ca	excess Ca	THF	1	96	0.35	38
Cp_2TiCl_2 + La	excess La	THF	1	72	0.46	38
Cp_2TiCl_2 + Ce	excess Ce	THF	1	40	0.64	38
$CpTiCl_3$ + Na	1/4	THF	1	5	0.47	38
$CpTiCl_3$ + Mg	1/2	THF	1	24	0.46	38
$TiCl_4$ + Na	excess Na	THF	1	144	0.44	38
Cp_2ZrCl_2 + Li	excess Li	THF	1	14	0.12	38
Cp_2TiCl_2 + Li/Hg	1/10	THF	1	72	0.70	27
Cp_2TiCl_2 + $C_{10}H_8^{\dot{-}}Li^{+a}$	1/6	THF	1	16	0.96	15
$TiCl_4$ + $C_{10}H_8^{\dot{-}}Li^+$	1/15	THF	120	0.5	1.7	15
VCl_3 + $C_{10}H_8^{\dot{-}}Li^+$	1/7	THF	120	0.5	2.0	15
VCl_3 + $C_{10}H_8^{\dot{-}}Li^+$	1/10	THF	1	0.5	0.9	15
$CrCl_3$ + $C_{10}H_8^{\dot{-}}Li^+$	1/10	THF	120	0.5	1.2	15
$CrCl_3$ + $C_{10}H_8^{\dot{-}}Li^+$	1/10	THF	1	0.5	0.4	15
$Ti(O\text{-}i\text{-}Pr)_4$ + $C_{10}H_8^{\dot{-}}Na^+$	not given	THF	1	0.5	1.3	16

[a] $C_{10}H_8^{\dot{-}}Li^+$ = lithium naphthalide.

in line with the diminishing strength of the metal—nitride bond [20]. However, iron compounds are as a rule more efficient than manganese compounds. Zr compounds are usually less active than those of Ti. Of low activity or totally inactive are systems based on Co, Ni, Pd, Pt and Cu.

The ligand environment of the transition metal can vary within rather wide limits. Systems based on halides, alkoxides, acetylacetonates and π-cyclopentadienyl complexes have been reported. Phosphine complexes have also been tried [21].

Another important factor is the reducing agent. At present a wide variety of such agents have been tested, among them organometallic compounds (RMgX, RLi, R_3Al), metal hydrides ($LiAlH_4$, LiH), metals (alkali, alkaline earth, rare earth), amalgams (Li/Hg, Na/Hg), aromatic radical anions and dianions, and molecular hydrogen [17,19,22—25]. It has also been reported that dinitrogen can be reduced electrochemically [16,26]. To achieve maximum reaction rates the reducing agent is often taken in considerable excess with respect to the transition metal compound (up to 10—60/1). The stoichiometric ratios required for the maximum possible ammonia production are much lower (see, e.g. refs. 27, 28). If the transition metal compound is in a sufficiently reduced state, under certain conditions it can itself reduce dinitrogen, as has been observed for the complexes $C_6H_6 \cdot TiCl_2 \cdot 2\,AlCl_3$ [25,29,30] and $[Cp_2TiH]_2$ [31] and in the thermolysis of Cp_2TiR_2 (R = Ph, Me) [17,23], Cp_2TiR (R = 2-MeC_6H_5, 2,6-$Me_2C_6H_3$) [32], and Cp_2ZrPh_2 [33] under N_2.

If the reductive processes in the system are retarded (for example, by lowering the temperature or by using smaller amounts of reducing agent) the formation of incomplete N_2 reduction products, yielding hydrazine on hydrolysis, can be detected. Hydrazine formation in these reactions was first observed by Van Tamelen et al. [34] (in the reaction of N_2 with $Ti(O\text{-}i\text{-}Pr)_4 + C_{10}H_8^{\dot{-}}Na$), by Shilov et al. [35,12] (in the systems Cp_2TiCl_2 + RMgX) and in our laboratory [25] (on heating N_2 with the complex $C_6H_6 \cdot TiCl_2 \cdot 2\,AlCl_3$ and with the mixture Al and $AlBr_3$ in the presence of $TiCl_4$). Subsequently hydrazine was found in numerous other studies (for reviews see refs. 12, 19).

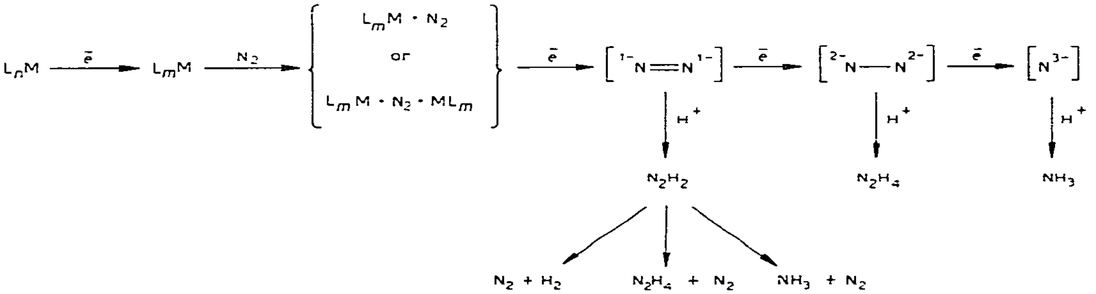
In order to compare the systems described here with the biological systems, the effect of nitrogenase inhibitors on the chemical reduction of dinitrogen was investigated. It was found that the two processes possess a number of common features. Thus, carbon monoxide and acetylenes inhibit both the chemical and the biological fixation of dinitrogen [36,8,17,37]. A similar effect is displayed by isonitriles and KCN [37]. Olefins are much weaker inhibitors of the chemical reduction of dinitrogen than are acetylenes [8,17], and in the enzymatic reaction generally have no inhibiting effect on the reduction of N_2 [36]. A definite similarity between these processes is observed also in the way they are affected by molecular hydrogen. As is well known, dihydrogen usually acts as an inhibitor of nitrogen fixation in the enzymatic reaction [36]. However, in artificial biological systems, clostridial ferredoxins and flavodoxins are capable of transferring electrons from H_2 via hydrogenase to various nitrogenases and further to N_2 [36]. A similar effect is exerted by dihydrogen on chemical N_2 fixation. Depending on the type of the system and on the reaction conditions, dihydrogen can again either effectively inhibit fixation of dinitrogen [17,19,29,28,38] or participate in its reduction [17,19,22,24,25].

Despite their high activities, all the systems discussed above are non-catalytic. Kinetic experiments reveal that the curves depicting the time dependence of the NH_3 yield are of similar character whatever the system. In all cases, an increase in the NH_3 yield is observed only up to a certain limit, after which it remains constant even in the presence of a large excess of the reducing agent. The limiting yield of NH_3 depends on the type of system, but never exceeds 1 or 2 mol per atom of transition metal (M).

The stoichiometric ratio $NH_3/M = 1$ may indicate that reduction of dinitrogen proceeds via an intermediate binuclear complex $[M \cdot N_2 \cdot M]$. Evidently this is the case in the systems Cp_2TiCl_2 + RMgX in ether [8,12], $Cp_2TiCl_2 + C_{10}H_8^-Li^+$ in THF [15], $VCl_3(THF)_3$ + Mg and $TiCl_3(THF)_3$ + Mg in THF [28]. If, however $NH_3/M = 2$ (as for $VCl_3 + C_{10}H_8^-Li^+$ in THF [15]) a mononuclear complex $[M \cdot N_2]$ (or the corresponding dimer $[M \cdot N_2]_2$) is apparently formed at the stage preceding the N_2 reduction. At present a large number of mono- and bi-nuclear dinitrogen complexes are known [13], many of which were isolated from just these types of system.

The reaction mechanism can be expressed by the general Scheme 1 *.

SCHEME 1



In the first stage the initial transition metal compound (L_nM) is reduced to a lower-valent derivative (L_mM) forming a complex with dinitrogen, which is thus activated.

Reduction of the coordinated N_2 molecule proceeds in at least three steps. First there is formed a diazene intermediate, then a hydrazine intermediate, and finally the end nitride which yields ammonia on hydrolysis.

The assumption that dinitrogen reduction proceeds via a step involving N_2 coordination to the transition metal compound was made even in the first studies of molecular nitrogen fixation in solution [1,8,14]. Experimental confirmation of this was obtained in a study of systems based on cyclopentadienyl derivatives of titanium. Upon bringing N_2 into contact with the systems Cp_2TiCl_2 (Cp_2TiCl) + i-PrMgCl in ether at low temperatures (—70— —100°C), Shilov et al. [35,12,18] observed the formation of an unstable dark blue dinitrogen complex of the composition $[(Cp_2Ti\text{-}i\text{-}Pr)_2N_2]$, apparently an intermediate in N_2 reduction by these systems. Similar, but more stable complexes $[(Cp_2TiAr)_2N_2]$ were obtained by Teuben [39,40,32], whereas Brintzinger and Bercaw et al. [31] described a complex $[(Cp_2Ti)_2N_2]$ which might have been formed as an interme-

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* In Scheme 1 the symbols $[{}^{1-}N{=}N^{1-}]$, $[{}^{2-}N{-}N^{2-}]$ and $[N^{3-}]$ designate the diazene, hydrazine and nitride levels of N_2 reduction, respectively.

diate in the fixation of dinitrogen by systems based on Cp_2TiCl_2 and metals or naphthalides as reducing agents. All these complexes apparently have an "end-on" bridge structure, Ti—N≡N—Ti *, and readily undergo reduction (for instance by Grignard reagents or by sodium naphthalide) with the formation of hydrazine and/or ammonia on hydrolysis.

That reduction of dinitrogen proceeds via a diazene intermediate is confirmed by the results described in refs. 12, 18, 40, and 42. Hydrolysis of the reaction mixture at this stage yields free diazene which then rapidly decomposes to a mixture of N_2 and N_2H_4, N_2 and H_2 and/or N_2 and NH_3 (depending on the conditions). Products corresponding to the hydrazine level of N_2 reduction and giving hydrazine on hydrolysis have also been reported [12,18,40]. Finally, in a number of cases the end products corresponding to complete rupture of the N≡N bond could be isolated. One such product, a nitride of the composition $[N(TiCl_2 \cdot 2\ AlCl_3)_3 \cdot C_6H_6]$, was obtained in our laboratory on heating dinitrogen with the complex $C_6H_6 \cdot TiCl_2 \cdot 2\ AlCl_3$ [25,29,30]. By bringing N_2 in contact with the systems $TiCl_3(THF)_3$ + Mg and $VCl_3(THF)_3$ + Mg in THF, Yamamoto et al. obtained black diamagnetic nitrides formulated as $[MNMg_2Cl_2(THF)]\cdot$ (M = Ti, V) [28]. On hydrolysis all these compounds yield stoichiometric amounts of ammonia.

Catalytic nitrogen-fixing systems

As already mentioned, all the above systems are non-catalytic. The absence of a catalytic effect might in some cases have been due to instability of the lower-valent transition metal compound responsible for the N_2 activation. However, this is evidently not a crucial factor, since the catalytic process also cannot be achieved with relatively stable nitrogen fixing systems.

A more general reason for the non-catalytic character of these reactions is that the transition metal compound which activates the dinitrogen is irreversibly lost in the form of the end nitride. The high affinity of the metal for nitrogen (favourable for scission of the N_2 molecule) hinders regeneration of the active species, and consequently makes the N_2 reduction process non-catalytic. Thus in order for the catalytic cycle to be realized, conditions had to be found under which the transition metal—nitrogen bonds in the nitride products would split readily.

These considerations formed the basis of our work on the development of the first catalytic nitrogen-fixing systems in solution. Here the N_2 reactions were carried out in aprotic solvents, strong aprotic acids such as aluminium bromide being used for breaking the nitride bonds, while metallic aluminium served as reducing agent and titanium compounds as the catalysts [29,30,25]. Some of the results obtained are given in Table 2, from which one can immediately see sharp difference between these systems and those of the previous section.

On heating dinitrogen with a mixture of Al and $AlBr_3$ in the presence of $TiCl_4$, $TiBr_4$ or $Ti(OBu)_4$, the yields of ammonia formed by hydrolysis constantly increase with increase in the amount of Al and $AlBr_3$ and can be brought up to 200 and more mol per mol of titanium compound. In the absence of TiX_4,

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* For $[(Cp_2TiAr)_2N_2]$ (Ar = p-MeC_6H_4) this was recently established by an X-ray analysis [41].

TABLE 2

CATALYTIC REDUCTION OF N_2 BY ALUMINIUM AND LITHIUM ALUMINIUM HYDRIDE[a]

System	Molar ratio of reagents	Reaction time (h)	Ammonia yield	
			(mol/g-at. of Ti)	referred to reducing agent (%)
$TiCl_4 + Al + AlBr_3$	1/6/0	8	0.02	0.4
	1/6/2	8	1.3	23
	1/12/33	14	10.7	92
	1/150/200	30	95	64
	1/600/1000	30	286	48
$TiBr_4 + Al + AlBr_3$	1/116/370	45	74	64
$Ti(OBu)_4 + Al + AlBr_3$	1/150/250	36	105	70
$C_6H_6 \cdot TiCl_2 \cdot 2\ AlCl_3 + Al + AlBr_3$	1/150/250	30	115	77
$TiCl_4 + LiAlH_4 + AlBr_3$	1/4/44	14	3.7	74
	1/8/44	24	9.8	95
	1/16/90	14	17.8	85
	1/16/90	40	19.2	92
	1/16/120	40	19.8	94
	1/300/1500	40	125	31
$Ti(OBu)_4 + LiAlH_4 + AlBr_3$	1/16/90	40	17.6	84
$TiCl_4 + LiAlH_4 + AlBr_3 + AlCl_3$	1/300/1500/690	35	100	25

[a] $P(N_2) \sim 100$ atm; with $TiCl_4 + LiAlH_4 + AlBr_3 + AlCl_3$ the reaction was carried out at 60—70°C; in the other cases at 130°C.

neither aluminium nor its mixture with $AlBr_3$ react with dinitrogen. Hence, titanium compounds are catalysts for the reduction of N_2 by aluminium. Other transition metal halides ($ZrCl_4$, VCl_3, $CrCl_3$, $MoCl_5$, WCl_6, $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiBr_2$) show practically no activity under these conditions.

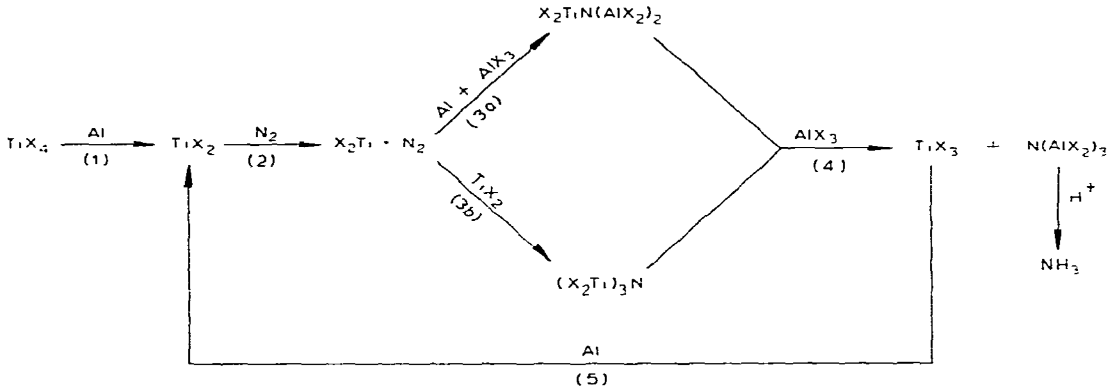
The best solvent for this reaction proved to be benzene. Ethers, which form stable complexes with aluminium bromide, sharply decrease the activity of the systems. The reaction can also be carried out in the absence of solvent, i.e. in molten aluminium bromide (m.p. 97.5°C).

Both the rate of the reaction and the maximum amount of fixed dinitrogen are strongly dependent on the aluminium bromide content. Complete conversion of aluminium into nitrides can be achieved only with a sufficient excess of $AlBr_3$ relative to Al (ca. 3/1). The necessity for large amounts of $AlBr_3$ is due to its consumption in the rupture of the metal—nitride bonds. It must be noted, however, that in the absence of $AlBr_3$, the systems not only lost their catalytic properties, but also in general no longer reduced dinitrogen. Evidently $AlBr_3$ also participates in other stages of the process.

The reaction mechanism apparently involves an initial reduction of titanium(IV) to titanium(II), which is the actual catalyst for reduction of N_2. This is supported by the fact that the complex $C_6H_6 \cdot TiCl_2 \cdot 2\ AlCl_3$, formed under similar conditions on heating $TiCl_4$ with a mixture of Al and $AlCl_3$ in benzene [44,45], is capable of reacting with N_2 to give the titanium(III) nitride of the composition $[N(TiCl_2 \cdot 2\ AlCl_3)_3 \cdot C_6H_6]$ [29,30,25]. Hydrolysis of this compound yields a stoichiometric amount of ammonia. On the other hand, the same complex $C_6H_6 \cdot TiCl_2 \cdot 2\,AlCl_3$ when added in small amounts to a mixture of aluminium and aluminium bromide gives rise to the catalytic reduction of N_2 (Table 2) [29,30,25]. Probably complexes of type $C_6H_6 \cdot TiX_2 \cdot 2\,AlBr_3$ act as N_2-reduction catalysts when the reaction is carried out in benzene. In the $AlBr_3$ melt the catalytic function is evidently assumed by titanium(II) halide in the form of an aluminium bromide adduct: $TiX_2 \cdot 2\,AlBr_3$. That such adducts are formed on heating $TiCl_4$ (or $TiCl_3$) with Al in the presence of aluminium halide has been shown in ref. 46.

Combination of all these results leads to Scheme 2 for the reaction mechanism *: stage 1 formation of the catalyst; stage 2 complexing of dinitrogen; stage 3a reduction of the coordinated N_2 molecule by titanium(II) and aluminium or 3b by titanium(II) only; stage 4 cleavage of the titanium—nitride bonds by $AlBr_3$ to give titanium(III) halide and the end nitride (yielding ammonia on hydrolysis) and stage 5 regeneration of the catalyst.

SCHEME 2



Reduction of dinitrogen at stages 3a and 3b proceeds stepwise, as is indicated by detection of hydrazine among the hydrolysis products when the reaction is carried out at lower temperatures.

The overall process can be expressed by the following equation:

$$N_2 + 2\,Al + 4\,AlX_3 \xrightarrow{Ti^{II}} 2[N(AlX_2)_3]$$

Effective catalytic systems can be obtained by replacing aluminium by $LiAlH_4$ as reducing agent (Table 2) [25]. Reduction of N_2 by lithium aluminium hydride to ammonia (after hydrolysis) is also catalysed by titanium compounds. Here too, a prerequisite for quantitative yields of ammonia (with reference to $LiAlH_4$) is the presence of a sufficient excess of $AlBr_3$ (up to 5—6 mol per mol of $LiAlH_4$) Interestingly, in these reactions $LiAlH_4$ acts as donor of four electrons, i.e. the stoichiometric ratio $LiAlH_4/N_2$ equals 3/2. In the absence of $AlBr_3$ the yields of NH_3 do not exceed 1 mol/Ti atom even in the presence of large amounts of lithium aluminium hydride, and in the absence of titanium compounds, ammonia is not formed at all.

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* In Scheme 2 the reaction mechanism is illustrated for N_2 activation in a mononuclear complex; for simplicity $AlBr_3$ is not shown in the products.

The use of temperatures above 100°C is necessary to prevent solidification of the aluminium bromide melt (which serves as the reaction medium). However, if $AlBr_3$ is used in a eutectic mixture with $AlCl_3$ ($AlBr_3/AlCl_3$ 2.17/1; m.p. 67°C) the system will operate efficiently at 60—70°C, giving up to 100 mol of NH_3 per mol of catalyst (Table 2), and with the ternary low melting mixture $AlBr_2/AlCl_3/$benzene the reaction can be carried out even at 30°C ($NH_3/Ti = 5$). The temperature needed for catalytic N_2 reduction by aluminium can be lowered in a similar way.

The results described show that in the presence of a sufficiently strong aprotic acid a number of systems acquire the ability to reduce dinitrogen catalytically. The efficiency of the reactions is determined by the nature of the transition metal compound and of the Lewis acid, and by other factors. Under optimal conditions the yields of the N_2 reduction products can reach hundreds of mol per mol of catalyst and, the conversion of the reducing agent approaches 100%.

In further studies Shilov et al. found catalytic nitrogen-fixing systems which functioned in protic media [12,18]. The catalyst here are molybdenum compounds, and the reducing agents titanium(III) hydroxide or sodium amalgam. It is reasonable to assume that the role of the protons in these reactions is also to split the metal—nitrogen bonds in the reduction products, and that the basic features of the catalytic mechanism are generally the same for both types of systems.

Nitrogen fixation with formation of organic nitrogenous compounds

The ability of transition metal compounds to activate molecular nitrogen and induce its reduction under mild conditions opens the way to various transformations of dinitrogen within the coordination sphere of the metal. Of particular interest are reactions of N_2 which would give nitrogen-containing organic compounds.

In attempts to find ways of carrying out such reactions, we began from the assumption that dinitrogen would be capable of reacting with σ-aryl and alkyl derivatives of transition metals to insert into the transition metal—carbon bond. The key role played by insertion into the metal—carbon bond in various catalytic transformations of unsaturated molecules is well known. We believed that if conditions could be established whereby a similar reaction would take place with N_2, this would lead to organic nitrogenous compounds.

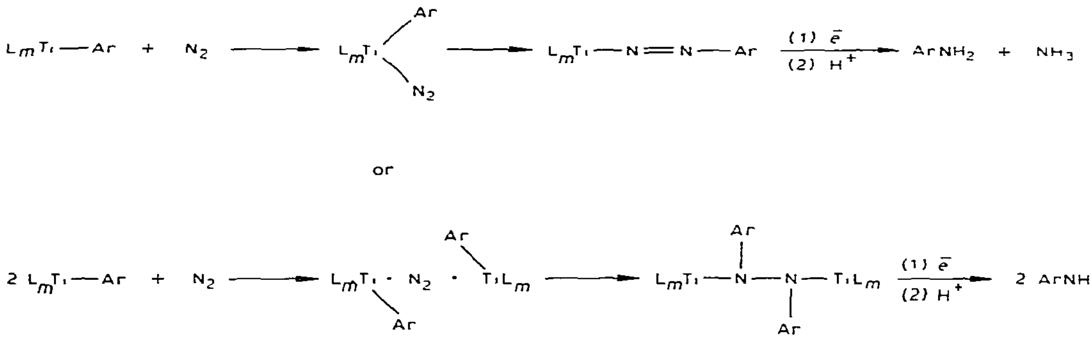
The first example of such reactions was observed in 1966 when we found that in interaction of N_2 with Cp_2TiCl_2 (or Cp_2TiPh_2) and excess PhLi in ether the products after hydrolysis contain significant amounts of aniline along with ammonia [47]. The formation of aniline in this reaction proceeds even at room temperature and atmospheric pressure ($PhNH_2/Ti$ 0.03; NH_3/Ti 0.17). Increasing the N_2 pressure markedly enhances the yields of both aniline and ammonia ($PhNH_2/Ti$ 0.10—0.15; NH_3/Ti 0.65; $P(N_2)$ 80—100 atm). Subsequently it was shown that approximately the same amounts of aniline are obtained with other titanium compounds: $CpTiCl_3$, $Ti(OBu)_4$, $TiCl_4$ [48]. Chlorides of vanadium(IV), chromium(III), molybdenum(V) and tungsten(VI) are only poorly effective in the formation of aniline, although ammonia can be produced in these cases in rather large quantities (e.g. up to 0.4—0.5 mol in the case of VCl_4). The halides of zirconium(IV), manganese(II), iron(III), cobalt(II) and nickel(II) are practically inactive for the formation of either aniline or ammonia.

Other aromatic organolithium compounds as well as phenyllithium are reactive, and the following pattern can be observed. In the case of *para*- and *meta*-substituted aryllithium, dinitrogen adds practically only to the carbon atom which was bound to the metal in the original organolithium compound [48]. Thus, on treatment of N_2 with *p*-tolyllithium in the presence of Cp_2TiCl_2 *p*-toluidine is formed, only traces of *m*-toluidine being detectable. Under the same conditions *m*-tolyllithium yields *m*-toluidine and only traces of the *p*-isomer. A different picture is observed with *ortho*-substituted aryllithiums. In that case rearrangements of the intermediate *o*-substituted σ-aryl derivatives of titanium take place, leading to mixture of isomeric amines [48]. Thus, from *o*-tolyllithium and N_2 a mixture of *o*- and *m*-toluidine and small amounts of *p*-toluidine is obtained; *o*-diphenyllithium yields *o*- and *m*-aminodiphenyls together with small amounts of *p*-aminodiphenyl, and with α-naphthyllithium a mixture of α- and β-naphthylamines is formed.

When aryllithium in these systems is replaced by aliphatic organolithium or organomagnesium compounds, amines are either not formed at all or are formed only in trace amounts. Arylmagnesium halides in combination with Cp_2TiAr_2, Cp_2TiCl_2, $TiCl_4$ or $Ti(OBu)_4$ in ether give small amounts of aromatic amines (not exceeding 0.01 mol/Ti atom) only on heating (80—100°C).

Marked amine-forming capacity is also displayed by systems obtained by treating diaryltitanocenes, Cp_2TiAr_2, with some alkali and alkaline earth metals such as Li, Na and Mg [49]. The reactions proceed at room temperature in ethereal solution (THF, diethyl ether etc.), Cp_2TiPh_2 giving rise to aniline, $Cp_2Ti(p\text{-}MeC_6H_4)_2$ to *p*-toluidine, and $Cp_2Ti(m\text{-}MeC_6H_4)_2$ to *m*-toluidine. Besides the amines quite large amounts of ammonia are also obtained. The highest activity in amine production is displayed by the system Cp_2TiPh_2 + Li in THF where 0.10—0.15 mol of aniline (per mol of Cp_2TiPh_2) are formed together with ~1.1 mol of ammonia (20°C, $P(N_2)$ 100 atm). Here a change in the dinitrogen pressure has different effects on the yields of $PhNH_2$ and NH_3. When the N_2 pressure is lowered to atmospheric the aniline yield falls sharply (to 0.01—0.03 mol) whereas that of ammonia remains practically constant. A similar effect on the $PhNH_2$ yield is observed when the temperature is raised.

The formation of amines in these reactions possibly proceeds via insertion of dinitrogen into the Ti—Ar bond of some lower-valent titanium derivative formed during reduction of the initial titanium compound by ArLi, Li etc. [47,48].

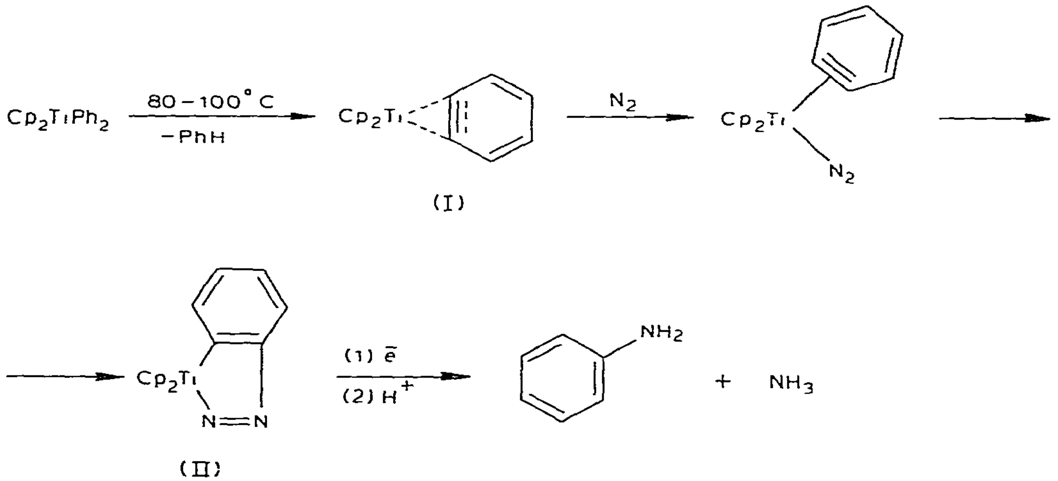


Another possible mechanism involves direct nucleophilic attack on the N_2 ligand in the intermediate dinitrogen complex by an arylcarbanion (from ArLi) followed by reduction of the ArN=N group bound to the titanium [47]. The possibility of such nucleophilic attack was recently demonstrated by Sellmann et al. for the manganese dinitrogen complex [$CpMn(CO)_2N_2$] [50].

Formation of amines can also take place in the reactions of N_2 with σ-aryltitanium derivatives alone, i.e. without an added reducing agent [51,52,33].

The thermal decomposition of Cp_2TiPh_2 in ether or in aromatic hydrocarbons at 80—100°C under pressure of N_2 gives products which liberate ammonia and small amounts of aniline on hydrolysis [23,51,52,33]. In this case aniline is formed by a different route from that in the reactions, described above, of N_2 with the systems $CpTiPh_2$(Cp_2TiCl_2) + PhLi and Cp_2TiPh_2 + Li. Investigation of the behaviour of the isomeric ditolyltitanocenes, $Cp_2Ti(p\text{-}MeC_6H_4)_2$, $Cp_2Ti(m\text{-}MeC_6H_4)_2$ and $Cp_2Ti(o\text{-}MeC_6H_4)_2$, under conditions of their thermolysis has shown that they all react with N_2 to form mixtures of isomeric toluidines: *p*- and *m*-toluidines (~35/65) from both $Cp_2Ti(p\text{-}MeC_6H_4)_2$ and $Cp_2Ti(m\text{-}MeC_6H_4)_2$, and *o*- and *m*-toluidines (46/54) from $Cp_2Ti(o\text{-}MeC_6H_4)_2$ [52,33]. These results together with the data on thermolysis of $Cp_2Ti(p\text{-}MeC_6H_4)_2$ and $Cp_2Ti(m\text{-}MeC_6H_4)_2$ under CO_2 [53] provide a basis for the assumption that aniline formation from dinitrogen and Cp_2TiPh_2 proceeds via reaction of N_2 with benzyne in the titanium coordination sphere, according to Scheme 3.

SCHEME 3



The formation of I during the thermolysis of Cp_2TiPh_2 has been shown in ref. 54. This complex is capable of reacting with tolane and CO_2 to give cyclic products analogous to the postulated II * [55,56].

A similar mechanism apparently operates in the reaction of N_2 with the system Cp_2TiCl_2 + Mg + *o*-fluorobromobenzene in THF, where aniline and ammonia are also produced even at room temperature [33]. The reaction of *o*-fluorobro-

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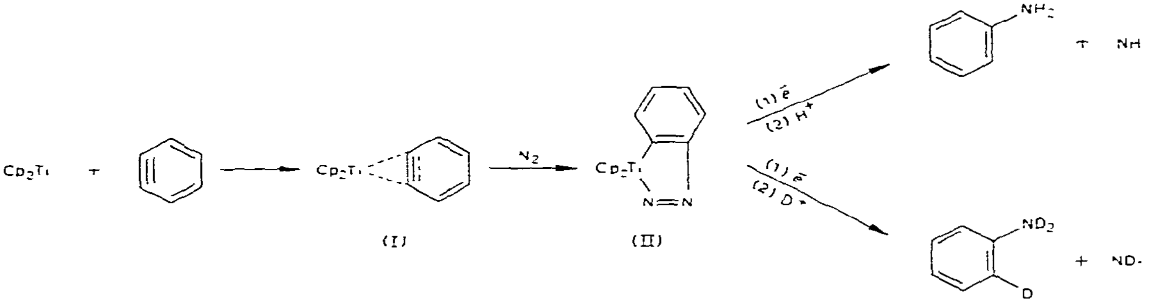
* Reductive splitting of the N=N bond in II leading to aniline formation can be brought about by lower-valent titanium complexes which are formed in the final stages of Cp_2TiPh_2 decomposition.

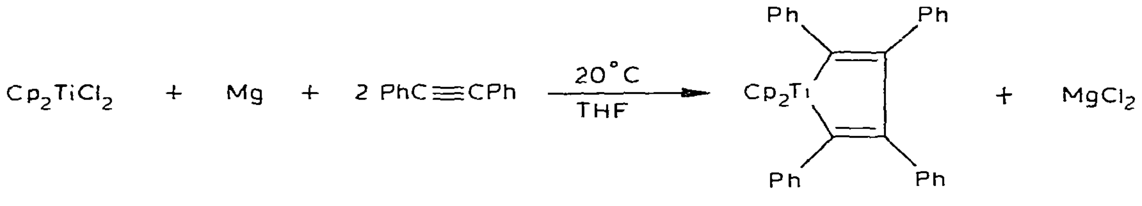
mobenzene with Mg, as is well known, generates benzyne [57], and the reaction of Cp_2TiCl_2 with Mg can yield Cp_2Ti.

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

There are thus conditions for the formation of the benzyne complex I, and for its reaction with N_2:



In this connection it is noteworthy that replacement of *o*-fluorobromobenzene by the corresponding *o*-dibromo and *o*-chlorobromo derivatives (which are less efficient sources of benzyne [57]) lowers the yield of $PhNH_2$. Of significance also is the fact that if the products from the reaction of N_2 with Cp_2TiCl_2, Mg, and *o*-fluorobromobenzene are decomposed by D_2O, *o*-deuteroaniline is formed. Similar treatment in the case of Cp_2TiCl_2 + PhLi yields aniline which does not contain deuterium in the aromatic ring. The formation of Cp_2Ti during reduction of Cp_2TiCl_2 by metallic magnesium in THF is evidenced by isolation of III from the reaction products of Cp_2TiCl_2 with Mg in the presence of tolane:



(III)

A study of the mechanism of amine formation using ^{15}N precision mass spectrometry showed [33] that in the reactions of N_2 with the systems Cp_2TiCl_2 + PhLi and Cp_2TiPh_2 + PhLi there is a kinetic ^{15}N isotope effect (similar for NH_3 and $PhNH_2$), which results in a lower ^{15}N content in both products than in the initial dinitrogen. At the same time, in the case of the "benzyne" system $Cp_2TiCl_2 + Mg + o\text{-}FC_6H_4Br$ the ^{15}N isotopic effects for aniline and ammonia differ considerably from each other; aniline, in contrast to ammonia, turning out to be more enriched with ^{15}N than the initial N_2. Evidently the aniline, and at least a major part of the ammonia, in this case com from different N_2 complexes.

The ability of N_2 to react with σ-aryl derivatives of titanium raises the possibility of carrying out analogous reactions in which aromatic hydrocarbons could be utilized for the synthesis of amines from dinitrogen. For this it is necessary that in the reaction system, in addition to activation of N_2, splitting of the C—H-bonds of the aromatic hydrocarbons with formation of σ-aryl hydride complexes must also take place. We investigated the possibility of synthesizing amines from dinitrogen and aromatic hydrocarbons under the action of transition metal compounds.

On treating N_2 at room temperature with a mixture of naphthalene and excess lithium (or sodium) in THF in the presence of $TiCl_4$ in addition to ammonia, the following amines were found: α-naphthylamine, 5,8-dihydro-α-naphthylamine, 5,6,7,8-tetrahydro-α-naphthylamine and β-naphthylamine. Under the same conditions *o*- and *p*-aminodiphenyls were obtained from dinitrogen and diphenyl [58,59].

The formation of small amounts of amines from benzene and toluene was observed in the above reactions of N_2 with diaryltitanocenes [33]. It appears that if thermolysis of $Cp_2Ti(p\text{-}MeC_6H_4)_2$ is carried out in benzene under N_2 pressure (100°C), besides *p*- and *m*-toluidines, aniline is formed, the source of which is the aromatic solvent. Similarly *p*- and *m*-toluidines (ca. 1/1) in addition to aniline are detected among the products of the reaction of N_2 with Cp_2TiPh_2 in toluene. Evidently the lower-valent titanium complexes, formed in the thermolysis of Cp_2TiAr_2, split the C—H bonds of the aromatic hydrocarbons used as solvent with the formation of σ-arylhydride derivatives of titanium. This is confirmed by the fact that Cp_2TiAr_2 (Ar = Ph, $p\text{-}MeC_6H_4$) and Cp_2TiMe_2 catalyse isotope exchange between aromatic hydrocarbons (benzene, toluene, anisole, fluorobenzene) and D_2 at 100—130°C [60]. In the case of toluene exchange occurs in both the aromatic ring and the methyl group. According to IR spectra, the deuterium in the aromatic ring of toluene is localized in the *p*- and *m*-positions, corresponding to the formation of *p*- and *m*-toluidines in the thermal decomposition of Cp_2TiPh_2 in toluene under N_2.

Conclusion

Investigations of recent years have modified our view that dinitrogen is an inert gas. Now we know how to activate it and this provides us with a firm basis for future research.

One of the important problems in the present stage of development of this field is to bring about catalytic hydrogenation of dinitrogen by molecular hydrogen under mild conditions. The first attempts to use the above systems for that purpose showed the possibility of utilizing dihydrogen for the reduction of N_2 in the presence of transition metal compounds [17,19]. The result is promising and gives rise to the hope that such an approach will lead to the creation of catalysts for the low-temperature synthesis of ammonia.

Also of considerable interest are reactions in which molecular nitrogen forms organic nitrogenous products. Such reactions have been considered above. If the efficiency of these reactions could be raised so as to make them catalytic, important new possibilities would be opened for the synthesis of nitrogen-containing organic compounds.

Finally, still another important direction is modelling of the biological fixation of dinitrogen. The known chemical nitrogen-fixing systems already show certain functional properties resembling those of nitrogenase (see above and ref. 12, 19). It can be assumed that further investigations in this area will bring us closer to an understanding of the mechanism of this vital biological process.

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