trans-[Na(thf)][V(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂]: Structural Characterization of a Dinitrogenvanadium Complex, a Functional Model for Vanadiumnitrogenase

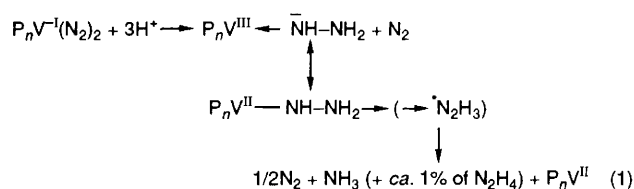**Dieter Rehder,* Claus Woitha, Wolfgang Priebsch and Hartmut Gailus**

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Reduction of $VCl_3(thf)_3$ (thf = tetrahydrofuran) by Na in the presence of bis(phosphines) and N_2 yields the complexes trans-$[V(N_2)_2L_2]^-$, which have been structurally characterized by X-ray crystallography for L = $Ph_2PCH_2CH_2PPh_2$, and in solution by ^{51}V NMR spectroscopy for L = $Me_2PCH_2CH_2PMe_2$; 25% of the coordinated N_2 is reductively protonated to NH_3 and a small amount of N_2H_4 by HBr.

The discovery and first characterization of an alternative, *i.e.* vanadium-containing nitrogenase (V-nase) encoded along with the common molybdenum nitrogenase in nitrogen-fixing bacteria such as *Azotobacter*[1] and *Anabaena*[2] has prompted investigations into the chemistry, structure and function of vanadium complexes containing dinitrogen fragments either in the form of formally neutral N_2 or in reduced (and protonated) states. Examples are $[V(CO)_5N_2]^-$,[3] which is stable in solution and below 220 K only, and hydrazine complexes of the general formula η^5-$C_5H_5V(CO)_3$ hydrazine.[4] More recently, a dinuclear compound of composition $[\{(py)VL_2\}_2\mu$-$N_2]$ [where L is o-$(Me_2NCH_2)C_6H_4$] has been structurally characterized by Gambarotta *et al.*[5] The N–N bond length in this complex is 1.228(4) Å [d(NN) in free nitrogen: 1.098 Å]. The compound should hence be considered to be a diazene rather than a dinitrogen complex. It has been demonstrated by Leigh *et al.*[6] that half of the N_2 can be converted into NH_3 on treatment with acids. Nevertheless, the compound is of restricted value as a model, since it is not likely, in the light of recent structural evidence for molybdenum nitrogenase,[7] that the FeVa-cofactor in vanadium-nitrogenase contains two closely linked vanadium centres.

While dinitrogen complexes of molybdenum(0), stabilized by phosphines, and containing the N_2 ligand in the end-on coordination mode have been known[8] and thoroughly investigated[9] for more than two decades, only a singular account on the corresponding, valence-isoelectronic vanadium(−ı) complexes, elucidating spectroscopic characteristics, has so far

appeared.[10] We have now been able to grow crystals of one of the basic complexes, *viz.* $[Na(thf)][V(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), $[Na(thf)]$-**1**,† and to determine the

$$P_nV^{-I}(N_2)_2 + 3H^+ \longrightarrow P_nV^{III} \longleftarrow \overline{N}H\text{--}NH_2 + N_2$$

$$P_nV^{II}\text{---}NH\text{--}NH_2 \longrightarrow (\longrightarrow {}^\bullet N_2H_3)$$

$$1/2N_2 + NH_3 (+ \text{ca. 1% of } N_2H_4) + P_nV^{II} \quad (1)$$

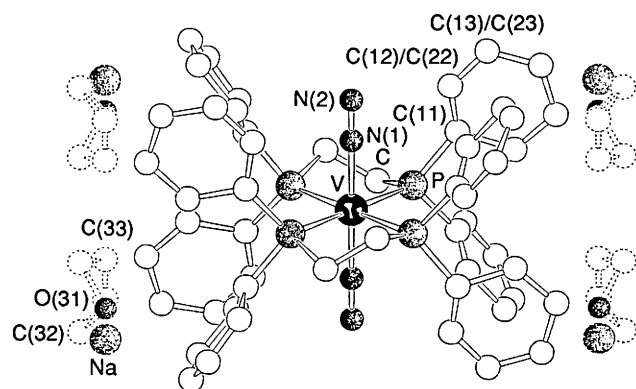**Fig. 1** SCHAKAL plot of [Na(thf)]-**1**. The space group is *Immm*. Atoms defining the asymmetric unit are numbered. The octahedral $V(N_2)_2P_4$ core of the anion is emphasized by shaded calottes. The phenyl rings and the ethylene back-bone are disordered. The cation [Na(thf)]$^+$ (thf is disordered) is statistically distributed between four equivalent site positions. There is a bonding interaction between Na$^+$ and N(2) with formation of a V–N≡N···Na bridge. Selected distances (Å) and angles (°): V–N(1) 1.915(11), N(1)–N(2) 1.130(16), V–P 2.419(3), P–C 1.829(12), P–C(11) 1.816(8), Na···N2 2.445(11), Na···O31 2.349(12); N(1)–V–P 90.0(0), V–N(1)–N(2) 180.0(30), C–P–C(11) 110.6(5), V–P–C 108.2(4), V–P–C(11) 122.7(3).

Fig. 2 93.7 MHz ^{51}V NMR spectrum of **2**. $\delta(^{51}V) = -1123$ (relative to $VOCl_3$), $J(^{51}V-^{31}P) = 314$, $J(^{51}V-^{15}N) = 57$ Hz

crystal and molecular structures by X-ray diffraction analysis.‡

The structure of [Na(thf)]-**1** (Fig. 1) was solved and refined in the space group *Immm*. Regarding the anion **1**, the asymmetric unit is defined by the atoms V, N(1), N(2), C, P, C(11) and C(12) [C(22)] to C(16)[C(26)]. The overall structure and the bonding parameters of **1** (for a selection see legend to Fig. 1) are very much the same as for the neutral molybdenum complex *trans*-[Mo(N$_2$)$_2$(dppe)$_2$].[11] The counter ion Na$^+$ has bonding contacts to the tetrahydrofuran oxygen [d(Na-O) = 2.35 Å]. There is also a non-negligiable contact between sodium and the terminal nitrogen of **1** [d(Na-N(2)) = 2.45 Å], hence a contact-ion pair interaction through a V–N≡N···Na bridge.

This structure of the anion is also preserved in thf solution, as shown in Fig. 2, depicting the ^{51}V NMR spectrum of *trans*-[V(^{15}N)$_2$(dmpe)$_2$]$^-$, **2**, (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$). The spectrum shows a well-resolved quintet [$^1J(^{31}P-^{51}V)$ coupling] of triplets [$^1J(^{15}N-^{51}V)$ coupling].

As dry Na-**1** or Na-**2** is treated with an excess of HBr, one of the four nitrogens is converted into NH$_4^+$. A small amount of hydrazine is also formed. No hydrogen, an important additional product in natural nitrogen fixation by V-nase, has been detected. Small but significant amounts of free N$_2$H$_4$ are also
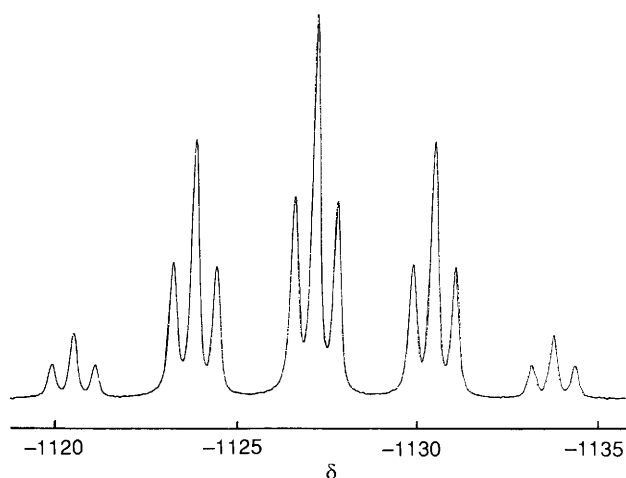
produced during N$_2$ reduction by V-nase.[12] The electrons in this reductive protonation are delivered by V^{-I}, which is converted to chlorophosphine vanadium complexes of, according to oxidimetric titration, V^{II} and small but varying amounts of V^{III}. Compounds **1** and **2** may hence be considered functional models of the nitrogenase activity of V-nase. The overall balance can be represented by eqn. (1).

Eqn. (1) incorporates some aspects of a tentative mechanism for NH$_3$ production, based on the assumption that a hydrazido(1−) and a hydrazinyl intermediate are formed, with concomitant disproportionation of the latter. Complexes containing the N$_2$H$_3$ (hydrazinyl) radical have recently been characterized.[13,14] Investigations to further elucidate this mechanism are presently under way.

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