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Reactions of Ligating Dinitrogen in Dinuclear Complexes

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I. Introduction

DINUCLEAR dinitrogen complexes have been reported for all transition metals with the exception of Hf, V, Ta, Tc and Ir. The field has been extensively reviewed recently,[1,2,3] and this chapter will be limited to the reactivity of the dinitrogen ligand in complexes in which the units $M–N_2–M$, $M–N_2–M'$ (M and M' = transition metal) are present and also to complexes $M–N_2–A$ where A = Lewis acid. The reactivity of the dinitrogen ligand in dinuclear complexes has been subject of intense research for only a small number of complexes and is limited mainly to Ti, Zr, and Fe.

In Section II aspects of bonding and reactivity of the dinitrogen ligand are discussed, while in Section III an account is given of successful and unsuccessful attempts to cause this ligand to react.

II. Bonding and Reactivity

The theoretical considerations for the binding of dinitrogen in dinuclear complexes are in principle the same as those which apply for mononuclear complexes. Dinitrogen, being a weak σ-donor and moderate π-acceptor, will build up electronic charge as a consequence of bonding and this will lead to a rather unstable dinuclear complex if there is not a secondary effect that helps to relieve this charge build-up. An indication for the flow of charge to dinitrogen can be inferred from the XPE spectrum of the asymmetric dinuclear complex $[MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}]$.[4] The position of the N(1s) bond energy (398·6 eV) indicates that the electron density in both N atoms in this complex is about the same as found for the non-coordinated and more

negatively charged N atom in the mononuclear complex $[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), which can be protonated or alkylated quite easily.[1] Unfortunately other XPE data on the bridging dinitrogen molecule are not known at the moment.

More evidence for the activation of the dinitrogen ligand is obtained from X-ray structural and vibrational spectroscopic data. In Table 1 the data for a number of relevant, dinuclear complexes are given. With the exception of the

Table 1. X-ray structural and vibrational spectroscopic data for some dinuclear dinitrogen complexes

Complex	N–N (Å)	M–N–N (deg)		$\nu(N_2)$ $(cm^{-1})^a$	Ref.
$[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]$	1·160(14)^b	178·8(4)^b		—	5
$[\{Ti(\eta^5\text{-}C_5H_5)_2R\}_2(N_2)]$	1·162(12)	176·5(5)		—	6
$[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$	1·182(5)	176·7(3)		—	7,8
$[\{Mo(\eta^6\text{-}C_6H_3Me_3)(dmpe)\}_2(N_2)]$	1·145(7)	175·6(4)		1989	9,10
$[MoCl_4(OMe)\{(N_2)ReCl(PMe_2Ph)_4\}]$	1·18(3)	179·6(14) 178·7(9)	(M = Re) (M' = Mo)	1660	11
$[MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2]$	1·154(29)	177·1(22) 178·6(21)	(M = Re) (M' = Mo)	1800	12,13
$[\{Mn(\eta^5\text{-}C_5H_4Me)(CO)_2\}_2(N_2)]$	1·118(7)	176·5(4)		1971	14
$[\{Ru(NH_3)_5\}_2(N_2)](BF_4)_4$	1·124(15)	178·3		2100	15
$[\{Co(PMe_3)_3(N_2)\}_2Mg(thf)_4]$	1·18	linear 158	(M = Co) (M' = Mg)	2068	16
$K[Co(N_2)(PMe_3)_3]$	1·16-1·18	linear	(M = Co)	1795 1758	17
$[\{Ni(PCy_3)_2\}_2(N_2)]$	1·12	178·2		—	18
$[\{(PhLi)_6Ni_2(N_2)(Et_2O)_2\}_2]$	1·35(2)	—^{c}		—^{d}	19
N_2	1·0976^e	—		2331	
MeN=NMe	1·23^f	—		—	
H_2N–NH_2	1·46^f	—		—	

^{a} $\nu(N_2)$ is normally not IR-active in the centrosymmetric complexes; Raman spectroscopy is frequently impossible due to decomposition of the samples during irradiation. ^{b} Average value from two independent molecules in the unit cell. ^{c} The dinitrogen ligand is "edge-on" bonded to a Ni-Ni moiety. ^{d} $\nu(N_2)$ is possibly below 1550 cm^{-1}. ^{e} P. G. Wilkinson and N. B. Houk, *J. Chem. Phys.* (1956) **24**, 528. ^{f} "Interatomic Distances", The Chemical Society, London (1958).

Mn, Ru and Ni-PCy_3 complexes, which show N–N distances very similar to those of mononuclear dinitrogen complexes,[1] all the complexes show a substantial lengthening of the N–N bond compared with free dinitrogen to about 1·14-1·18 Å. The M–N–N–M moiety is essentially linear, with exception of Co–N–N–Mg–N–N–Co, where the transition metal-dinitrogen grouping is linear, but the magnesium-dinitrogen group is bent. In the very complicated molecule $[\{(PhLi)_6Ni_2(N_2)(Et_2O)_2\}_2]$, the dinitrogen is "edge-on" bonded to a Ni–Ni moiety and interacts simultaneously with the Li

atoms. The result of this multiple interaction is a very long N–N distance (1·35 Å).

The $\nu(N_2)$ data clearly are in agreement with the substantial decrease in bond order of the dinitrogen molecule as follows from the long N–N distances. The shifts of $\nu(N_2)$ relative to free dinitrogen are large (of the order of 350-650 cm^{-1} to lower energy).

To explain these observations, a number of qualitative MO schemes have been suggested [for detailed discussions of these theories see the references given in the review by Chatt *et al.*[1] and Chapter 6.] One essential aspect however should be emphasized at this point. The weak σ-donation from the dinitrogen to the metal and the relatively stronger back-donation into the π^* orbitals of dinitrogen could easily lead to a too high charge build-up on dinitrogen. This unfavourable situation can be relieved by delocalization into empty π-type orbitals of the transition metal. It is evident that this mechanism will work effectively for complexes with few d electrons, e.g. early transition metals like Ti and Zr[8] or acceptor-type molecules like $[MoCl_3(thf)_3]$ which can function both as π-donors and as π-acceptors.

A consequence of this type of bonding may be an additional weakening of the N≡N bond and an increase in multiple bond character of the M–N bond, with ultimately cleavage of the N–N bond and formation of a transition metal nitride. Other ligands on the metal may participate in the bonding scheme and can even play an essential role in the bonding of the bridging dinitrogen ligand. This is the case in the complexes $[\{(\eta^5\text{-}C_5Me_5)_2M(N_2)\}_2(N_2)]$, (M = Ti, Zr).[5,8]

Based on the foregoing arguments one may expect quite a high reactivity of the bridging dinitrogen ligand. It is however impossible to predict whether this reactivity will be towards electrophilic (π-donor properties of the metal dominating) or nucleophilic reagents (π-acceptor properties dominating). The nature of the additional ligands may be decisive. Moreover, in most dinuclear complexes the dinitrogen ligand is in the inside of the complex, and reactions that are feasible electronically may be sterically blocked. It is also possible that in reactions initially aimed at the dinitrogen ligand, attack on peripheral ligands takes place and this may change the electronic conditions for the bonding of the dinitrogen so that the N–N bond order increases and dinitrogen is liberated.

III. Reactions

A. Unsuccessful experiments

Very few publications on dinuclear dinitrogen complexes of the transition metals mention explicitly experiments exploring the reactivity of the ligated

dinitrogen molecule. The very long N–N distance (1·35 Å) in [{(PhLi)$_6$-Ni$_2$(N$_2$)(Et$_2$O)$_2$}] suggests a strong increase in the electron density of the dinitrogen molecule and consequently a high reactivity of this ligand to protons or other electrophilic agents, but up to now no such reactions have been reported for this and a related complex.[20,21] From these publications a rather disappointing picture emerges. In practically all of the experiments reported, the dinitrogen is simply substituted by other ligands and is evolved as dinitrogen gas or simply remains bound to the metal.

The molybdenum complex [{Mo(η^6-C$_6$H$_6$)(PPh$_3$)$_2$}$_2$(N$_2$)] does not produce any N-containing products on reaction with H$_2$O, LiAlH$_4$ or BuLi.[22] The analogous complex [{Mo(η^6-C$_6$H$_3$Me$_3$)(dmpe)}$_2$(N$_2$)] (dmpe = Me$_2$PCH$_2$-CH$_2$PMe$_2$) is protonated at the metal with HBF$_4$ giving [{Mo(η^6-C$_6$-H$_3$Me$_3$)(H)(dmpe)}$_2$(N$_2$)] (BF$_4$)$_2$, which on further protonation (with HCl) or reaction with FeSO$_4$/H$_2$SO$_4$ also forms no nitrogen derivatives.[9] This protonation reaction suggests that in the Mo-dinitrogen complex, the electron density at the metal is higher than at the dinitrogen molecule.

The iron complexes [{Fe(η^5-C$_5$H$_5$)(L$_2$)}$_2$(N$_2$)] (L$_2$ = dmpe or dppe) also do not give N–H bond formation on reaction with reducing agents (e.g. LiAlH$_4$ or NaBH$_4$), or on protonation.[23,24] The dinitrogen ligand in [{RuL$_5$}$_2$(N$_2$)]$^{2+}$ (L = NH$_3$, H$_2$O) does not react with oxidizing and reducing agents and attempts to protonate it also fail.[25] An unsuccessful attempt to reduce the dinitrogen ligand in K$_2$[{Rh(NO$_2$)$_3$(NH$_3$)(OH)}$_2$(N$_2$)] with sodium dithionate has been reported.[26]

B. Reduction and protonation of the ligated dinitrogen molecule

The discovery by Vol'pin and Shur[27] in 1964, that combinations of transition metal compounds and an excess of reducing agents take up and reduce dinitrogen under mild conditions and give substantial amounts of ammonia on hydrolysis, started off intense research on these and related systems. Titanium compounds were especially effective and systems based on [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] have been investigated by a number of research groups, varying such reaction conditions as temperature, dinitrogen pressure, and nature of the reducing agents. There is substantial evidence that in these systems, which are very complicated and difficult to study systematically dinitrogen is reduced to titanium nitrides via dinuclear dinitrogen complexes (see Chapter 3). A number of mechanisms have been suggested to explain the complicated reactions that take place in the [Ti(η^5-C$_5$H$_5$)$_2$]-based systems and much confusion has resulted.

A survey of this early work will not be given here; this has already been covered in the review literature.[2,28]

C. Systems based on dicyclopentadienyl compounds of Ti and Zr

Since about 1970, research on the reduction of dinitrogen by Ti- and Zr-based systems has been limited to $M(\eta^5\text{-}C_5H_5)_2$-derivatives. Although considerable progress concerning the mechanism of complexation and reduction of the dinitrogen molecule has been made, the results obtained so far do not permit discussion in terms of an all-inclusive mechanism.

The reason for this may in part be that although various related dinitrogen complexes may have almost identical physicochemical properties, they quite often show very different chemical behaviour. This is well known for mononuclear dinitrogen complexes and it may also be true for dinuclear dinitrogen complexes.[29] Secondly, although the intermediates in the system under discussion here have not been fully characterized, it is quite possible that due to the high reactivity of cyclopentadienyl groups in low-valent Ti and Zr compounds, various different structures may exist which are not easily distinguishable but may have different chemical properties. In this respect the reported structures of species formerly referred to as "titanocene" have to be mentioned here[30,31,32] (Fig. 1).
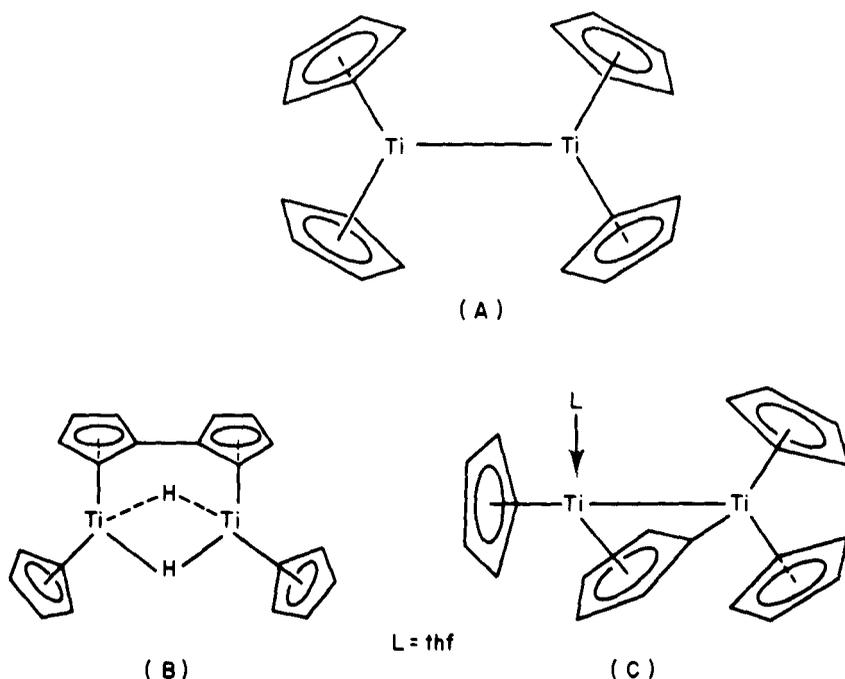
Fig. 1. Some forms of "titanocene", (A) metastable dimer[30] (structure unknown), (B) fulvalene bridged dimer,[31] (C) cyclopentadienyl bridged dimer.[32]

Authentic titanocene $[Ti(\eta^5\text{-}C_5H_5)_2]$ is most probably generated as an intermediate in the alkali metal (amalgam, naphthalene anion or metal) reduction of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$. It is not stable as such, but Brintzinger *et al.*[5,30] showed that it can dimerize to give the metastable $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2]$, which forms a dinuclear dinitrogen complex $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$. The dinitrogen ligand is not sufficiently activated to produce ammonia or hydrazine on protonation, but the addition of a strong reductor like lithium-naphthalene (1 Li/Ti) is sufficient to give a stoichiometric yield of NH_3 (0·95 mol NH_3 per Ti atom) after protonation.

A complex with the same stoichiometry but quite different properties was obtained by Shilov *et al.*[33] from $[\{Ti(\eta^5\text{-}C_5H_5)_2Cl\}_2]$ and MeMgI in ether under dinitrogen. In contrast to the former complex, this complex shows a band at 1280 cm^{-1}, which is assigned to $\nu(N_2)$. This low value of $\nu(N_2)$ suggests that the complex is a diazene derivative and consequently a non-linear Ti–N=N–Ti unit is proposed.[34] Protonation studies support this view. Reaction with HCl (in methanol) at -60°C give dinitrogen and hydrazine (1:1 molar ratio) and reaction with HCl (in ether) at the same temperature produces dinitrogen and ammonia (30% based on the complexed dinitrogen). The difference in product formation is ascribed to disproportionation of the initially formed diazene under the different reaction conditions. The presence of the dicyclopentadienyl-titanium moiety follows from the formation of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ on reaction with HCl (Scheme (**1**)). Complete reduction of the
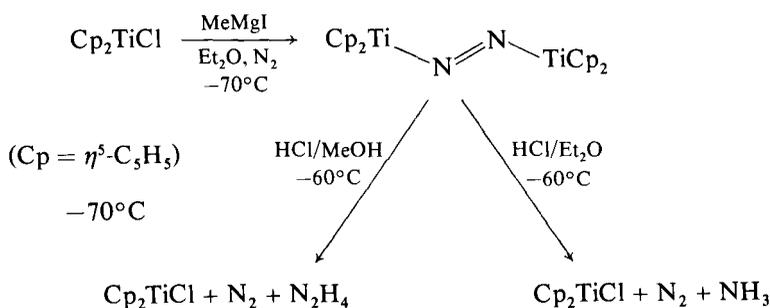
Scheme (1)

ligated dinitrogen and formation of a nitrido-titanium complex takes place on reaction with PhLi (in ether). Conversion of this complex to a hydrazine precursor under the action of Pr^{i}MgCl was claimed in a reduction scheme.[35] It is not clear from the paper whether this observation was made on the complex itself or whether it has been assumed as an intermediate in the system $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]/Pr MgCl/N_2$ in ether.

Pez[32] reports that the dimeric titanocene-type compound $[(\eta^5\text{-}C_5H_5)_2\text{-}$ Ti-μ-$(\eta^1,\eta^5\text{-}C_5H_4)\text{Ti}(\eta^5\text{-}C_5H_5)]$, obtained by low-temperature potassium-naphthalene reduction of $[\text{Ti}(\eta^5\text{-}C_5H_5)_2Cl_2]$ in thf under argon, reacts with dinitrogen to give a deep-blue complex $[\{\text{Ti}_2(C_5H_5)_3(C_5H_4)\}_2(N_2)]$ (Fig. 2).[36] This complex shows no $\nu(N_2)$ in the infrared spectrum and therefore a centrosymmetric dinuclear structure is proposed with the dinitrogen bridging the titanocene parts of two dimers. In this respect the complex is very similar to $[\{\text{Ti}(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$ reported by Brintzinger *et al.*[30]
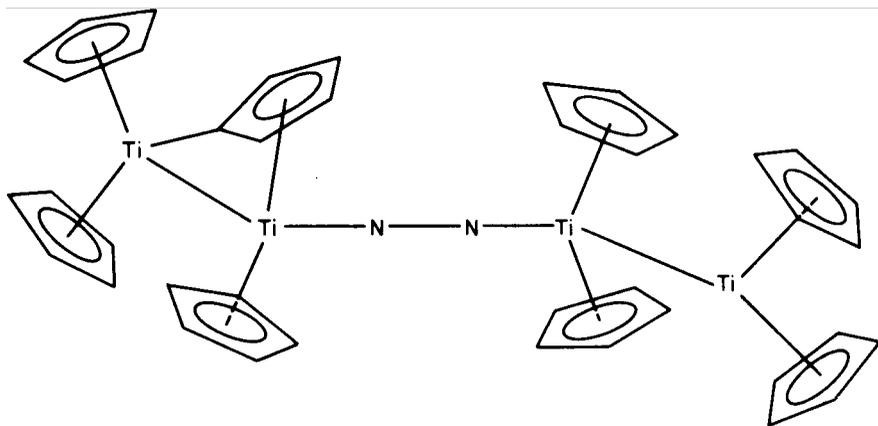
Fig. 2. Possible structure of dinitrogen complex of cyclopentadienyl bridged titanocene dimer.[36]

This similarity is also found in the reactivity of the dinitrogen ligand. It does not react with H_2, but a strong reducing agent (e.g. potassium-naphthalene) reduces it to an ammonia precursor. About 70% of the originally complexed dinitrogen is formed as ammonia after hydrolysis.[36]

The high reactivity of the cyclopentadienyl rings in low-valent dicyclo-pentadienyltitanium compounds prompted Bercaw *et al.*, to study the more stable permethylcyclopentadienyl analogues. $[\text{Ti}(\eta^5\text{-}C_5Me_5)_2]$ at 0°C forms $[\{\text{Ti}(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]$ with a linear bridging dinitrogen as was shown by X-ray structure determination (Fig. 3).[5] The long N–N distance (1·160 Å) indicates a reduction of the dinitrogen bond order, but this is not substantiated by an easy protonation of the dinitrogen; additionally, further reduction of this ligand (e.g. with Mg/Hg or a N_2/H_2 mixture) cannot be achieved.[37]

At low temperature (-80°C) the titanium complex takes up extra dinitrogen and an equilibrium is established:

$$[\{\text{Ti}(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)] \underset{}{\overset{N_2}{\rightleftharpoons}} [\{\text{Ti}(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)] \qquad (1)$$
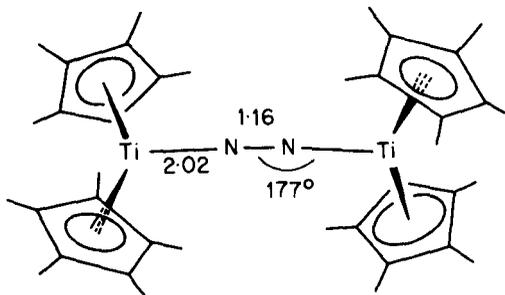
Fig. 3. Structure of $[\{Ti(\eta^5\text{-}C_5Me_5)_2\}_2(N_2)]$.

giving a dinuclear dinitrogen complex with terminal dinitrogen ligands. The structure was based on analogy with the corresponding zirconium complex (see below) and on ^1H and ^{15}N NMR spectra.[38] Surprisingly these complexes produce a nearly quantitative yield of hydrazine when treated with HCl.[5]
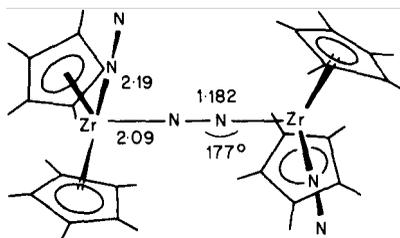
Fig. 4. Structure of $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$.

Permethylzirconocene forms a dinitrogen-containing complex both terminal and bridging, $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)]$, the structure of which has been determined[8] as that shown in Fig. 4. With HCl in toluene at -80°C it reacts to give hydrazine (0·86 mol)[8] (equation (**2**).

$$[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(N_2)] + 4HCl \rightarrow 2[Zr(\eta^5\text{-}C_5Me_5)_2Cl_2] + 2N_2 + N_2H_4 \quad (2)$$
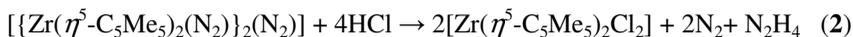
A study of the reaction of hydrogen chloride with the complex having terminal $^{15}N_2$ shows that half of the hydrazine arises from terminal dinitrogen and the other half from the originally bridging dinitrogen.[8] It is not likely that the bridging dinitrogen is attacked first, since the related complex $[\{Zr(\eta^5\text{-}C_5Me_5)_2(CO)\}_2(N_2)]$ does not give hydrazine on reaction with hydrogen chloride.[39] The mechanism proposed is one in which first a terminal dinitrogen is protonated, then the other terminal ligand is lost and a symmetric bis-diazenido complex $[Zr(\eta\text{-}C_5Me_5)_2(N_2H)_2]$ is formed. Further protonation of the latter gives diazene, which disproportionates to give dinitrogen and hydrazine.[8,38]

Shilov *et al.*[33,35] have studied systems based on ethereal mixtures of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ and alkyl-Grignard reagents at low temperatures (-80°C) under N_2. With MeMgI (Mg:Ti = 2) the previously discussed dinitrogen complex $[\{Ti(\eta^5\text{-}C_5H_5)_2\}_2(N_2)]$ was obtained. With Pr^iMgCl (Mg:Ti = 4) a Mg- and Cl-containing complex of stoichiometry $[\{Ti(\eta^5\text{-}C_5H_5)_2\}(N_2MgCl)]$ having $\nu(N_2)$ at 1255 cm^{-1}, was isolated. Treatment of this complex with HCl (in MeOH) at -60°C gave hydrazine in about 80% yield. Structures with a MgCl fragment bound to two titanium atoms bridging the dinitrogen molecule were proposed. The reduction of dinitrogen in these systems is suggested to proceed according to Scheme (**2**). In this scheme the conservation of the dicyclopentadienyltitanium unit throughout the reduction process is essential.
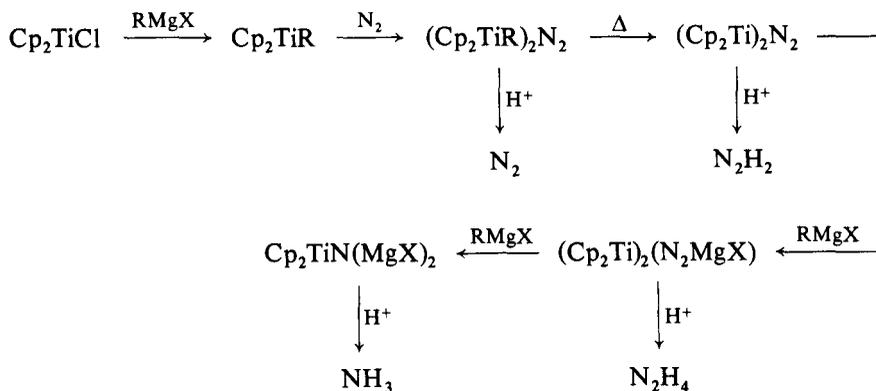
$Cp = \eta^5\text{-}C_5H_5$; R = alkyl; X = halide.

Scheme (2)

This Shilov mechanism, however, is probably not the only one operative in these systems. Van der Weij *et al.*[40,41] studied related systems $[\{Ti(\eta^5\text{-}C_5H_5)_2R\}(N_2)]$ with R = aryl, CH_2CMe_3 and gave evidence for a reduction mechanism in which loss of a $(\eta^5\text{-}C_5H_5)$ group is essential (see below). They observed that for the system $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]/4$ Pr^iMgCl in ether under dinitrogen at -80°C this mechanism also works and can at least account for part of the ammonia and hydrazine obtained. The loss of cyclopentadienyl groups was confirmed by the isolation of $[Mg(\eta^5\text{-}C_5H_5)_2]$ from the reaction mixture. The Pr^iMgCl system is very labile and the results are strongly dependent on the reaction conditions.[41] Based on experimental evidence and by analogy with the sodium-naphthalene reduction of $[\{Ti(\eta^5\text{-}C_5H_5)_2R\}_2(N_2)]$ they suggest the mechanism shown in Scheme (**3**).

The complexity of the systems under discussion here, and the variety of products that can be expected under various reaction conditions is also

$$Cp_2TiCl \xrightarrow{RMgX} Cp_2TiR \xrightarrow{N_2} (Cp_2TiR)_2N_2 \longrightarrow$$

$$(CpTiR)NMgX \xleftarrow{\Delta} (CpTiR)_2N_2(MgX)_2 \xleftarrow{RMgX} (CpTiR)_2N_2 \xleftarrow{RMgX}$$

$$\downarrow H^+ \qquad\qquad\qquad \downarrow H^+$$

$$NH_3 \qquad\qquad\qquad N_2H_4$$

Cp = η^5-C$_5$H$_5$; R = alkyl; X = halide.
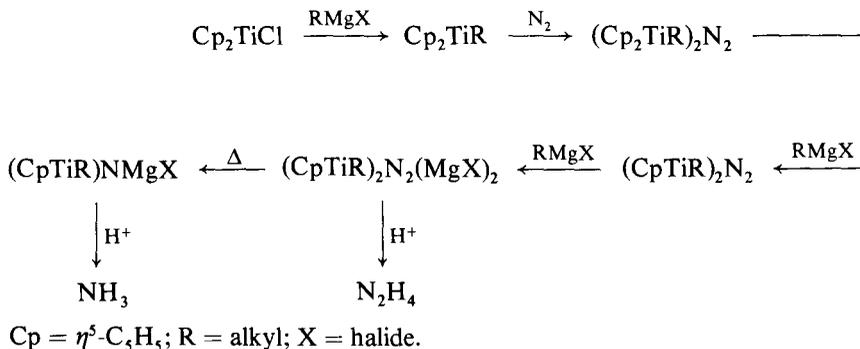
Scheme (3)

illustrated by the work of Bercaw *et al.*[30] They isolated [{Ti(η^5-C$_5$H$_5$)$_2$-(Et)}$_2 \cdot$ 6MgCl$_2 \cdot$ 7Et$_2$O] from a mixture of [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] and EtMgCl in ether at 20°C under Ar. The structure of this complex is unclear. It reacts directly with dinitrogen (230 atm. in 1,2-dimethoxyethane) and gives a nitride formulated as [{Ti(η^5-C$_5$H$_5$)$_2$}$_3$(N)$_2$], which gives ammonia and [Ti(η^5-C$_5$H$_5$)$_2$Cl$_2$] (2:3) on reaction with HCl gas.

It is clear that further work under carefully controlled reaction conditions is necessary to solve the problem of the mechanism of dinitrogen reduction in these systems.

Unlike the alkyldicyclopentadienyltitanium dinitrogen complexes, the analogous complexes [{Ti(η^5-C$_5$H$_5$)R}$_2$(N$_2$)] (R = Ph, *o-*, *m-*, *p*-CH$_3$C$_6$H$_4$, C$_5$F$_5$ and CH$_2$Ph) are completely characterized crystalline compounds.[42] Recently an X-ray structure determination on [{Ti(η^5-C$_5$H$_5$)$_2$(*p*-CH$_3$C$_6$-H$_4$)}$_2$(N$_2$)] (Fig. 5) showed the presence of a linear Ti–N–N–Ti unit as has been found for the other well characterized dinuclear dinitrogen complexes. The N–N distance (1·162 Å) is the same as reported for [{Ti(η^5-C$_5$-Me$_5$)$_2$}$_2$(N$_2$)],[5] and slightly shorter than that (1·182 Å) in the complex [{Zr(η^5-C$_5$Me$_5$)$_2$(N$_2$)}$_2$(N$_2$)].[8] The dinitrogen ligand in [{Ti(η^5-C$_5$H$_5$)R}$_2$-(N$_2$)] cannot be protonated directly. It would be interesting to know the behaviour towards protonation of the bridging dinitrogen in the recently published[43] complex [{Zr(η^5-C$_5$H$_5$)$_2$R}$_2$(N$_2$)] (with R = CH(SiMe$_3$)$_2$), but no such study has yet been reported.

Further activation of the dinitrogen ligand in [{Ti(η^5-C$_5$H$_5$)$_2$R}$_2$(N$_2$)] can be achieved by the use of reducing agents (e.g. sodium-naphthalene, BuLi or Pr^{i}MgCl). Sodium-naphthalene is the most reactive, Pr^{i}MgCl the least,[44] but its effectiveness increases for the alkyl complexes (e.g. R = CH$_2$CMe$_3$).[41] Van der Weij *et al.*[40] have thoroughly investigated the system [{Ti(η^5-C$_5$-H$_5$)$_2$R}$_2$(N$_2$)]/sodium-naphthalene (R = *m*-CH$_3$C$_6$H$_4$) at low temperature (-78°C) in thf. They propose a mechanism (Scheme (**4**)) in which the bridging

$(Cp_2TiR)_2N_2 \xrightarrow{NaC_{10}H_8} (CpTiR)_2N_2 \xrightarrow{NaC_{10}H_8} [(CpTiR)_2N_2]^{2-}$

$(CpTiR)_2N_2 \downarrow H^+$

N_2H_2

$[(CpTiR)_2N_2]^{2-} \downarrow H^+$

N_2H_4

$[(CpTiR)N]^- \xleftarrow{\Delta}$

$\downarrow H^+$

NH_3

Cp = η^5-C$_5$H$_5$; R = aryl; NaC$_{10}$H$_8$ = sodium naphthalene.

Scheme (4)

Fig. 5. Structure of $[\{Ti(\eta^5\text{-}C_5H_5)_2(p\text{-MeC}_6H_4)\}_2(N_2)]$.

dinitrogen is reduced stepwise via a diazene precursor to a dianion which gives hydrazine when treated with HCl. In the first step the essential reaction is the abstraction of a cyclopentadienyl group from titanium and the formation of $(C_5H_5)Na$. In the second step electrons of the naphthalene anion are transferred into the $[\{Ti(\eta^5\text{-}C_5H_5)R\}_2(N_2)]$ system and a dianion is generated. Both reactions proceed quite easily even at -78°C. In the hydrazine precursor the dinitrogen molecule is so far modified (reduced) that it is thought to possess an essentially single N–N bond. Both intermediates are very reactive and react easily with a variety of substrates (e.g. solvent or slightly acidic hydrogen on organic molecules) or extra sodium-naphthalene to give a very complicated mixture which is very difficult to unravel. Warming of the hydrazine precursor to room temperature results in the splitting of the N–N bond and formation of a nitrido compound. Ammonia is produced when this nitrido species reacts with protons. Reaction with extra sodium-naphthalene proceeds with degradation of the cyclopentadienyltitanium structure, without increasing the total yield of reduced dinitrogen. The various intermediates have not been isolated or detected in solution. The evidence for their existence and identity is indirect and based on the following observations:

(i) Substantial amounts of $[Ti(\eta^5\text{-}C_5H_5Cl_3]$ are obtained after reacting the reduced mixtures with HCl/ether.
(ii) $(C_5H_5)Na$ was demonstrated to be present in the solutions (by IR and ^1H NMR spectroscopy).
(iii) Ferrocene was obtained in yields corresponding to the amounts of $(C_5H_5)Na$ present; it was demonstrated that $[FeCl_2]$ did not interfere with the reduction process itself.
(iv) When DCl/D_2O was used to quench the reduced mixtures RD was formed, thus demonstrating retention of the Ti-R bond.

Other reducing agents like BuLi and Pr^iMgCl give reaction mixtures which are very similar to those with sodium-naphthalene and it is assumed that the same mechanism applies.

From the work discussed in this section it may be inferred that in dinuclear dinitrogen complexes with a linear M–N–N–M unit (M = Ti, Zr), the ligated dinitrogen cannot be protonated directly despite the fact that the N–N distance is quite long and is intermediate between that found in free dinitrogen and MeN=NMe. Further reduction is an essential condition for obtaining N-H compounds. On the other hand, terminal dinitrogen in Ti and Zr complexes may be just as reactive as in other transition metal compounds[1] as is suggested by the smooth formation of hydrazine from the complexes $[\{M(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2N_2]$ M = Ti, Zr.

C. Carbon-nitrogen bond formation

A number of publications have appeared in which the (mostly low yield) formation of carbon-nitrogen bonds is reported. The systems under investigation normally consist of Ti compounds mixed with an excess of strong reducing agent and are normally considered as containing nitrido-metal species. It is very unlikely that in these systems the N–N group is still present and therefore they fall outside the scope of this section, and are discussed in Chapter 3.

D. Dinuclear complexes of niobium, chromium and iron

The formation of a dinuclear dinitrogen complex of niobium, $[\{NbCl(dmpe)_2\}_2(N_2)]$, has recently been reported. It gives a small amount of hydrazine (10%) on reaction with HCl in thf. Details of structure and the reactivity of the dinitrogen ligand are not yet known.[1]

Sobota *et al.*[45] report the formation of the complexes $[(Cr(dppe)_2)_2(N_2)]$ and $[Cr_2N_2Mg_4Cl_4(thf)_5]$ in the system $CrCl_2/Mg/N_2$ in thf (in the presence or absence of dppe respectively). Hydrolysis of the first complex gives small amounts of ammonia and hydrazine, whereas the latter gives these compounds in higher yields (60% and 25% respectively). These complexes are poorly characterized and the presence of bridging dinitrogen was not clearly established. However, the formation of hydrazine from the thf complex indicates that although the major part of the complex mixture probably is a nitride, at least a minor part contains N–N bonds. Whether this is a dinitrogen ligand in a reduced form or a hydrazido-derivative is not clear, but the system is very interesting.

Other systems in which the reduction of dinitrogen is observed (probably via dinuclear dinitrogen complexes) are formed by $FeCl_3$ and reducing agents in ether under dinitrogen. A dinuclear complex $[(PPh_3)_2(Pr^i)HFe(N_2)Fe(Pr^i)(PPh_3)_2]$ is formed from $[(PPh_3)_2FeCl_3]$ with Pr^iMgCl in ether.[46] A band at 1761 cm^{-1} is attributed to $\nu(N_2)$ and indicates a low N–N bond order. This is illustrated in its reactivity towards HCl (in ether), where a low yield of hydrazine is obtained (10% based on the complexed dinitrogen). The mechanism shown in Scheme (**5**) is postulated. Kinetic studies on the system

$$L_n\overset{\text{H}}{Fe}\cdots N\underline{\cdots}N\cdots FeL_n \xrightarrow{\text{H}^+} L_n Fe-\overset{\text{H}}{N}=\overset{\text{H}}{\underset{+}{N}}-FeL_n \longrightarrow$$

$$L_n\overset{+}{Fe}-NH-NH-FeL_n \xrightarrow{\text{H}^+} N_2H_4$$

Scheme (5)

FeCl$_3$/PhLi/N$_2$ in ether suggest the formation of a dinuclear iron-dinitrogen complex.[47] The nature of this complex is still unknown, EPR spectra indicate that the iron part of the complex is probably an Fe(I) derivative. On treatment with HCl, part of the dinitrogen is liberated as hydrazine (about 20% of the complexed dinitrogen) and the remainder as dinitrogen gas. In the presence of LiBr this system also forms ammonia on hydrolysis while the yield of hydrazine drops; in the absence of LiBr only hydrazine (and dinitrogen) is obtained.[48]

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