Dinitrogenvanadates(−I): Synthesis, Reactions and Conditions for their Stability

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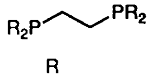
Reduction of $[VCl_3(thf)_3]$ by Na or Li (M) in the presence of phosphines (L^m) and N_2 yielded the complexes $Na[V(N_2)_n(PMe_2Ph)_{6-n}]$ (n = 1 or 2), $M[V(N_2)_nL^2_{4-n}]$ [n = 1 or 2, $L^2 = Me_2PCH_2CH_2PMe_2$ (dmpe) or $Ph_2PCH_2CH_2PPh_2$], $Na[V(N_2)(dmpe)L^3]$ {$L^3 = PhP[(CH_2)_2PPh_2]_2$, $MeP[(CH_2)_3PMe_2]_2$ (bdmpm) or $MeP[(CH_2)_3PEt_2]_2$} and $Na[V(N_2)_2L^4]$ {$L^4 = P[(CH_2)_2PPh_2]_3$, $P[(CH_2)_3PMe_2]_3$ or $P[(CH_2)_3PEt_2]_3$}. Generally, the complexes are labile, with a maximum stability for *cis*- and *trans*-$M[V(N_2)_2(dmpe)_2]$. In the presence of CO or $CNBu^t$, N_2 is replaced by these ligands. The compounds have been characterized by their ν(NN) pattern and by ^{51}V, ^{23}Na and ^7Li NMR spectroscopy. The ^{51}V NMR spectra exhibit well resolved multiplets. All spectroscopic data, in particular ^7Li NMR of *cis*-and *trans*-$[Li(thf)_x][V(N_2)_2(dmpe)_2]$ in tetrahydrofuran, are indicative of close contact ion-pair interaction of the kind $V{-}N{\equiv}N\cdots M^+$. The potassium ion and large cations such as $[NEt_4]^+$ do not provide stable complexes, and complexation of Li^+ and Na^+ by crown ethers leads to immediate decomposition of the N_2 complexes. The reductive protonation of part of the co-ordinated N_2 to NH_4^+ (plus small amounts of $N_2H_5^+$) is discussed in terms of similar reactivity features to the analogous complexes, and in the context of these N_2 complexes as functional models for nitrogenases. The compound $[V_2(bdmpm)_2Cl_3]$, isolated as an intermediate product of the reduction of VCl_3, reacted with $LiNHNH_2$ to yield ammonia.

Since the initial preparation and characterization of phosphine-stabilized dinitrogen complexes of molybdenum(0) by Hidai and co-workers,[1] and their comprehensive investigation by Chatt *et al.*[2a] and others,[2] these complexes have been considered as functional models for the reaction site in the Mo-containing cofactor centre (FeMoco) of molybdenum nitrogenase. Accordingly, the corresponding complexes of vanadium(−I) have been introduced as functional models for the FeVco (the vanadium analogue of FeMoco) in vanadium nitrogenase.[3] This view has been challenged over the past few years, partly by the discovery of iron-only nitrogenases and, more recently, by calculations which favour an Fe–Fe centred site for nitrogen fixation.[4] These calculations also show that the heterometal (Mo or V) attains a non-negligible role in tuning the electronic properties of the iron–sulfur core, which is also apparent from certain functional dissimilarities between Mo- and V-nitrogenase. Thus, the latter uses up 50% of the electron flux in hydrogenase activity (the former 25%),[5] and a small amount of hydrazine is liberated along with ammonia during turn-over by V-nitrogenase, but not by Mo-nitrogenase.[6] Further, acetylene is partly reduced to ethane by V-nitrogenase[5] while, with Mo-nitrogenase, reductive protonation leads to ethylene only. Irrespective of the question of whether the heterometal is the site where coupling of N_2 and its reduction occurs, or whether the heterometal influences nitrogen fixation indirectly, a comparison of the stability and reactivity patterns of the two series of 'functional' models of Mo^0 and V^{-I} complexes is of interest in the context of nitrogen fixation. We have therefore extended earlier work[3] on the dinitrogen vanadium complexes.

To date, the complexes of general composition $[V(N_2)_n(L^m)_x]^-$ (where L is a mono- to tetra-dentate phosphine and m represents the number of co-ordinated phosphorus functions; $xn + m = 6$, where x = 1–5) have been the only vanadium complexes with the N_2 ligand in the end-on co-ordination mode (low-temperature compounds disregarded), documented by a crystal structure analysis of $[Na(thf)][V(N_2)_2(dppe)_2]$ (thf = tetrahydrofuran, dppe = $Ph_2PCH_2CH_2PPh_2$).[3b] Only four other N_2 complexes, all of which contain bridging dinitrogen or diazenide(2−), respectively, have been structurally characterized, *viz.* $[\{V(py)(C_6H_4CH_2NH_2\text{-}o)_2\}_2(\mu\text{-}N_2)]$ (py = pyridine) where 2-(2-aminomethyl)phenyl co-ordinates through the amino group and the deprotonated sp^2 carbon,[7] $Na[\{V(C_6H_2Me_3\text{-}1,3,5)_3\}_2(\mu\text{-}N_2)]$,[8] $[\{V(CH_2CMe_3)_3\}_2(\mu\text{-}N_2)]$[9] and $[\{V(NR_2)_3\}_2(\mu\text{-}N_2)]$ (R = Pr^i or C_6H_{11}),[10] two of which, the mesitylene and the 2-(2-aminomethyl)phenyl complex, have been shown to liberate ammonia on treatment with acids.[8,11] Less well defined vanadium-containing systems capable of reductive protonation of N_2 to ammonia and/or hydrazine have been known for longer. Thus, N_2 is converted to $N_2H_5^+$ by V^{2+} in the presence of α,ω-dicarboxylic acids,[12] and NH_3 or N_2H_4 is generated under pressure in the system V^{2+}–Mg–OH^-.[13] Shilov and co-workers[14] have recently isolated and structurally characterized a V^{II}–V^{III} catecholate complex from a similar nitrogen fixing system.

Results and Discussion

Preparation and General Properties.—The anionic dinitrogen complexes are prepared by reduction of VCl_3 in thf in the presence of phosphine and in a normal pressure N_2 atmosphere at temperatures between 195 and 230 K [equation (1)]. The



R
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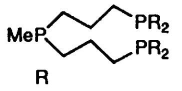
Ph dppe



R
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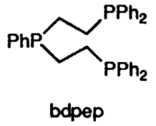
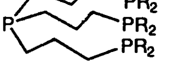
Et bdepm



bdpep



R
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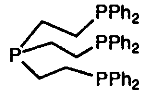


tdpe

$$[VCl_3(thf)_3] + 2dmpe + 4Na/Li + 2N_2 \longrightarrow Na/Li[V(N_2)_2(dmpe)_2] + 3Na/LiCl \quad (1)$$

reducing agent is either sodium sand or lithium foil. Naphthalene, mentioned in earlier reports as a necessary mediator in these reductions,[3] is not essential. The reduction proceeds *via* blue V^{II} intermediates $[VCl_2(L^m)_x]$ ($xm = 4$)[15–17] to yield brown solutions containing mono- and, chiefly, bis-(dinitrogen) complexes of V^{-I}. With magnesium, reduction does not go beyond V^{II}. Potassium also yields brown solutions containing low-valent vanadium, but does not provide, for reasons discussed below, N_2 complexes sufficiently stable to be characterized. An optimum stability is achieved with dmpe, but spectroscopic data have also been obtained for several other di- to tetra-dentate phosphines (see the following section). Monodentate phosphines such as PPh_3, PMe_3 and PEt_3 do not form stable N_2 complexes, but PMe_2Ph does. This phosphine combines appropriate electronic properties (it is a strong σ base and π acid by virtue of the two methyl substituents) with a restricted ability of steric shielding apparently essential for the stability of the complexes. Solutions of mono(dinitrogen) complexes have been obtained by combining bi- and tri-dentate phosphines [equation (2)]. In this reaction a mixed-valent

$$[VCl_3(thf)_3] + bdmpm \longrightarrow [VCl_3(bdmpm)] \xrightarrow{+\,dmpe,\ +\,N_2,\ +\,4Na} Na[V(N_2)(bdmpm)(dmpe)] + 3NaCl \quad (2)$$

V^{II}–V^{I} intermediate of composition $[\{V(bdmpm)_2\}_2(\mu\text{-}Cl)_3]$ (formulated in analogy to $[\{V(thf)_3\}_2(\mu\text{-}Cl)_3]^+$[18]) has been isolated when conducting the reaction with insufficient sodium for reduction of V^{III} to V^{-I}, equation (3).

$$[VCl_3(bdmpm)] + 2Na \xrightarrow{+dmpe} \tfrac{1}{2}[V_2(bdmpm)_2Cl_3] \quad (3)$$

Below *ca.* 230 K, the compounds are stable in solution for several weeks. In the case of the dmpe complexes, the solutions may be kept at ambient temperatures without substantial decomposition for a couple of days. The less stable mono-(dinitrogen) complexes convert to the bis(dinitrogen) complexes within hours. The ratio between *cis* and *trans* products depends on the temperature, and at low temperature, the formation of the *cis* complex is favoured. For $Na[V(N_2)_2(dmpe)_2]$, the *cis–trans* ratio at 195 K is 12:1, whilst this ratio changes to 4:1 at 250 K (statistical *cis–trans* distribution for the second substituent step), and to 3:1 at 290 K. The interconversion between the *cis* and *trans* forms with varying temperature is reversible.

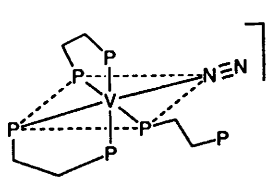
Under reduced pressure, the complexes lose N_2 even in solution. In contact with air, immediate decomposition and liberation of N_2 occurs. Precipitation of the bis(dinitrogen) complexes with pentane or hexane at low temperatures yields black, pyrophoric powders, insoluble in all common solvents and inaccessible to reliable elemental analyses due to admixtures of MCl and partial loss of N_2 during work-up even when handled under N_2. Nitromethane decomposes the complexes with incandescence. Efforts to recover the mono-(dinitrogen) complexes formed according to equation (2) led to the isolation of small amounts of *cis*- and *trans*-$Na[V(N_2)_2(dmpe)_2]$. Large cations such as $[NEt_4]^+$ and $[PPh_4]^+$ do not stabilize the anions, and addition of crown ethers capable of co-ordinating Li^+ and Na^+ initiate immediate decomposition. The reasons for this incapability to stabilize the anions with soft cations, an observation which has also been reported by Leigh and co-workers,[15] will be discussed below.

Spectroscopic Properties.—(*a*) *IR and* ^{51}V *NMR results.* An unambiguous characterization of the N_2 complexes and their interconversion has been carried out by IR and NMR (^{51}V, ^{23}Na and ^{7}Li) spectroscopy; IR and ^{51}V NMR data are collated in Table 1.

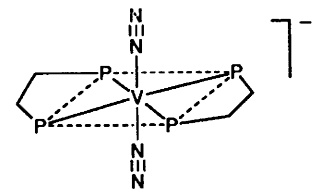
With dmpe or PMe_2Ph, mixtures of mono(dinitrogen), *cis*- and *trans*-bis(dinitrogen) complexes are obtained (shown in **I**–**III** for diphosphines) which exhibit the expected ν(NN) patterns. The solution IR spectra show five absorptions, the assignment of which has been carried out on the basis of the reactivity features and analogy to the corresponding molybdenum complexes where, for the bis(dinitrogen) complexes, the bands at higher wavenumbers have been associated with the *cis* configuration.[19] Comparison of ν(NN) in *trans*-$Li[V(N_2)_2(dmpe)_2]$ (1758 cm^{-1}; $\Delta\nu = 573\ cm^{-1}$, where Δν is the difference in the stretching frequencies between free and complexed ligand) and ν(CO) in *trans*-$Li[V(CO)_2(dmpe)_2]$ (1731 cm^{-1}; $\Delta\nu = 424\ cm^{-1}$) suggests equally effective π-acceptor properties for the ligands N_2 and CO in these V^{-I} complexes. The hypsochromic shift by 27 cm^{-1} of ν(NN) in *trans*-$Na[V(N_2)_2(dmpe)_2]$ relative to *trans*-$Li[V(N_2)_2(dmpe)_2]$ is indicative of contact ion-pair formation. Contact ion-pair formation has been reported as a common feature in carbonyl chemistry.[20–22]

The contact-ion interaction is also apparent from the differences of the ^{51}V chemical shifts of *trans*-$Li/Na[V(N_2)_2(dmpe)_2]$ (*cf.* Table 1). Also noteworthy is the considerably stronger effect of the cation on ^{51}V shielding in *trans*- as compared to *cis*-$Li[V(N_2)_2(dmpe)_2]$, compatible with the greater stability of the former and indicative of the importance of the nature of the cation for the existence of these dinitrogen complexes.

A feasible diagnostic tool in revealing the speciation in complex mixtures is ^{51}V NMR spectroscopy. As an example, Fig. 1 shows spectra over a temperature range of 100 K of the mixture of N_2 complexes obtained by reduction of VCl_3 with Na in the presence of dmpe. The spectra exhibit the signals for the mono- and the bis-(dinitrogen) complexes, with the resonance for $[V(N_2)(dmpe)_3]^-$ vanishing above 240 K and the (high-field) resonance for *trans*-$[V(N_2)_2(dmpe)_2]^-$ gaining in intensity at the expense of *cis*-$[V(N_2)_2(dmpe)_2]^-$ as the temperature rises. The signals for the bis(dinitrogen) complexes are well resolved at low temperature, showing the expected ^{31}P–^{51}V coupling patterns, *viz.* a quintet for the *trans*- and a



I



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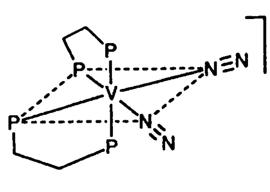
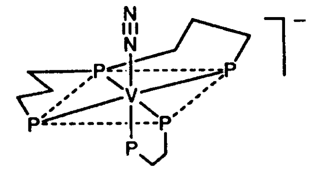
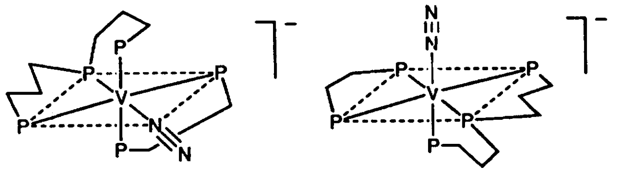


III



IV



V

Table 1 IR and ^{51}V NMR data for the N_2 complexes Na/Li[V(N_2)$_n$L^m]

Complex	$\tilde{\nu}$(NN)[a]/cm^{-1}	δ(^{51}V)[b]	$\Delta\delta$/dT[c] (ppm K^{-1})	J(^{51}V–^{31}P)/Hz
Na[V(N_2)(PMe_2Ph)$_5$]	1880	−473*	−1.07	
Na[V(N_2)(dmpe)$_3$]	1880	−1032 (sxt)		275
Na[V(N_2)(dmpe)(bdmpm)]	1725	−1022 (d qnt)[d]		222, 291
Na[V(N_2)(dmpe)(bdepm)][e]	1760–1720 (br)	−873 (d qnt)		224, 287
		−814 (d qnt)		238, 273
Na[V(N_2)(dmpe)(bdpep)]	1750	−881		
cis-Na[V(N_2)$_2$(PMe_2Ph)$_4$]	1813s, 1781vs	−620*	−0.79	
cis-Na[V(N_2)$_2$(dmpe)$_2$][f]	1805s, 1769vs	−982 (tt)	−0.49	245, 290
cis-Li[V(N_2)$_2$(dmpe)$_2$]		−950 (m)		208
cis-Na[V(N_2)$_2$(tdmp)]	1778s, 1674vs[f]	−866 (qnt)		264
cis-Na[V(N_2)$_2$(tdep)]	1830s, 1730s	−772		250
cis-Na[V(N_2)$_2$(tdpe)]	1833s, 1713vs[g]	−851		
trans-Na[V(N_2)$_2$(PMe_2Ph)$_4$]	1706	−910*	−0.32	
trans-Na[V(N_2)$_2$(dmpe)$_2$][f]	1721	−1138 (q)	−0.49	285
trans-Li[V(N_2)$_2$(dmpe)$_2$]	1758	−982 (q)		275
trans-Na[V(N_2)$_2$(dppe)$_2$]	1790[g]	−710*	−0.80	

[a] In thf, if not indicated otherwise. [b] In [$^2H_8$]thf. All values are given for room temperature. Where data were collected at low temperature (indicated by *), δ was projected to 293 K with the temperature gradients given in the fourth column. Multiplicity: q = quartet, qnt = quintet, sxt = sextet, tt = triplet of triplets, d qnt = doublet of quintets, m = multiplet; broad singlet, where not indicated. [c] Temperature gradient. The negative sign indicates deshielding with increasing temperature. The temperature dependence is essentially linear over the temperature range 195 to 290 K. [d] Other, minor resonances are present. [e] Two isomers. [f] Data corrected with respect to those reported in ref. 3. [g] Nujol mull.

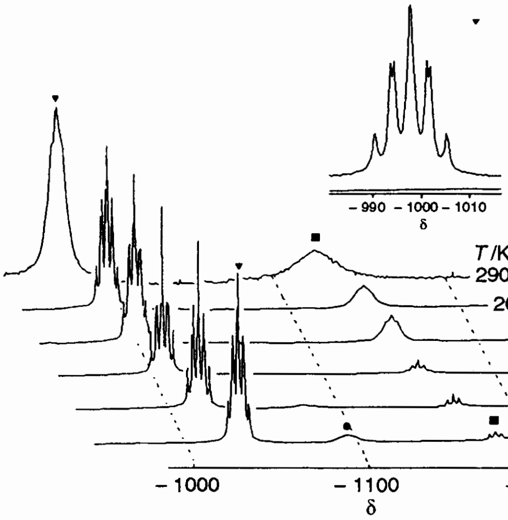


Fig. 1 Temperature-dependent 94.73 MHz ^{51}V-{^{1}H} NMR spectra of thf solutions containing mixtures of Na[V(N_2)(dmpe)$_3$] (●), *cis*-Na[V(N_2)$_2$(dmpe)$_2$] (▼) and *trans*-Na[V(N_2)$_2$(dmpe)$_2$] (■). The insert shows the signal of *cis*-Na[V(N_2)$_2$(dmpe)$_2$] at 260 K. The δ scale is relative to $VOCl_3$

(partially resolved; see insert in Fig. 1) triplet of triplets for the A_2B_2X spin system in the *cis*-complex. The broadening at higher temperatures reflects exchange phenomena. In the case of complexes Na[V(N_2)(dmpe)(bdmpm)] and Na[V(N_2)(dmpe)(bdepm)] the resonance is resolved into a doublet of quintets, corresponding to an idealized A_4BX spin system (**IV** and **V**), where B is the phosphorus *trans* to N_2 and the four remaining phosphorus functions are equivalent in a first approximation. In the case of the bdepm complex, two of the three possible isomers have been observed. Where phenyl substituents are attached to phosphorus, relatively broad and unresolved signals are observed over the whole temperature range.

The ^{51}V chemical shifts of the N_2 complexes are similar to those of the CO complexes, again demonstrating the similar electronic properties of the two ligands. General trends in the spectra of the N_2 complexes compare with those reported earlier for carbonyl complexes:[23] (*i*) shielding of the ^{51}V nucleus is lower in mono- than in bis-(dinitrogen) complexes, and (*ii*) the ^{51}V nucleus is deshielded in complexes with phosphines carrying phenyl substituents with respect to those containing pure alkyl phosphines. Relatively large shift differences within this latter group of complexes point towards steric influences on ^{51}V shielding.[23,24] In accord with the theory of nuclear shielding,[25] the ^{51}V nucleus is dehielded as the temperature rises. The temperature gradients (Table 1) are of the predicted order of magnitude, and they increase as ^{51}V shielding decreases {*cis*-Na[V(N_2)$_2$(dmpe)$_2$], δ −982, $\Delta\delta/\mathrm{d}T = -0.49$; *cis*-Na[V($N_2$)$_2$($PMe_2Ph$)$_4$], δ −620, $\Delta\delta/\mathrm{d}T = -0.79$ and Na[V(N_2)(PMe_2Ph)$_5$], δ −473, $\Delta\delta/\mathrm{d}T = -1.07$}, again as predicted.[25]

(*b*) *^{7}Li and ^{23}Na NMR results, and structure.* In order to obtain more direct evidence for the contact ion-pair formation, we have also investigated the ^{23}Na and ^{7}Li NMR spectra of the dmpe complexes. The ^{23}Na NMR spectra of thf solutions of mixtures of dinitrogen dmpe complexes show a broad signal (half width $w_{\frac{1}{2}}$ = 4.8 kHz) centred at δ 5.3 (relative to NaCl in H_2O), which remains unchanged in the temperature range 190–293 K and corresponds to a signal representing fast Na^+ exchange between sodium chloride and the sodium vanadate. The ^{7}Li NMR data are summarized in Table 2; for the ^{7}Li NMR spectra of the dinitrogen complexes see also Fig. 2.

At ambient temperatures, a broad signal at about δ 1.5 is observed, which splits into two signals as the temperature decreases. The relatively sharp high-field component at δ 1.2 corresponds to Li^+ (solvated by thf) with Cl^- as the counter ion.[26] We allocate the broad low-field component at δ 1.9 to the contact ion-pair Li^+[V(N_2)$_n$(dmpe)$_{4-n}$]$^-$. The low-field shift relative to solvated Li^+ is a consequence of contacts of the kind $Li^+ \cdots N{\equiv}N{-}V^-$, with the lithium ion possibly partly depleted of its thf sphere. We have briefly reported on this kind of interaction in a communication on the crystal structure analysis of *trans*-[Na(thf)]$^+$[V(N_2)$_2$(dppe)$_2$]$^-$,[3b] demonstrating that, in the solid state, $V{-}N{\equiv}N \cdots Na$ chains are formed in which the anions [V(N_2)$_2$(dppe)$_2$]$^-$ are linked by Na^+ (*cf.* Fig. 3). Contacts between Na^+ and μ-N_2 have also been reported for Na[{V($C_6H_2Me_3$-1,3,5)$_3$}$_2$(μ-N_2)].[8]

The overall situation in solution may be described by equation (4). At room temperature, equilibration is too fast

$$[Li^*(thf)_y]^+Cl^- + [Li(thf)_x]^+[V(N_2)_2(dmpe)_2]^- \rightleftharpoons [Li(thf)_y]^+Cl^- + [Li^*(thf)_x]^+[V(N_2)_2(dmpe)_2]^- \quad (x < y) \quad (4)$$

Table 2 Lithium-7 NMR data of dmpe complexes[a]

	203 K		233 K		283 K	
Compound	δ	$w_{\frac{1}{2}}$/Hz	δ	$w_{\frac{1}{2}}$/Hz	δ	$w_{\frac{1}{2}}$/Hz
LiCl	1.20	4				
$Li[V(N_2)_n(dmpe)_{4-n}]$[b]	1.18	53	1.12	190	1.53[d]	330
	1.9	310	c			
$Li[V(CO)_n(dmpe)_{4-n}]$	0.82	185	1.01	115	1.34	50

[a] Admixed with LiCl, in [$^2H_8$]thf; $c(Li^+)$ *ca.* 0.1 mol dm^{-3}, $\delta(^7Li)$ are quoted relative to saturated aqueous LiCl; $w_{\frac{1}{2}}(^7Li)$ is the width of the ^7Li resonance at half-height; n = 1 or 2. [b] See also Fig. 2. [c] The broad low-field component is an unresolved shoulder. [d] One signal only.

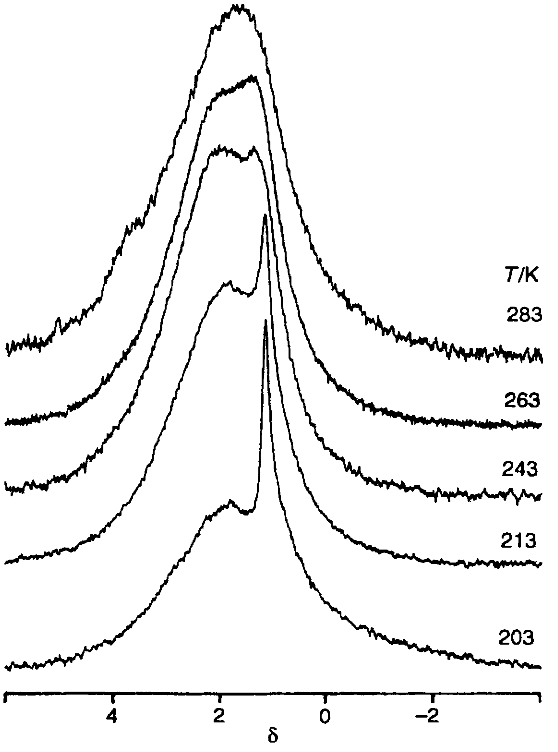


Fig. 2 Temperature-dependent 140.0 MHz ^7Li NMR spectra of thf solutions of $Li[V(N_2)_n(dmpe)_{4-n}]$ (n = 1 or 2) + LiCl, obtained by reduction of VCl_3 with lithium. The δ scale is relative to saturated, aqueous LiCl

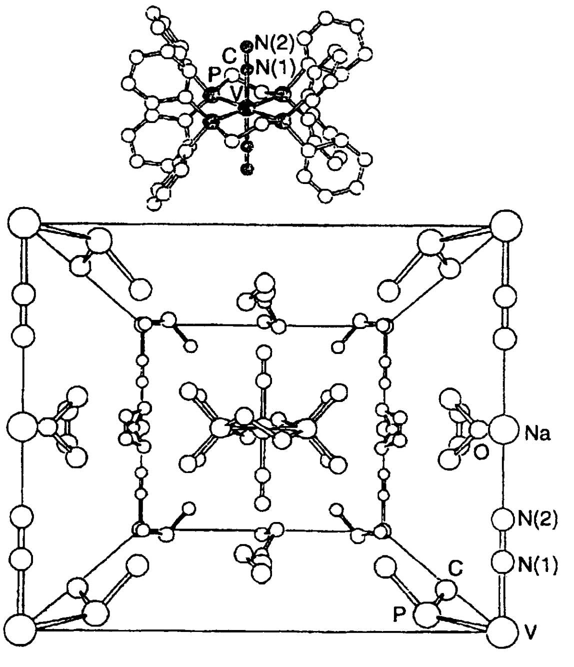


Fig. 3 Section of the crystal structure of *trans*-$[Na(thf)][V(N_2)_2(dppe)_2]$ (see insert at the top for the molecular structure). The structure was resolved in the space group *Immm*.[3b] Selected bonding parameters: *d*[V–N(1)] 1.915(11), *d*[N(1)–N(2)] 1.130(16), *d*-[Na···N(2)] 2.445(11), *d*[Na–O(thf)] 2.349(12) Å; V–N(1)–N(2) 180°

to be resolved; it slows down at low temperatures to show the two components of the system. The signal for $[Li(thf)_y]^+$ is still rather broad compared to that of a solution containing LiCl only, and hence demonstrates that there is exchange between the two components even at low temperature, diminishing the effective point symmetry at the ^7Li nucleus (nuclear spin $I = \frac{3}{2}$) of $[Li(thf)_y]^+$ and thus giving rise to effective quadrupole broadening. For the solutions containing the carbonyl complexes $Li[V(CO)_n(dmpe)_x]$ (n = 2 or 3, x = 2; n = 4 or 5, x = 1) and LiCl, exchange is fast over the whole temperature range. The variations in the ^7Li NMR parameters δ and $w_{\frac{1}{2}}$, however, unambiguously show that there is an exchange equilibrium between solvated Li^+ and Li^+ in contact interaction with the carbonyl group of the anion.

Reactions.—(*a*) *Introduction of large cations.* Our NMR results show that contact-ion interaction similar to that revealed for the solid state also prevails in solution. Contact ion-pair formation seems in fact to be essential for the relative stability of the dinitrogen complexes. This is demonstrated by the unsuccessful preparation of such complexes with potassium as reducing agent, K^+ does not have a sufficiently high polarizing ability, a prerequisite for the formation of strong contact ion-pairs. The necessity of the presence of a cation with a high polarizing effect is also demonstrated by efforts to stabilize the dinitrogenvanadates with large (soft) cations, which have successfully been employed in stabilizing carbonylvanadates.[27] Stirring the Li/Na vanadates with $[E]^+Cl^-$ [E = NEt_4, NEt_3Ph, PPh_4 or $N(PPh_3)_2$] in thf does not stabilize the solutions, and addition of tetramethylethylenediamine, 12-crown-4 (in the case of the Li salt) or 15-crown-5 (Na salt) leads to immediate decomposition even at 195 K, due to removal of the cation by complexation.

(*b*) *Ligand exchange.* Not unexpectedly, the N_2 complexes are substitution labile. When a solution containing the complexes $Na[V(N_2)_n(PMe_2Ph)_{6-n}]$ (n = 1 or 2) is warmed to 40 °C under a normal pressure CO atmosphere, all N_2 is exchanged for CO within *ca.* 50 min and the anions *trans*-$[V(CO)_2(PMe_2Ph)_4]^-$ and small amounts of $[V(CO)_6]^-$ are detected spectroscopically. The carbonyl complex undergoes further substitution, and after 3 d reaction time, *cis*-$[V(CO)_4(PMe_2Ph)_2]^-$ (δ −1712) has formed as the main product along with small amounts of $[V(CO)_5(PMe_2Ph)]^-$ (δ −1860) and $[V(CO)_6]^-$ (δ −1957). In the case of $Na[V(N_2)_n(dmpe)_{4-n}]$ (n = 1 or 2), the final products of reaction are *cis*-$[V(CO)_4(dmpe)]^-$ (δ −1714), $[V(CO)_5(dmpe)]^-$ (δ −1858) and $[V(CO)_6]^-$.

Fig. 4 shows a series of IR spectra which indicate the step-wise substitution of N_2 in $Na[V(N_2)_n(dmpe)_{4-n}]$ by $CNBu^t$ at room

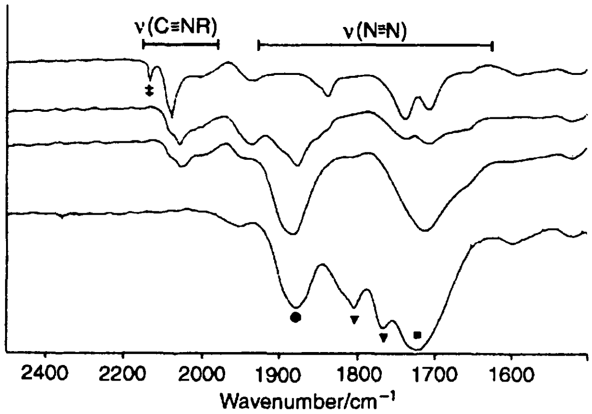


Fig. 4 IR spectra of the ν(NN) and ν(CN) regions of a thf solution of $Na[V(N_2)(dmpe)_3]$ (●), *cis*-$Na[V(N_2)_2(dmpe)_2]$ (▼) and *trans*-$Na[V(N_2)_2(dmpe)_2]$ (■) before (bottom trace) and after portionwise addition of $CNBu^t$. The top spectrum represents the situation after an addition of an excess of $CNBu^t$ and standing for 45 min. ‡ Indicates unco-ordinated $CNBu^t$

temperature. The first ν(NN) bands to disappear are those of the more labile *cis*-$[V(N_2)_2(dmpe)_2]^-$, followed by *trans*-$[V(N_2)_2(dmpe)_2]^-$ and $[V(N_2)(dmpe)_3]^-$. An intermediate mixed-ligand complex $[V(N_2)(CNBu^t)(dmpe)_2]^-$ with ν(CN) at 2054 cm^{-1} [ν(NN) not unambiguously assigned] can be detected; the final substitution product obtained with excess of the cyanide is $[V(CNBu^t)_2(dmpe)_2]^-$, with a characteristic ν(CN) at 2077 cm^{-1}, hence a bathochromic shift of 57 cm^{-1} with respect to unco-ordinated $CNBu^t$. Due to the concomitant formation of paramagnetic impurities, ^{51}V NMR spectroscopy could not be employed here for further characterization.

(*c*) *Reductive protonation.* In the context of viewing the N_2 complexes as functional models of the nitrogenases, the reaction of bis(dinitrogen)molybdenum(0) complexes with acids has been investigated intensively and, based on the various intermediates which have so far been characterized,[28] a stepwise reductive protonation of N_2 to NH_3 such as shown in equation (5) can be proposed. Small amounts of hydrazine are also formed; in non-polar solvents, N_2H_4 is the main product. The overall reaction of the formation of ammonia can be formulated as shown in equation (6). Alternatively to what is noted in equation (5), an intermediate hydrazido(2−) complex of Mo^{IV} has been proposed which, after further protonation, undergoes intramolecular electron reorganization (formation of a hydrazinyl intermediate) and disproportionation to form Mo^{III}, ammonia and nitrogen [equation (7)]. Such a mechanism

$$\begin{aligned}L_4Mo^{O}(-N{\equiv}N)_2 &\longrightarrow N_2 + \{L_4Mo^{I}{-}N{=}NH\} \longrightarrow \\ &\{L_4Mo^{II}{=}N{-}NH_2] \longrightarrow \{L_4Mo^{II}{=}N{-}NH_3\}^+ \longrightarrow \\ &\qquad \{L_4Mo^{III}{=}NH\}^+ + NH_3 \quad (5)\end{aligned}$$

$$\{Mo^{O}(N_2)_2\} + 3H^+ \longrightarrow \{Mo^{III}\} + NH_3 + 1.5N_2 \quad (6)$$

$$\begin{aligned}L_4Mo^{O}(-N{\equiv}N)_2 &\longrightarrow N_2 + \{L_4Mo^{IV}{=}N{-}NH_2\} \longrightarrow \\ &\qquad \{Mo^{III}\} + NH_4^{\ +} + \tfrac{1}{2}N_2 \quad (7)\end{aligned}$$

is backed up by the observation that two-electron reducing agents such as $SnCl_2$ fulfil the role of reducing agent for the hydrazido(2−) ligand, circumventing disproportionation,[29] and by the discovery of hydrazinyl complexes.[30]

The compounds $Na[V(N_2)_2(dppe)_2]$ and $Na[V(N_2)_2(dmpe)_2]$ react with dry HBr to form ammonia and a small amount of hydrazine[3] [equation (8)]. A mechanism *via* a hydrazine and hydrazido(2−) complex has been proposed, backed up by the existence of hydrazine complexes of V^{II} and V^{III}.[31] Again, the succeeding steps may be either reductive protonation of $N_2H_2^{\ 2-}$ to form NH_3 or N_2H_4 [equation (9)], or disproportionation of an intermediate hydrazinyl complex [equation (10)]. The latter mechanism is favoured by the overall stoichiometry of reductive protonation as indicated by equation (8). The intermediacy of a hydrazide complex is supported by the observation that ammonia is formed in the reaction between $[V_2(bdmpm)_2(\mu\text{-}Cl)_3]$ and lithium hydrazide (see Experimental section).

$$\{V^{-I}(N_2)_2\} + 3H^+ \longrightarrow \{V^{II}\} + NH_3 + 1.5N_2 \quad (8)$$

$$\begin{aligned}L_4V^{-I}(-N{\equiv}N)_2 &\longrightarrow N_2 + \{L_4V^{III}{=}N{-}NH_2\} \longrightarrow \\ &\qquad \{V^{III}\} + NH_3/N_2H_4 \quad (9)\end{aligned}$$

$$\begin{aligned}L_4V^{-I}(-N{\equiv}N)_2 &\longrightarrow N_2 + \{L_4V^{III}{-}NH{-}NH_2\} \longrightarrow \\ &\{L_4V^{II}(-NH{-}NH_2^{\bullet})\} \longrightarrow \{V^{II}\} + \tfrac{1}{2}N_2 + \tfrac{1}{2}NH_3 \quad (10)\end{aligned}$$

Conclusion

The synthesis of phosphine-stabilized mono- and bis-(dinitrogen) complexes of V^{-I} by reduction of VCl_3 is applicable to a variety of mainly oligodentate alkylphosphines. Of the phosphines checked in this study, dmpe yields the more stable complexes. Where only dmpe is employed, the (kinetically favoured) *cis*- and the (thermodynamically favoured) *trans*-bis(dinitrogen) complexes are obtained. Mono(dinitrogen) complexes can be prepared by combining dmpe with a tridentate phosphine.

Sodium and lithium are appropriate reducing agents to generate the N_2 complexes, and the presence of Na^+ or Li^+ as the counter ion is a prerequisite for the relative stability of the anionic complexes. This is due to close contact ion-pair interaction both in solution and in the solid crystalline state. In the solid state, *trans*-$[Na(thf)][V(N_2)_2(dppe)_2]$ and possibly other complexes as well form polymers (insoluble in all common solvents) with linear V–N≡N ··· Na units arranged in chains. In thf solution, stable contact ion-pairs of the kind V–N≡N ··· Li have been detected below *ca.* 250 K by ^7Li NMR spectroscopy. At ambient temperatures Li^+ in contact interaction with vanadate(−I) exchanges with solvated Li^+.

Even under these conditions optimized for the existence of $V^{-I}(N_2)$ complexes, the compounds are labile and lose N_2 under slightly reduced pressure. In the presence of carbon monoxide or isocyanides, N_2 is replaced. As in the analogous $Mo^0(N_2)$ complexes, 25% of the co-ordinated N_2 can be converted to $NH_4^{\ +}$ (plus a small amount of hydrazine) with acids. The reductive protonation of N_2 to NH_3 possibly proceeds *via* the formation of a hydrazido and/or hydrazinyl intermediate. The electrons for the reduction are delivered by the metal, hence a 'true' functional model for nitrogenases. While the Mo and V complexes react similarly towards H^+, dinitrogenvanadium complexes, in contrast to the Mo complexes, are thermally labile. The lability of the V–N_2 bond in particular is a good approach (in the sense of the model character of these complexes) towards the first step of nitrogen fixation, *viz.* the (reversible) binding of N_2 to the active site.

Experimental

General and Spectroscopic Measurements.—All operations were carried out under nitrogen and in absolute, oxygen-free solvents. The following compounds were synthesized according to literature procedures: $[VCl_3(thf)_3]$,[32] bdmpm, bdepm, tdmp or tdep.[33] Sodium sand was prepared by dispersing sodium, heated just beyond its melting point, in hot xylene, removal of the xylene with a pipette after cooling to room temperature and washing with thf. Lithium foil was obtained by rolling out lithium and using pieces of size *ca.* 1 cm^2. All other starting materials were obtained from commercial sources.

The IR spectra were run on a Perkin-Elmer 1720 FT spectrometer as thf solutions in 0.1 mm CaF_2 cuvettes or (low-temperature measurements) 0.1 mm Irtran (ZnS) cuvettes, or as Nujol mulls (KBr or CsI plates); NMR spectra were scanned as thf solutions (thf–[$^2H_8$]thf 2:1) in rotating 10 mm diameter vials on a Bruker 360 MHz spectrometer with the following typical measuring parameters: ^{51}V, frequency (SF) 94.73 MHz, sweep width (SW) 125 kHz, time domain (TD) 8200 K, pulse angle 20°, no relaxation delay (RD), line-broadening factor (LB) 30 Hz, average scan number (NS) 30 000, reference $VOCl_3$, ^{23}Na, SF 95.26 MHz, SW 50 kHz, TD 8200 K, pulse angle 4 µs, RD 2 s, LB 12 Hz, NS 400, reference saturated aqueous (D_2O) NaCl, ^7Li, SF 139.96 MHz, SW 2800 Hz, TD 8200 K, pulse width 4 µs, RD 2 s, LB 0.7 Hz, NS 80, reference saturated aqueous (D_2O) LiCl.

Preparation and Reactions of Complexes.—(*a*) $Na[V(N_2)_n(PMe_2Ph)_{6-n}]$ *and* $M[V(N_2)_n(dmpe)_{4-n}]$ (*n* = 1 *or* 2, M = Na *or* Li). The compound $[VCl_3(thf)_3]$ (374 mg, 1.00 mmol) was dissolved in thf (20 cm^3) and treated with PMe_2Ph (540 µl, 552 mg, 4.00 mmol) or dmpe (334 µl, 300 mg, 2.00 mmol), respectively. The green solution thus obtained was cooled to dry-ice temperature, and an excess of the metal reductant (100 mg Na sand or Li foil) was added. After a few minutes of stirring at −78 °C, the solution turned blue (V^{II}), after about 1 d dark brown. The solution was then filtered at −78 °C and used directly for spectroscopic characterizations and reactivity studies.

Addition of pentane (200 cm^3), filtration of the precipitate and drying in a N_2 stream yielded a black-brown, pyrophoric powder containing varying amounts of Na–LiCl along with the N_2 complexes. Efforts to remove these admixtures led to decomposition of the dinitrogen complexes.

Tetrahydrofuran solutions of the bis(dinitrogen) complexes with tdmp and tdep were prepared similarly to $Na[V(N_2)_2(dmpe)_2]$. Addition of naphthalene (*ca.* 15 mg) to the reaction mixture facilitates the reduction.

(*b*) *Formation of ammonia from* $Na[V(N_2)_2(dmpe)_2]$ *and* HBr. The reaction was carried out with a dry sample prepared by precipitation with pentane as described above, and containing, based on the elemental nitrogen analysis, 54% of the bis(dinitrogen) complex. The sample (38.7 mg) was cooled to −196 °C, dry HBr (2 cm^3) was condensed onto it, and the mixture was slowly warmed to room temperature. The solution was stirred as soon as the HBr melted. The HBr was allowed to evaporate, and the residue was dried under high vacuum for 1 h to yield 81.8 mg of a brown powder (nitrogen content 0.98%). Of this 22.0 mg were treated with 10 mol dm^{-3} aqueous NaOH (5 cm^3) and the evolving gas transferred to a Schlenk tube containing 0.1 mol dm^{-3} H_2SO_4 as absorbent. Photometric determination of NH_3[34] and N_2H_4[35] gave 0.257 mg of NH_3 and 9.6 µg of N_2H_4. This corresponds to a complete volatilization of all of the nitrogen in the brown powder, and to a 25% conversion of the dinitrogen in the N_2 complex to essentially NH_3. A blank using $Na[V(CO)_{6-n}(dmpm)_{\frac{n}{2}}]$ (*n* = 2–4) was negative.

(*c*) *Reduction of* VCl_3 *in the presence of* bdmpm *and* dmpe. (*i*) $Na[V(N_2)(dmpe)(bdmpm)]$. The compounds $[VCl_3(thf)_3]$ (374 mg, 1 mmol) and bdmpm (260 µl, 1 mmol) were dissolved in thf (40 cm^3). After 1 h stirring, the green solution was concentrated to 12 cm^3, cooled to −30 °C and treated with dmpe (165 µl, 1 mmol), Na sand (200 mg) and naphthalene (20 mg). The solution was stirred for a few minutes and then allowed to react at −78 °C for 1 d and at −40 °C for an additional day. The brown solution thus obtained contained $Na[V(N_2)(dmpe)(bdmpm)]$.

After addition of hexane (13 cm^3), the solution was filtered through a short Celite column (2.5 cm diameter, 1 cm height) and the filtrate treated with hexane (100 cm^3) to yield small amounts of *cis*-$Na[V(N_2)_2(dmpe)_2]$. From the filtrate, small amounts of *trans*-$Na[V(N_2)_2(dmpe)_2]$ separate within a couple of days.

Tetrahydrofuran solutions of the mono(dinitrogen) complexes containing dmpe along with bdepm and bdpep were prepared accordingly.

(*ii*) $[V_2(bdmpm)_2Cl_3]$ *and its reaction with* $LiNHNH_2$. When the reduction of VCl_3 in the presence of bdmpm and dmpe is carried out in a molar ratio of VCl_3 : Na = 1:2, $[V_2(bdmpm)_2Cl_3]$ is obtained instead of the dinitrogen complex: the compound $[V(bdmpm)Cl_3]$ (408 mg, 1 mmol) {prepared from $[VCl_3(thf)_3]$ and bdmpm in analogy to the dmpe complex[36]} was dissolved in thf (40 cm^3), cooled to −40 °C and treated with dmpe (165 µl, 1 mmol), Na sand (46 mg, 2 mmol) and naphthalene (10 mg). The reaction was terminated after 10 h. After addition of hexane (15 cm^3), the brown solution was filtered, the filtrate concentrated to 5 cm^3, cooled to −78 °C and treated with hexane (50 cm^3) to yield a brown powder $[V_2(bdmpm)_2Cl_3]$. Yield: 200 mg (56%) (Found: C, 37.20; H, 7.70; P, 26.30; V, 13.95. $C_{22}H_{54}Cl_3P_6V_2$ requires C, 37.05; H, 7.60; P, 26.10; V, 14.30%). IR: ν_{max}/cm^{-1} (Nujol mull) 311 (V–Cl).

A thf solution (10 cm^3) containing $[V_2(bdmpm)_2Cl_3]$ (0.5 mmol) cooled to −40 °C, was treated with a suspension of $LiNHNH_2$ (19.0 g, 0.5 mmol) in thf (5 cm^3), and stirred for 4 h, after which time the solution had turned red. Warming to room temperature led to decomposition and liberation of gas. All volatile compounds were condensed (liquid-nitrogen temperature) into a Schlenk tube containing concentrated hydrochloric acid (2 cm^3). After warming to room temperature, the solution was evaporated to dryness *in vacuo*, yielding 26.1 mg of residue. The IR spectrum indicated the presence of NH_4Cl and dmpe·HCl. Based on the elemental analysis (C, 16.7; H, 7.8; N, 12.0%), 13 mg of the residue were attributable to NH_4Cl, corresponding to a conversion of *ca.* 50% of the hydrazide to ammonia.

(*d*) *trans*-$Li[V(CO)_2(dmpe)_2]$. The compound $[VCl_3(thf)_3]$ (374 mg, 1.00 mmol) was dissolved in thf (20 cm^3) and treated with dmpe (334 µl, 300 mg, 2.00 mmol). The green solution was cooled to −78 °C, and an excess of lithium foil (100 mg) was added. Dinitrogen was removed by evacuation and replaced by dried CO. The solution turned blue after a few minutes and dark brown after 1 d. The filtered solution, containing *trans*-$Li[V(CO)_2(dmpe)_2]$ [$\delta(^{51}V)$ −1063 *J*(VP) 161 Hz; $\tilde{\nu}$(CO) 1731 cm^{-1}] and small amounts of $[V(CO)_6]^-$ and *cis*-$[V(CO)_4(dmpe)]^-$, was directly used for spectroscopic investigations.

(*e*) *Ligand-exchange reactions.* In a flask containing a solution of $Na[V(N_2)_n(PMe_2Ph)_{6-n}]$ (*n* = 1 or 2) prepared as described in section (*a*) and cooled to −60 °C, the N_2 atmosphere was exchanged for a CO atmosphere and the contents warmed to room temperature within 3 h. From time to time, a light CO stream was passed over the solution to remove N_2, released by the exchange reaction. The colour of the solution gradually turned from dark to light brown. The main product after 3 h was *trans*-$[V(CO)_2(PMe_2Ph)_4]^-$; $[V(CO)_6]^-$ was present as a minor product. Prolonged exposure to CO led to partial replacement of phosphine. The main product present after 3 d was *cis*-$[V(CO)_4(PMe_2Ph)_2]^-$ (^{51}V NMR evidence).

A similar behaviour towards CO was observed for $Na[V(N_2)_n(dmpe)_{4-n}]$ (*n* = 1 or 2). In this case, the exchange was conducted at 40 °C.

A thf solution of $Na[V(N_2)_n(dmpe)_{4-n}]$, prepared as described in section (*a*), was treated (room temperature), at 45 min intervals with six 0.5 cm^3 portions of *tert*-butyl isocyanide. The solution gradually became lighter. For discussion see the preceding section.

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