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Invited review

Dinitrogen fixation and activation after 30 years: a puzzle still unsolved

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Abstract

The most relevant literature in the field of dinitrogen activation/fixation promoted by early transition metals is critically reviewed in the occasion of the 30th anniversary of its discovery. Our contribution to this research is also reviewed.

Keywords: Dinitrogen fixation; Zirconium; Vanadium; Titanium; Niobium; Tantalum

The aim of the present review is to survey part of the most relevant literature in the field of dinitrogen activation or fixation promoted by early transition metals, and to summarize our contribution to this research during the past five years. Excellent and more comprehensive reviews are available on this topic [1].

Dinitrogen is the most abundant component of the atmosphere and is an essential element for life. A high inertness is its salient characteristic which makes it an efficient and readily available agent for protecting reactive chemicals. Today, dinitrogen is used not only by chemists for blanketing Schlenk vessels and to fill dry-boxes, but even in the food industry to retard the degradation of goods. The high stability of N_2 is to be ascribed both to the

$$N_2(g) \rightarrow 2N(g) \quad \Delta H = +945.2 \text{ KJ mol}^{-1}$$

presence of a N≡N triple bond (1.10 Å) and to the fact that N_2 is very difficult to oxidize or reduce. Dinitrogen oxidation to form nitrogen oxides requires very high temperatures (typically NO_x are formed in significant amounts during the combustion of fuels). Conversely, the reduction of N_2, although very difficult ($E_{red} = -7.8$ eV), is more promising, since the resulting highly reactive nitride or hydrazide anions may be reasonably expected to provide a wider range of controllable reactivity. Thus far, the only reactions available for the reduction of N_2 are provided by variations of the original Haber process which are presently used for the production of very large amounts of NH_3 (23 million tons per year in the US). The severity of the conditions employed in

$$N_2(g) + H_2(g) \xrightarrow{\text{cat.}} NH_3(g)$$

these catalytic processes contrasts spectacularly with the catalytic reduction performed by the naturally occurring nitrogenase under very mild condition [2]. In this natural system, the coordination of dinitrogen is followed by electron transfer from the pyruvate electron pool which takes the dinitrogen molecule through the several steps of reduction (diazenido → hydrazido → nitride). Complete transformation to NH_3 requires at least six electrons to be provided to N_2. Therefore, it is not surprising that the efficiency and the mild conditions displayed by nitrogenase have stimulated considerable research in this field [3], and that understanding the detailed mechanism of the action of nitrogenase remains a primary goal in this chemistry. In fact, in respect of finding more viable and easy-to-prepare synthetic alternatives to nitrogenase, the insights obtained from the naturally occurring systems might provide crucial information about the fundamental steps in which dinitrogen is efficiently coordinated and reduced. This is not only important for creating possible alternatives to the Haber process, but also for the ambitious goal of using dinitrogen as a source of nitrogen atoms for the preparation of organic molecules (formation of heterocycles, nitriles, carbamates, hydrazines, ureas, etc.).

Given this scenario, the initial discovery in 1965 by Allen and Senoff [4] that a simple $[Ru(NH_3)_5]^{2+}$ com-

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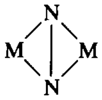
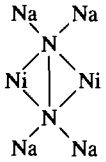
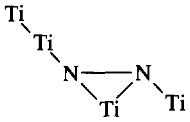
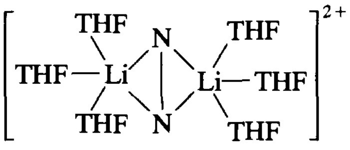
plex could reversibly coordinate dinitrogen represented a true landmark in the development of modern coordination chemistry. A major input was given to this chemistry by Chatt and his coworkers, at the Nitrogen Fixation Unit at the University of Sussex, who synthesized a series of zero-valent Group VI metal dinitrogen complexes (end-on coordinated) and successfully performed the first elemental transformation of coordinated dinitrogen [5]. In the aftermath of the tremendous interest generated by these findings, studies flourished in this field, and as a result many dinitrogen complexes have been discovered for a number of transition metals [1f,5a]. Significant breakthroughs have been made recently, for example, in the stoichiometric preparation of *N*-aminopyrrole directly from dinitrogen [6a] and the catalytic conversion of N_2 into amines [6b]. Although these metal-promoted processes are certainly not financially viable for the production of heterocycles or amines, they do have the merit of demonstrating that incorporation of dinitrogen into organic substrates is indeed a realistic goal.

There is a general agreement that the coordination of dinitrogen to a metal center is a prerequisite for its further transformation and that the availability of d electrons and the presence of a strongly reducing metal are crucial for the interaction of the metal with an exceedingly stable molecule such as dinitrogen [7]. To date there is no reported example of coordination of dinitrogen performed by a d^0 transition metal. However, it should be noted that the recently reported reversible side-on coordination of dinitrogen to a Li^+ cation (Scheme 1) [8] contradicts these expectations, and opens interesting perspectives in the field of the reactions of dinitrogen with high valent transition metals. Since the type of bonding adopted by dinitrogen (Table 1) seems to be a crucial factor for further activation, the attention of researchers was mainly focussed on the preparation of new complexes containing dinitrogen bonded in a variety of modes. As a result, a plethora of compounds has been prepared containing end-on (both terminal and bridging) dinitrogen [1f,5a], while the side-on bonding mode remains relatively uncommon. Following the initial proposal by Lappert et al. that a Zr(III) complex might be able to coordinate dinitrogen in a side-on bonding fashion [9], this unusual bonding mode came to be regarded as particularly promising for activation purposes. In fact, this type of coordination implies a significant donation of charge from the metal to the π^* orbitals of N_2, which corresponds to significant reduction of the N≡N triple bond. This widely accepted idea was recently substantiated by the findings of Fryzuk and coworkers. The reduction of $[(Pr^i_2PCH_2SiMe_2)_2N]ZrCl_3$ afforded the dinuclear dinitrogen complex $\{[(Pr^i_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}N_2)$ in which the side-on bonded dinitrogen shows the longest observed N–N distance (N–N = 1.548 Å) [15] (Scheme 2). In addition, theoretical calculations [16] carried out on the closely-related side-on $\{[(Pr^i_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}N_2)$ and end-on $\{[(Pr^i_2PCH_2SiMe_2)_2N]ZrCp\}_2(\mu\text{-}N_2)$ complexes, have emphasized that the presence of suitable d orbitals, able to provide a δ overlap with the π^* orbital of the dinitrogen, is a factor capable of determining the coordination mode. However, aside from this elegant work, other literature data indicate that the side-on bonding mode does not necessarily imply reduction of dinitrogen. For example, the side-on dinitrogen complex of samarocene [17] shows a N–N distance (N–N = 1.088 Å) which is surprisingly short, and even shorter that in free N_2 (N–N = 1.10 Å). The puzzle becomes even more complicated when considering that, in the case of the aforementioned reversible side-on coordination of dinitrogen to lithium, the N–N distance (N–N = 1.06 Å) is even shorter [8]. This result also remains unexplained.

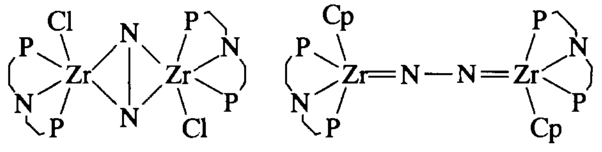
Table 1

Mode	Type	Reactivity	Ref.
$L_nM\text{-}N{\equiv}N$	stable, reversible	protonation, alkylation	[10]
$L_nM\text{-}N{=}N\text{-}ML_n$	stable, reversible	protonation, alkylation	[11]
	reversible	reduction	[12]
			[13]
	stable	reduction	[14]

Recent studies on nitrogenase [18] have indicated that vanadium, probably in a relatively high oxidation state, might be involved in dinitrogen reduction, thus



Scheme 1.



Scheme 2.

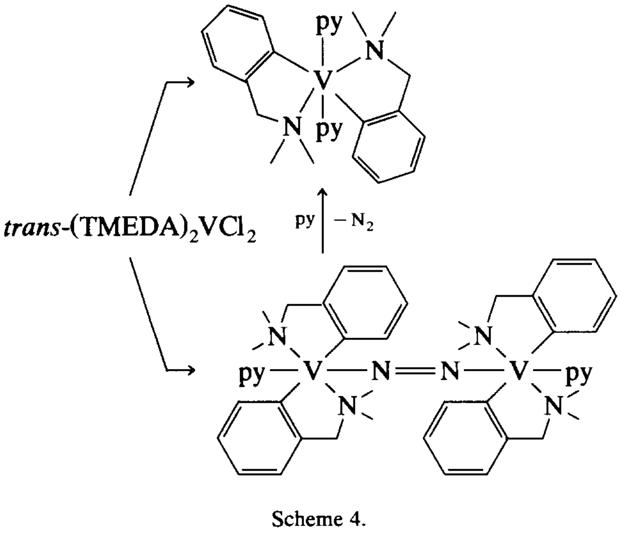
$$N_2 \xrightarrow[\text{MeOH}]{V(OH)_2/Mg(OH)_2} NH_3 + H_2NNH_2$$

$$N_2 \xrightarrow[\text{ROH}]{Ti(OBu^t)_2} NH_3$$

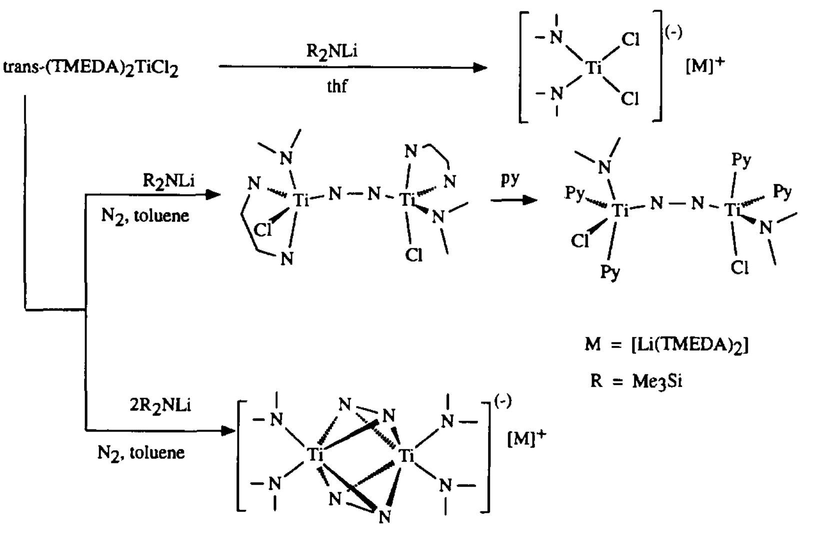
Scheme 3.

indicating that the presence of a low oxidation state (+2 or lower) is not necessarily a prerequisite for dinitrogen reduction [19]. These considerations raise questions about the factors which enhance the reactivity of V(III) and make this relatively stable species capable of interacting with dinitrogen. Is dinitrogen fixation the result of a favorable electronic configuration of the metal determined by the nature of the donor atoms, or is it rather the result of a favorable steric constraint and ligand geometry such as that in the cuboid structure of the nitrogenase cofactor [18]?

Our research in this field was stimulated by the initial finding that divalent titanium and vanadium complexes generated in situ may be able to catalytically transform dinitrogen in the presence of protic solvents to ammonia and hydrazine (Scheme 3) [19–21]. These observations provided a strong stimulus for developing the chemistry of these two divalent species in the hope that the characterization of families of their derivatives might enable clarification of the factors which promote or disfavor the coordination and, eventually, the activation of dinitrogen. Divalent vanadium and titanium were expected to be particularly suitable systems for this purpose, since a very high reactivity was predicted. The project required the preparation of suitable divalent starting salts from which divalent Ti and V complexes could be obtained by simple ligand exchange reactions. This was accomplished with the successful synthesis of monomeric and octahedral $MCl_2(TMEDA)_2$ ($M = Ti^{22}$, V^{23}) complexes. The role of the ligand donor atom was the first factor to be examined. In agreement with the findings by van Tamelen and Schrauzer and coworkers [19–21], ligands employing oxygen as a donor atom were the most promising in promoting reactivity with dinitrogen. For this reason we attempted the synthesis of a variety of Ti(II) [24] and V(II) [25] alkoxides and aryloxides, finding that surprisingly neither system undergoes any appreciable interaction with dinitrogen. Even when preformed dinitrogen complexes were employed as starting materials, dinitrogen was systematically liberated during the ligand replacement reactions. A great tendency to form complexes with the metal in a higher oxidation state was the general trend observed in this chemistry. In contrast, the employment of carbon-donor based ligands was, at least in the case of V(II), the appropriate strategy for promoting coordination of dinitrogen. The isolation and characterization of the first vanadium dinitrogen complex $[(Me_2NCH_2Ph)_2VPy]_2$-(μ-N_2) [26] was achieved via a simple chloride replacement reaction of $VCl_2(TMEDA)_2$ with LiPh(*o*-CH_2NMe_2) in the presence of pyridine (Scheme 4), thus confirming that divalent vanadium is indeed sufficiently reactive to interact with dinitrogen. Following this finding, another organometallic dinitrogen complex of V(II) was prepared and characterized [27]. A significant advance in the understanding of the reactivity of vanadium with dinitrogen was achieved with the successful preparation and characterization of Np_3V-N_2-VNp_3 [28]. The reversible coordination of dinitrogen on a trivalent vanadium center demonstrated the unprecedented ability of the oxidation state +3 to react with N_2, which is particularly interesting since the trivalent state of vanadium is accessible in natural systems, and a medium valent vanadium may be the active species responsible for the activation of dinitrogen in vanadium-nitrogenase. Trivalent vanadium is also responsible for other transformations that occur in some biovanadium systems [29]. However, although di- and tri-valent vanadium organometallic complexes can react with N_2, some characteristics, such as the very high reactivity, their thermal lability and the reversibility of the dinitrogen coordination, make these species unsuitable for further activation studies. For this reason, we have investigated the possibility that ligands based on donor atoms other than carbon (such as nitrogen for example) may also be able to promote coordination of dinitrogen. The preparation of low- and medium-valent Ti and V amides was considered to be an appropriate starting point for this research, even though the use of these species was expected to be limited by their air-sensitivity. Nevertheless the results in the case of Ti(II) were rather encouraging. As summarized in Scheme 5, reaction of *trans*-$TiCl_2(TMEDA)_2$ with $(Me_3Si)_2NLi$ gave two different dinitrogen complexes depending on the stoichiometry employed [30]. This reaction led to disproportionation, with formation of Ti(III) species,



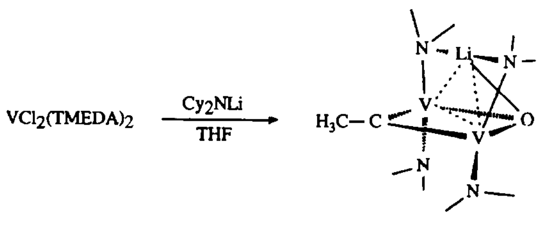
Scheme 4.



Scheme 5.

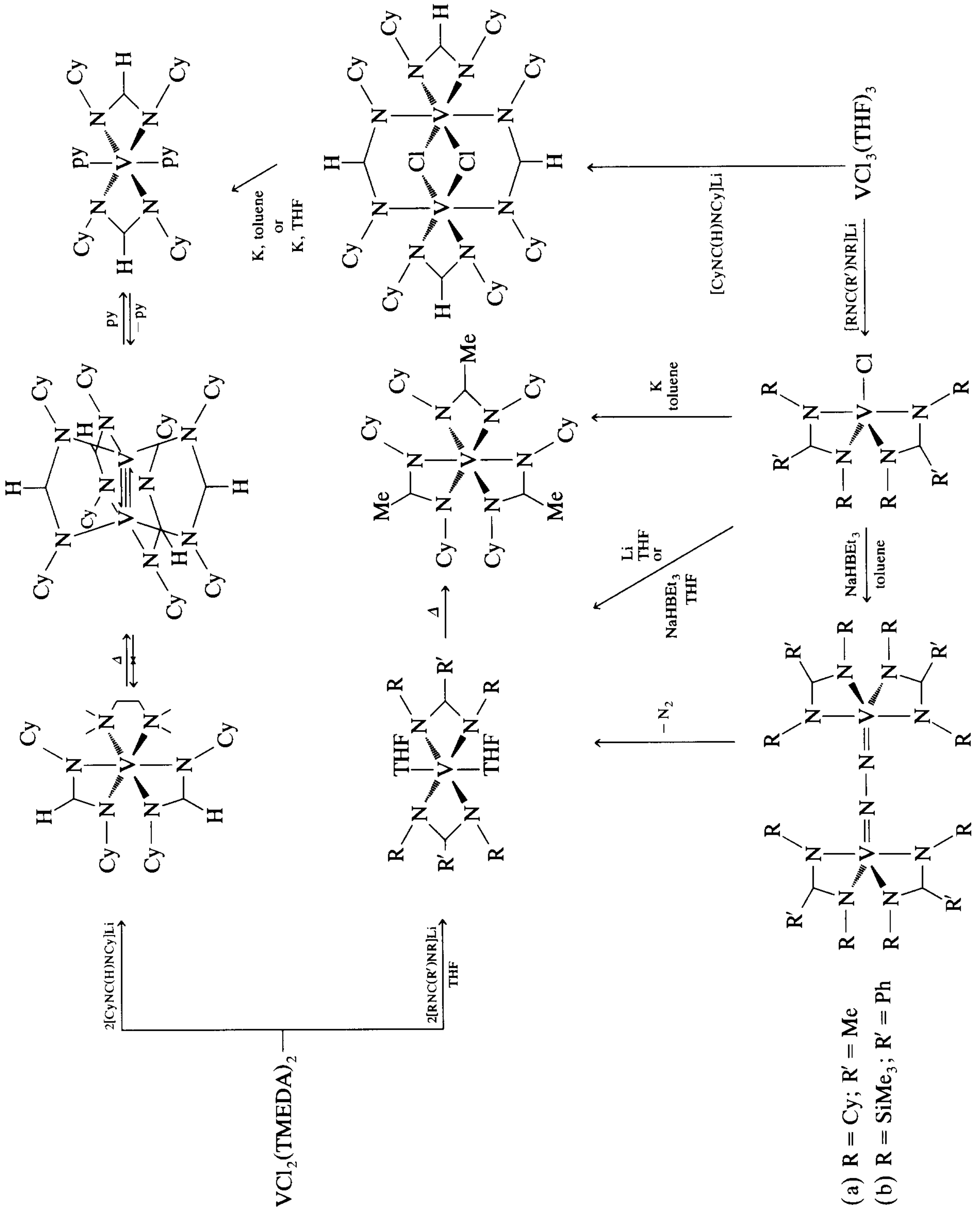
when carried out in polar solvents. By way of contrast, the corresponding reaction in toluene with one equivalent of amide yielded an exceedingly robust end-on dinitrogen complex [31]. The TMEDA ligands coordinated to the two titanium atoms were replaced by pyridine without demolishing the Ti–N_2–Ti core [30]. Reaction with two equivalents of amide in toluene gave an unprecedented side-on complex in which two molecules of dinitrogen were coordinated to two Ti centers to form a mixed valence anionic complex. Although in both cases the coordination of dinitrogen was irreversible, the N–N distances did not indicate any particularly great amount of N_2 reduction. Attempts to use other nitrogen-donor based ligands such as amidinate anions [32] resulted, as in the case of the aryloxides [24], only into a disproportionation and formation of Ti(III) complexes (notoriously poor substrates for dinitrogen fixation) [33].

In the case of divalent vanadium, attempts to prepare amide derivatives led to more complicated transformations (THF cleavage and fragmentation, etc.) and resulted in an increase of the metal oxidation state [35] (Scheme 6). However, in the case of the bidentate amidinate ligands it was possible to prepare a series of compounds (Scheme 7). A comparison of the crystal structures of these compounds revealed that the steric hindrance of the ligand might play a very significant role in determining both the stability of the +2 oxidation state and the occurrence of dinitrogen fixation. In the case of the less bulky formamidinates and acetamidinates it was possible to isolate, respectively, dimeric complexes with formal V≡V triple bonds, and solvated monomeric species. The steric contacts within the ligands were shown to be the factor capable of determining the nuclearity of these systems. Conversely, the employment of the sterically very demanding benzamidinate inhibited both dimerization and disproportionation, and allowed the isolation and characterization of a reversible end-on dinitrogen complex $\{[Me_3SiNC(Ph)NCSiMe_3]_2V\}_2(N_2)$. As in the case of the d^3 V(II) organometallic complexes the coordination of dinitrogen was quite labile, as shown by the fact that N_2 was easily displaced by weakly coordinating ligands such as THF.



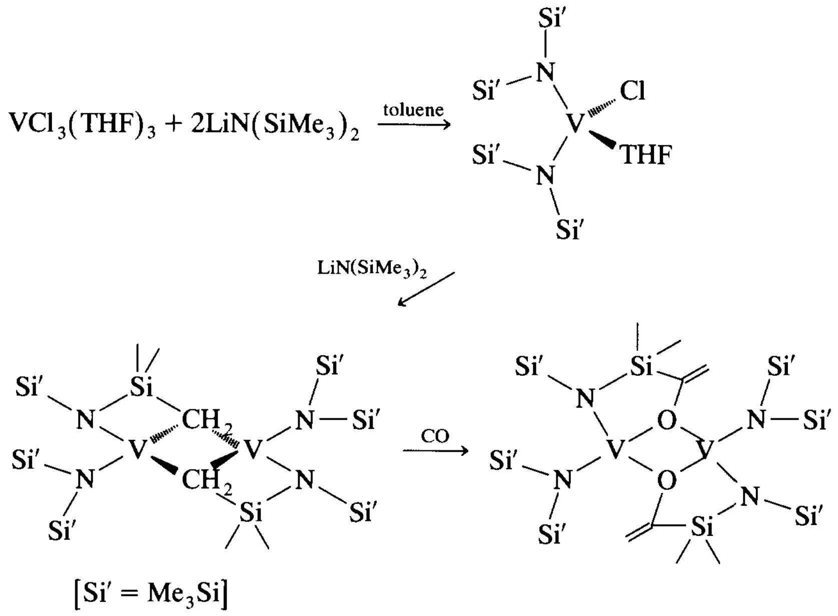
Scheme 6.

The most encouraging results were provided by trivalent vanadium which with monodentate and sterically demanding anionic amides formed exceedingly robust end-on dinitrogen complexes. Simple reaction of $VCl_3(THF)_3$ with three equivalents of $({}^{i}Pr)_2NLi$ gave the very robust $\{[({}^{i}Pr)_2N]_3V\}_2(N_2)$ [36]. The exceptional stability of this complex (which is unreactive towards a series of reagents such as pyridine, CO, RNC, Ph_2NH, olefins and alkynes) was rather surprising in view of the lability of the coordination of dinitrogen in $(Np_3V)_2(N_2)$ [28] and in all the other divalent vanadium dinitrogen complexes [26,27]. This result suggests that the d^2 electronic configuration in combination with the presence of nitrogen-donor based ligands is a possible arrangement for dinitrogen complexes with an exceptionally high stability.



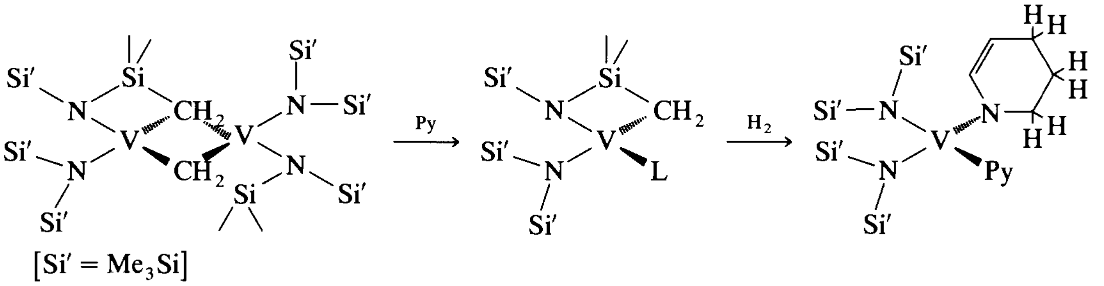
(a) R = Cy; R' = Me
(b) R = SiMe$_3$; R' = Ph

Scheme 7.

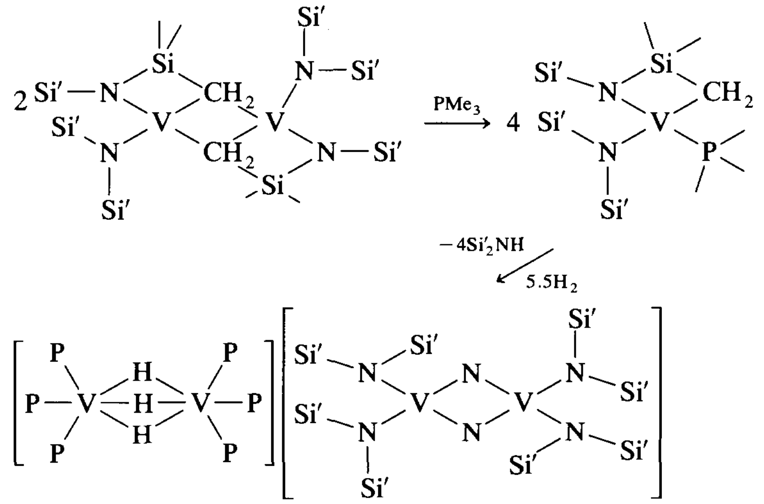


Scheme 8.

This rationale prompted us to carry out a broader investigation on the chemistry of species containing the $(R_2N)_3V$ framework. To our surprise, attempts to prepare the previously reported triangular $[(TMS)_2N]_3V$ complex [37], by reaction of $VCl_3(THF)_3$ with three equivalents of $(TMS)_2NLi$, actually led to the formation of $[(Me_3Si)_2NV(\mu\text{-}CH_2Si(Me)_2N(SiMe_3)]_2$ [38] in which a V–C bond was formed through C–H σ-bond metathesis involving the third amide group and one of the silyl groups. This organometallic species containing



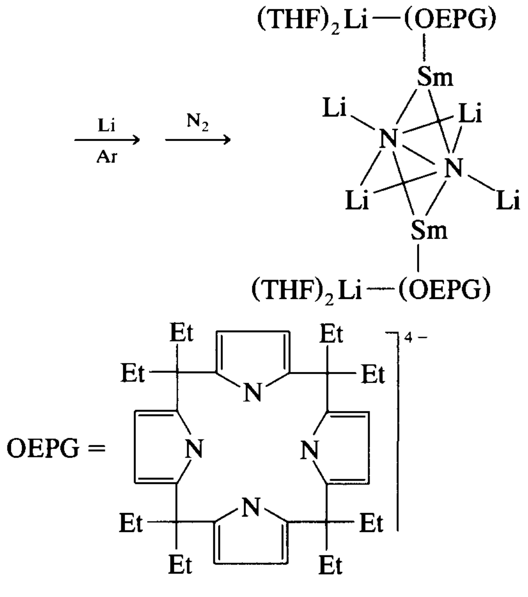
Scheme 9.



Scheme 10.

a vanadaazacyclobutane function (Scheme 8) was a particularly promising species for study of dinitrogen activation. In fact, simple hydrogenation of the V–CH_2 bond of the metallacycle might either give the highly reactive $[(TMS)_2N]_2VH$ species, able to reduce or complex dinitrogen, or lead to reduction of the metal center to the +2 oxidation state, also sufficiently reactive to interact with dinitrogen. This second possibility was particularly attractive since a side-on dinitrogen V(II) dinuclear complex has the potential of transferring the six electrons necessary for reducing dinitrogen to nitride. A search for this type of reactivity led to the discovery that the dinuclear structure of $[(Me_3Si)_2NV(\mu\text{-}CH_2Si(Me)_2N(SiMe_3)]_2$ can be cleaved by reaction with ligands such as PMe_3 or pyridine [39]. The resulting very reactive monomeric $[(Me_3Si)_2N]V[CH_2SiMe_2NSiMe_3]L$ [L = Py, PMe_3] complex, containing the intact vanadaazacyclobutane ring, was treated with H_2. In the case where the L = pyridine, the intermediate hydride species, presumably formed during the initial stage of the reaction, regioselectively hydrogenated the pyridine ring to give an eneamido vanadium species (Scheme 9) [39]. In contrast, when Me_3P was used as the ancillary ligand in place of pyridine, with the intention of preventing the ligand hydrogenation reaction, an unusual mixed valence species $\{[(Me_3P)_3V]_2(\mu\text{-}H)_3\}^+/\{([(Me_3Si)_2N]_2\text{-}V)_2(\mu\text{-}N)_2\}^-$ was isolated (Scheme 10) [40]. The formation of the $\{[(Me_3P)_3V]_2(\mu\text{-}H)_3\}^+$ cation and the quantitative recovery of $(TMS)_2NH$ from the mother liquor attest to the unprecedented possibility of cleaving the M–N bond by simple hydrogenolysis. This observation opens some interesting perspectives for the design of catalytic systems for the activation of dinitrogen. The $\{([(Me_3Si)_2N]_2V)_2(\mu\text{-}N)_2\}^-$ counter-anion of this complex is a dinuclear mixed valence V(IV)/V(V) species with the $(TMS_2N)_2V$ units bridged by two nitride moieties. The origin of the two nitrides has not been fully elucidated. However, the fact that no silicon compounds were present in the mother liquor and that this complex not was formed when the reaction and work-up were carried out under Ar, strongly pointed to N_2 as a possible source for these nitrides. It is worth mentioning in this respect, that this transformation is the converse of the formation of dinitrogen from a transition metal nitride obtained by Taube and coworkers upon oxidation of an Os–N complex [41]. The shape of the V_2N_2 core in the anion is somewhat reminiscent of a hypothetical side-on dinitrogen complex presumably obtained by reaction of the in situ generated $[(TMS)_2N]_2V$ with dinitrogen. However, the long N–N nonbonding distance between the two nitride atoms in the isolated complex obviously ruled out the presence of a N≡N bond. In order to form the two nitride moieties, the dinitrogen molecule of an hypothetical intermediate N_2-complex (probably side-on) would need to undergo a 6-electron reduction. The transformation of four molecules of $[(Me_3Si)_2N]V(CH_2SiMe_2NSiMe_3)(PMe_3)$ (containing V(III)) into one molecule of $\{[(Me_3P)_3V]_2(\mu\text{-}H)_3\}^+/\{([(Me_3Si)_2N]_2V)_2(\mu\text{-}N)_2\}^-$ (containing two V(II), one V(IV) and one V(V)) implies a disproportionation with concomitant loss of one electron. The remaining five electrons necessary for the 6-electron reduction of dinitrogen are provided by the oxidation of 2.5 molecules of H_2. This also produces five of the eight hydrogen atoms necessary to protonate the four CH_2 moieties and the four NR_2 groups to form four molecules of free amine. The remaining three protons are provided by three additional molecules of H_2 which at the same time supply the three hydrides necessary to form the cationic $\{[(Me_3P)_3V]_2(\mu\text{-}H)_3\}^+$ moiety.

$SmCl_3(THF)_3 + (OEPG)Li_4(THF)_4$

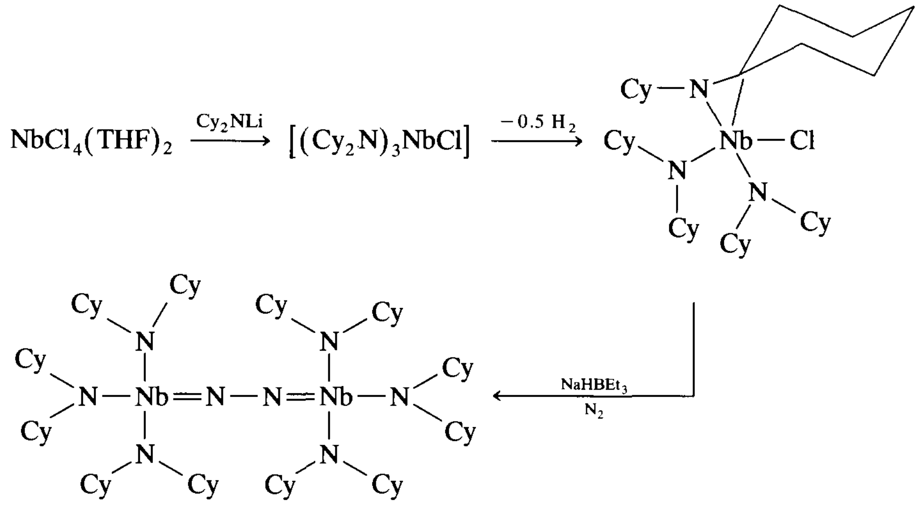


Scheme 11.

$$MCl_5 + (TMS)_2N\text{-}N(TMS)_2 \longrightarrow Cl_3M\text{-}N_2\text{-}MCl_3$$

Scheme 12.

An interesting type of anionic organic amide is provided by the porphyrinogen tetraanion in $OEPGLi_4$ [OEPG = octaethylporphyrinogen] [42]. This compound has in fact a remarkable steric and electronic flexibility which might be very versatile for both the stabilization of the lower oxidation states of the metal and for study of the reactivity of its metal complexes with dinitrogen. As mentioned above, the ability of divalent samarium to coordinate dinitrogen was observed only in the case of the bis-cyclopentadienyl systems, for which a labile side-on complex with an exceedingly short N–N distance was isolated and characterized [17]. During attempts to prepare a Sm(II) porphyrinogen complex we obtained a Sm(III) species in which two identical $OEPGSm[Li(THF)_2]$ units are connected to what is



Scheme 13.

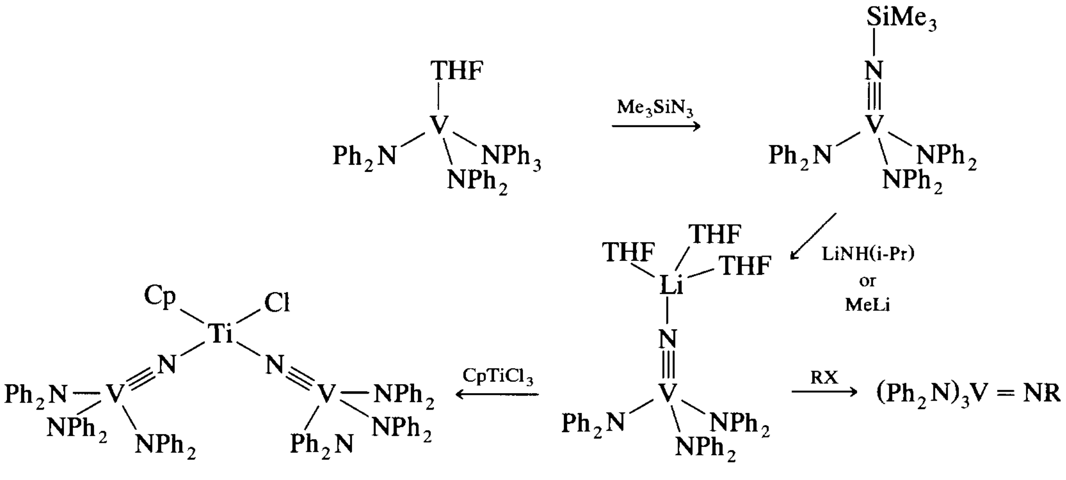
formally a hydrazine tetralithium salt (Scheme 11). In this species the N_2 moiety was encapsulated in the center of a Sm_2Li_4 octahedron [43]. The very long N–N distance (comparable to that observed by Fryzuk in the complex $\{[(Pr^i_2PCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}N_2)$ [15] and for which a considerable amount of N–N reduction was found to occur), along with the magnetic properties of this complex, strongly indicated the presence of Sm(III) centers and an N_2 molecule that had undergone considerable reduction.

Unfortunately, the reaction of this promising ligand with low- and medium-valent vanadium led only to a series of deoxygenation [44] and solvent fragmentation reactions [45], which (while of interest in respect of their unusual nature) have so far prevented further studies of the reactions of this metal with dinitrogen.

The heavier congeners of vanadium, namely niobium and tantalum, are well known to form exceedingly robust $M–N_2–M$ linkages [46]. Ligand replacement reactions may be commonly performed on the metal centers without affecting the coordinated dinitrogen moiety. Protonation reactions, leading to hydrazine, may be also performed with this type of complexes [1c,5b]. The high stability of this linkage is also demonstrated by the observation that it is frequently formed in an indirect manner, as for example by reaction of the high-valent metal halide with $(TMS)_2N–N(TMS)_2$ (Scheme 12) [47]. In only one instance has an in situ generated Ta(III) species

$$MCl_5 + (TMS)_2N\text{-}N(TMS)_2 \rightarrow Cl_3M\text{-}N_2\text{-}MCl_3$$

been proved to form a dinitrogen complex by direct reaction with N_2 [48]. Nevertheless, the coordinated N_2 moiety of these systems has been successfully transformed into simple organic molecules [49]. Therefore the results suggested to us that these systems might indeed be ideal for further activation studies. Having obtained the information about the exceptional stability of V(III) amide/N_2 complexes, we have examined the possibility of preparing Nb(III) and Ta(III) amides.



Scheme 14.

However, the reaction of $NbCl_4(THF)_4$ with R_2NLi, carried out in an effort to prepare $(R_2N)_3NbCl$ as a suitable precursor for reaching the trivalent state via further reduction, actually led to the formation of a pentavalent metallaziridine derivative obtained by oxidative addition of the ligand C–H bond to the tetravalent Nb (Scheme 13) [50]. Treatment of this species with hydride reagents led ultimately to the reduction of the metal center, subsequent dinitrogen coordination, and formation of an exceedingly stable $(Cy_2N)_3Nb\text{-}N_2\text{-}Nb(NCy_2)_3$ complex. Curiously, the behavior was considerably different in the case of the Ta analogues, for which similar reactions afforded an unprecedented dimeric complex $[(Cy_2N)_2TaCl]_2$ species containing a Ta–Ta single bond without bridging ligands [51].

A conclusive demonstration of the ability of transition metal complexes to generate nitride species via cleavage of the N≡N bond of coordinated dinitrogen, and an understanding of the reaction conditions under which this process may be achieved, remain primary goals in N_2 activation chemistry. The isolation and characterization of $\{[(Me_3P)_3V]_2(\mu\text{-}H)_3\}^+/\{([(Me_3Si)_2N]_2V)_2(\mu\text{-}N)_2\}^-$ [40] strongly indicated that such a process is possible, and that dinuclear V(II) amide complexes are sufficiently reactive and possess the appropriate electronic configuration to bring about complete reduction of dinitrogen. The next step is an extensive study of the chemistry of the nitride moiety, and in particular of the reaction steps and of the conditions under which this function may be attached to organic molecules. Homo- and hetero-dinuclear vanadium nitrides are already known and may be prepared by various routes [52]. We were interested in preparing vanadium nitride species that would be as close as possible to the fragment obtained upon reduction of the dinitrogen complex. For example, a 2-electron reduction on the $N_3V\text{-}N_2\text{-}VN_3$-complex would give a $[N_3V]N^-$ fragment. Although attempts to obtain this fragment directly by reduction of the dinitrogen-complex $(R_2N)_3V\text{-}N_2\text{-}V(NR_2)_3$ have so far been unsuccessful, it was possible to prepare the desired function by using the reaction sequence shown in Scheme 14 [53]. Oxidation of the $(Ph_2N)_3V(THF)$-complex with $TMSN_3$ led to the formation of the corresponding pentavalent imido species $(R_2N)_3V(=NTMS)$. Nucleophilic attack at the silicon atom by $LiNH(^iPr)$ or MeLi gave the extremely air-sensitive nitrido lithium salt $(R_2N)_3V{=}NLi(THF)_3$. This species displays a moderate nucleophilic power and can react with a number of organic and organometallic halides in halide replacement reactions. Interestingly, the reaction of $(Ph_2N)_3V{=}N\text{-}Li(THF)_3$ with $CpTiCl_3$ gave $CpTiCl[-N{=}V(NPh_2)_3]_2$, which may be regarded as the product of the oxidative insertion of a divalent "CpTiCl" species to the N≡N bond of coordinated dinitrogen of an $(R_2N)_3V\text{-}N_2V)NR_2)_3$ complex.

In conclusion, 30 years since the discovery of the first dinitrogen-complex, dinitrogen activation remains a very real and stimulating puzzle. The goal of providing an in-depth understanding of the transformations that may promote the incorporation of N_2 into organic substrates has not yet been achieved. However, chemists have certainly made spectacular advances in this field, and since a wide range of possible synthetic strategies are available important and exciting discoveries can be expected in the near future.

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