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Published in:
EPRINTS-BOOK-TITLE

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1982

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Teuben, J. H. (1982). Reaction of Dinitrogen in Dinuclear Complexes. In *EPRINTS-BOOK-TITLE* University of Groningen, Stratingh Institute for Chemistry.

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REACTION OF DINITROGEN IN DINUCLEAR COMPLEXES

by
 J. H. TEUBEN *

Dinuclear dinitrogen complexes are known for most of the transition metals; only for Hf, V, Ta and Tc no complexes have been reported until now. The reactivity of the complexed dinitrogen has not been widely studied but protonation to hydrazine or ammonia has been reported for a number of elements (Fig. 1). The bonding of the N₂-ligand is normally in a linear M-N-N-M arrangement. In two Ni-complexes a doubly side-on coordinated N₂ molecule has been found (Fig. 1, 2). In the reported structures the M-N

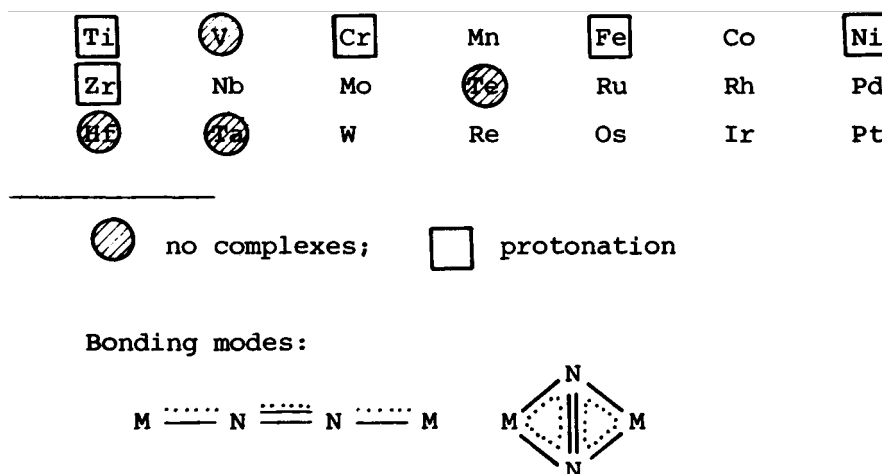


Fig. 1. Dinuclear dinitrogen complexes (transition metals involved, dinitrogen binding mode and occurrence of protonation).

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Complex	N-N	M-N-N	$\nu(\text{N}_2)$
$(\text{Cp}_2\text{Ti t ol})_2\text{N}_2$	1.16	177°	—
$(\text{Cp}^1_2\text{Ti})_2\text{N}_2$	1.16	179°	—
$\text{Cp}_3\text{C}_5\text{H}_4\text{Ti-N}_2\text{-Ti}_2\text{Cp}_2\text{C}_{10}\text{H}_8$	1.27	—	1282
$[\text{Cp}'_2\text{Zr}(\text{N}_2)]_2\text{N}_2$	1.18	177°	—
$[[(\text{PhLi})_3\text{Ni}]_2\text{N}_2\text{Et}_2\text{O}]_2$	1.35	—	—
$[\text{MeCpMn}(\text{CO})_2]_2\text{N}_2$	1.12	177°	1971
$[(\text{PCy}_3)_2\text{Ni}]_2\text{N}_2$	1.12	178°	—
N_2	1.10	—	2331
MeN = NMe	1.23	—	—
$\text{H}_2\text{N} - \text{NH}_2$	1.46	—	—


$\text{Cp}^1 = \eta^5\text{-C}_5\text{Me}_5$; $\text{C}_{10}\text{H}_8 =$  ; Cy = cyclohexyl.

Fig. 2. Structural and spectroscopic data for dinuclear dinitrogen complexes.

bond in the complex is longer than in free N_2 . For complexes of Ti and Zr the observed distances of 1.16-1.27 Å suggest a lowering of the bond order,

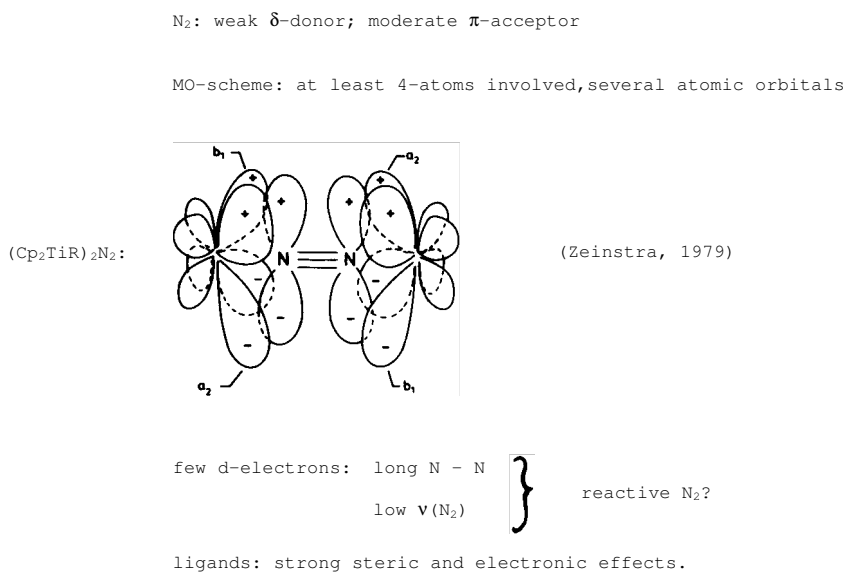


Fig. 3. Bonding and reactivity of dinitrogen in dinuclear complexes.

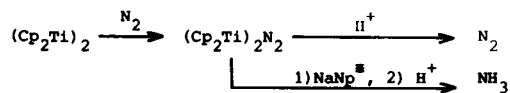
N_2 normally unreactive, easily displaced.

systematic studies:

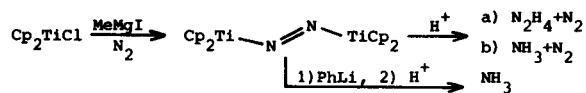
$[C_6H_6Mo(PPh_3)_3]_2N_2$	$H_2O, LiAlH_4, BuLi$	neg.
$[CpFe dppe]_2N_2$	$LiAlH_4, NaBH_4$	neg.
$[(NH_3)_5Ru]_2N_2^{2+}$	oxid, red., H^+	neg.
Cp_2Ti, Cp_2Zr systems	H^+	N_2H_4, NH_3
$[NbCl(dmpe)_2]_2N_2$	H^+	N_2H_4 (10%)
$[Cr(dppe)_2]_2N_2$	H^+	N_2H_4, NH_3 (low yield)
$[Cr_2N_2Mg_4Cl_4\cdot 5thf]$	H^+	N_2H_4, NH_3 (25, 60%)
$(PPh_3)_2(Pr^i)HFe-N_2-Fe(Pr^i)(PPh_3)_2$	H^+	N_2H_4 (10%)
$FeCl_3 PhLi N_2$	H^+	N_2H_4 (20%)
$[{(PhLi)_3Ni}_2N_2 \cdot Et_2O]_2$	H^+	NH_3 (30%)

Fig. 4. Reactivity of bridging dinitrogen.

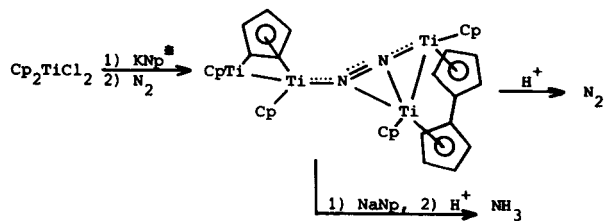
Bercaw (1972):



Shilov (1972):



Pez (1976, 1978):



$^{\#}Np$ = Naphthalene

Fig. 5. Titanocene-dinitrogen systems.

but this is not directly observable in the chemistry of the complexes (e.g. protonation studies) (Fig. 2). The bonding in dinuclear dinitrogen complexes is complicated and involves normally 4 or more atoms. From this a strong electronic effect of other ligands is expected, and in addition steric aspects are very important too (Fig. 3). The reactivity of bridging N_2 has not been studied extensively. From the reports the picture of a rather unreactive, but easily displaceable ligand emerges. Treatment with reducing agents and subsequent protonation sometimes give N-H products like N_2H_4 and NH_3 (Fig. 4).

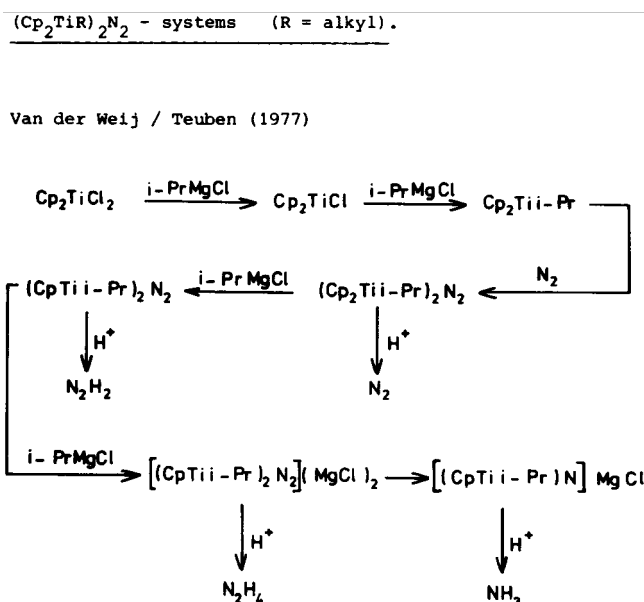


Fig. 8. Reduction of dinitrogen in the $[(Cp_2TiR)_2N_2]$ (R=alkyl) complexes (Teuben *et al.*).

Among the best studied systems are those which are based on titanocene and zirconocene derivatives. These systems are very complicated and difficult to study. Systems, which are basically the same have been investigated to give a variety of complexes with different properties and interpretations (Fig. 5). Permethyltitanocene and -zirconocene systems are less ambiguous. From the excellent work by Bercau and coworkers a very interesting, but still rather complicated mechanism for the reduction of N_2 in these systems has been suggested (Fig. 6).

For the reduction in the related compounds $(Cp_2TiR)_2N_2$ ($R = \text{alkyl}$), different and conflicting mechanisms have been put forward. The main difference between them is the retention or loss of the Cp_2Ti structure during the reduction (Fig. 7, 8).

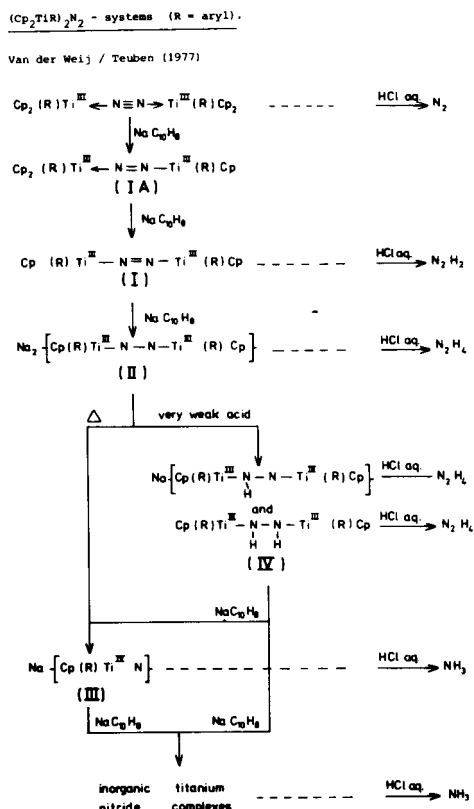


Fig. 9. Reduction of dinitrogen in the $[(Cp_2TiR)_2N_2]$ ($R = \text{aryl}$) complexes.

The aryl complexes $(Cp_2TiR)_2N_2$ have been extensively investigated. Meticulous work on the step-wise reduction of the ligand N_2 sodium-naphthalene has led to the reduction scheme presented in Figure 9.