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Cyclodivanadazene Alkyl and Aryl Complexes

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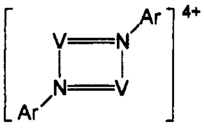
Summary: Both reduction and aryl/alkylation are involved in the reactions of aryl and alkyl Grignard reagents with the terminal (imido)vanadium(V) complex [ArNVCl$_3$] *to form diamagnetic cyclodivanadazene type species,* [(μ-*p*-MeC$_6$H$_4$N)$_2$V$_2$R$_4$] (R = CH$_2$Ph, 2,4,6-Me$_3$C$_6$H$_2$).

In the present report we are essentially concerned with the genesis, the properties, and the organic derivatives of the cyclodivanadazene core:



A

The most attractive features associated with skeleton **A** are (i) the two electrons of the core which can give rise to singlet or triplet states, *via* different mechanisms including a V—V single bond, (ii) its analogy with the corresponding dioxo [V$_2$O$_2$]$^{4+}$ species, (iii) the possibility of developing an organometallic chemistry of the divanadium(IV) diradical unit.

The imido ligand [RN]$^{2-}$ is currently having a considerable impact in organometallic chemistry, in two major areas: (i) the use of imido fragments as ancillary ligands isoelectronic with [C$_5$H$_5$]$^-$ for stabilizing high oxidation states[1] and (ii) the chemistry of the [M=NR] functionality,[1d,2] a particularly active area, one example being in the reaction with C—H bonds.

The imido group, behaving either as an ancillary ligand or as a reactive functionality, displays in general the terminal bonding mode. The few examples reported for bridging bonding modes are derived from a dimerization of the more reactive monomeric form.[1d,3]

Horton and de With have reported several examples in the chemistry of vanadium(V) imido complexes, in particular that of vanadium(V) bis(imido) and amido imido monomeric species.[2]

The organometallic chemistry derived from the mono(imido) species [RNVCl$_3$] has been perceived as leading to not fully characterized alkyl derivatives or to paramagnetic vanadium(IV) forms.[4] Very rare examples of dinuclear (imido)vanadium(IV) compounds containing alkyl and amido or alkoxo groups have been very recently reported. They are derived from the hydrogenation of the homoleptic [{η^2-C(Mes)=NBu^t}$_3$V],[5] though this was not reported as a preparative method, or from the photochemical decomposition of the corresponding mononuclear alkoxoalkylvanadium(V) derivatives [Bu^{t}NV(R)$_2$(OR′)].[6] We report here the results of the reductive aryl/alkylation of [*p*-MeC$_6$H$_4$NVCl$_3$] (**1**) leading to organometallic derivatives possessing skeleton **A**.

Treatment of **1** with PhCH$_2$MgCl or MesMgBr (Mes = 2,4,6-C$_6$H$_2$) in a mixture of tetrahydrofuran (THF) and dioxane at 253 K led to the corresponding diamagnetic divanadium(IV) species **3**[7] and **4**[8] (Scheme 1, pathway A).

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(7) Procedure for **3**: A 0.767 M solution of C$_6$H$_5$CH$_2$MgCl (2.60 g, 17.27 mmol) in THF (22.5 mL) was added dropwise under N$_2$ at 253 K to a solution of **1** (1.51 g, 5.76 mmol) in THF (150 mL)/dioxane (25 mL). After the addition was complete, the temperature was increased to room temperature and the mixture was stirred for a further 6 h. Filtration of the magnesium salts gave a green-brown solution. The solvent was removed and the residue extracted in diethyl ether to give **3** contaminated with an unidentifiable impurity (combined mass 1.06 g). Further extraction in diethyl ether of this mixture gave analytically pure crystalline **3** (37%). ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 7.1–6.6 (m, 28 H, C$_6$*H*$_5$CH$_2$, NC$_6$*H*$_4$-*p*-Me), 2.43 (br, 8 H, C$_5$H$_5$C*H*$_2$), 2.24 (s, 6 H, NC$_6$H$_4$-*p-Me*). ^{13}C NMR (C$_6$D$_6$): δ 142.6 (Ar), 135.25 (Ar), 125.5 (Ar), 120.36 (Ar), 26.5 (2Me), 21.8 (4CH$_2$). Anal. Calcd for C$_{42}$H$_{42}$N$_2$V$_2$: C, 74.55; H, 6.26; N, 4.14. Found: C, 74.33; H, 6.36; N, 4.01.

(8) Procedure for **4**: A 1.43 M solution of MesMgBr (6.81 g, 30.5 mmol) in THF (21.3 mL) was added dropwise under N$_2$ at 253 K to a solution of **1** (2.67 g, 10.2 mmol) in THF (150 mL)/dioxane (25 mL). After the addition was complete, the temperature was increased to room temperature and the solution stirred overnight. Filtration of the magnesium salts gave a red solution. Removal of the solvent and extraction in diethyl ether afforded **4** (48%) as a crystalline solid. ^{1}H NMR (CD$_2$Cl$_2$, 600 MHz): δ 6.88 (AB q, J_{AB} = 8.2 Hz, 8 H, NC$_6$*H*$_4$-*p*-Me), 6.61 (br, 8 H, C$_6$*H*$_2$-*o*-Me$_2$-*p*-Me), 2.28 (s, 12 H, C$_6$H$_2$-*o-Me*$_2$-*p*-Me), 2.27 (s, 12 H, C$_6$H$_2$-*o-Me*$_2$-*p*-Me), 2.23 (s, 6 Hz, NC$_6$H$_4$-*p-Me*), 1.67 (s, 12 H, C$_6$H$_2$-*o*-Me$_2$-*p-Me*). ^{13}C NMR (CD$_2$Cl$_2$): δ 148.1 (Ar), 144.8 (Ar), 142.3 (Ar), 140.0 (Ar), 132.9 (Ar), 132.3 (Ar), 131.7 (Ar), 130.8 (Ar), 124.7 (Ar), 31.2 (Me), 26.6 (Me), 25.9 (Me), 25.7 (Me). Anal. Calcd for C$_{50}$H$_{58}$N$_2$V$_2$: C, 76.17; H, 7.59; N, 3.80. Found: C, 76.12; H, 7.41; N, 3.50.

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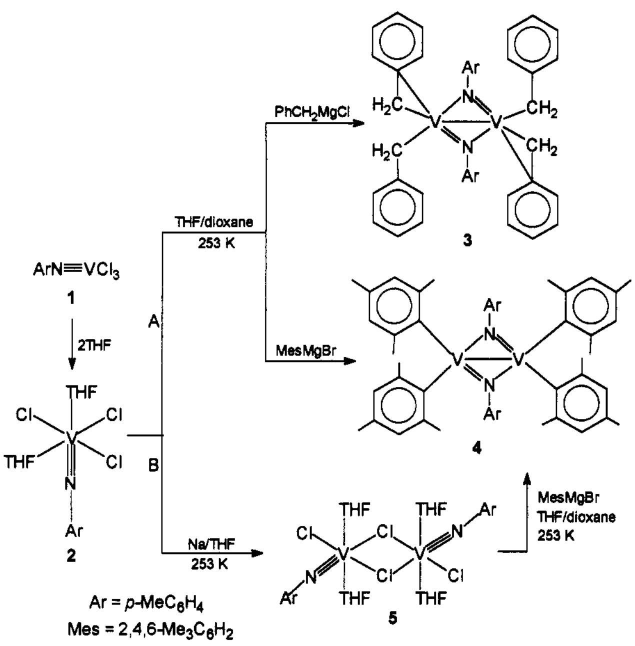
Scheme 1



Although the THF adduct of 1 p-MeC$_6$H$_4$NVCl$_3$·2THF[4,9] (2) was not isolated in these reactions, it is clear that this provides the first step in the reaction pathway. It is noteworthy that the reaction of 1 with PhCH$_2$MgCl did not proceed as cleanly as that with MesMgCl, a factor clearly limiting the synthetic utility of the former reaction.

The reductive arylation of 1 can be carried out using an alternative approach. Addition of 1 equiv of sodium sand to a THF solution of 1 led to the divanadium(IV) chloride-bridged species 5,[10] which was subsequently arylated to give 4[11] (Scheme 1, pathway B).

Microanalytical, ^{1}H NMR, and magnetic data are consistent with the formulations given for 3–5 and are further supported by single-crystal X-ray analyses. Only the molecular structures of 3[12] (Figure 1) and 4[13] (Figure 2) will be discussed in detail, however.

In each complex the two vanadium centers are bridged by two imido ligands and coordinated to two benzyl (3) and mesityl (4) substituents. The V$_2$N$_2$ core is planar in 3, having a C_i crystallographic symmetry, and very close to planarity in 4, having a C_2 symmetry. The very short V—V distances (2.449(19 Å for 3 and 2.487(1) Å for 4) are quite close to those found (2.460(1),[5] 2.472(3) Å[6]) in the other bis(imido)-bridged divanadium(IV) complex so far reported.

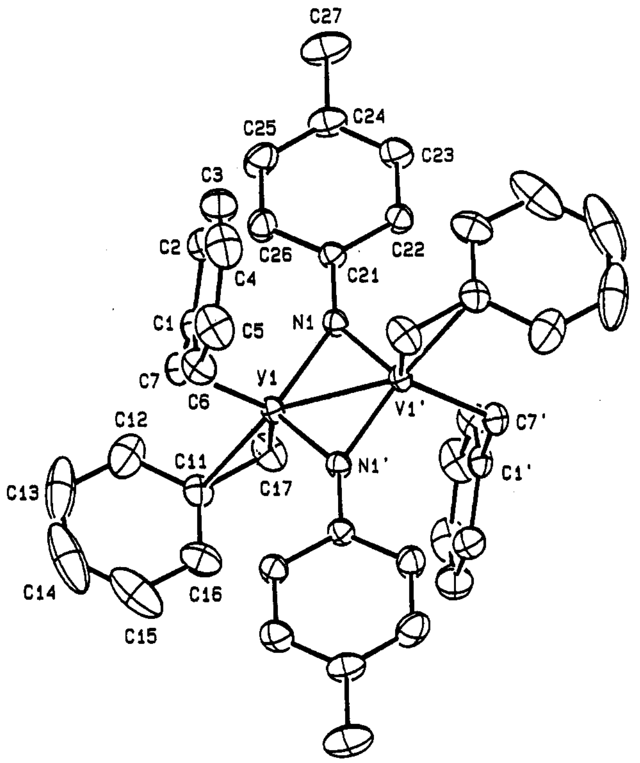


Figure 1. ORTEP drawing (30% probability ellipsoids) of complex 3. Selected bond distances (Å) and angles (deg) are as follows: V1—V1′ = 2.449(19), V1—N1 = 1.837(1), V1—N1′ = 1.862(2), V1—C7 = 2.082(3), V1—C17 = 2.065(2), V1—C11 = 2.443(2), V1···C1 = 3.056(3), N1—C21 = 1.408(2), C1—C7 = 1.475(3), C11—C17 = 1.451(3); N1—V1—C7 = 105.9(1), N1′—V1—C7 = 109.2(1), N1′—V1—C17 = 115.1(1), N1—V1—C17 = 99.4(1), N1—V1—N1′ = 97.0(1), C7—V1—C17 = 125.0(1), V1—N1—V1′ = 83.0(1), V1—C7—C1 = 117.4(1), V1—C17—C11 = 86.2(1). The prime refers to a transformation of $1 - x, -y, -z$.

The benzyl and mesityl bonding modes in 3 and 4 deserve a brief comment. The V—C bond distances in 3 (see caption for Figure 1) show unquestionably that an η^2 and η^1 bonding mode exists for the two benzyl groups on each metal and hence, that vanadium is formally five-coordinate, while in 4 the hydrogens from the o-methyl groups of the mesityls give rise above and below the V$_2$N$_2$ plane to rather short V—H distances (V—H71, 2.60 Å; V—H171, 2.62 Å). These structural features observed in the solid state have not been revealed in solution. In fact, the ^{1}H and ^{13}C NMR spectra at 293 K for 3 show respectively a

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[9] X-ray data for 5 and for [PhNVCl$_3$(THF)$_2$], related to 2, and theoretical calculations: unpublished results.

[10] Procedure for 5: Sodium sand (0.270 g, 11.7 mmol) was added to a solution of 1 (3.081 g, 11.7 mmol) in THF (100 mL) at 253 K. The solution was warmed to room temperature and stirred for a further 48 h. Filtration of sodium chloride and concentration of the filtrate gave red crystalline 5 (37%) on prolonged standing. Anal. Calcd for C$_{30}$H$_{46}$Cl$_4$N$_2$O$_4$V$_2$: C, 48.54; H, 6.25; N, 3.77. Found: C, 48.41; H, 6.48; N, 3.99.

[11] Transformation of 4 to 5: A 1.00 M solution of MesMgBr (1.03 g, 4.6 mmol) in THF (4.6 mL) was added dropwise to a solution of 5 (0.86 g, 1.2 mmol) in THF (100 mL)/dioxane (15 mL) at 253 K. The solution was warmed to room temperature and stirred for a further 5 h. Filtration of the magnesium salts gave a red solution. Removal of the solvent and extraction in diethyl ether afforded 4 (40%).

[12] Structure analysis of 3: C$_{42}$H$_{42}$N$_2$V$_2$, M_r = 676.7, triclinic, space group $P\bar{1}$, a = 10.315(1) Å, b = 10.561(1) Å, c = 9.549(1) Å, α = 105.26(1)°, β = 103.87(1)°, γ = 63.12(1)°, V = 886.3(2) Å^3, Z = 1, ρ_{calcd} = 1.268 g cm^{-3}; λ(Mo Kα) = 0.710 69 Å; μ(Mo Kα) = 5.40 cm^{-1}; crystal dimensions 0.26 × 0.35 × 0.45 mm. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and anisotropically refined by full-matrix least squares for all the non-hydrogen atoms. The hydrogen atoms were located from a difference Fourier map and refined in a cycle prior to the last stage of refinement. For 3650 unique observed structure amplitudes ($I > 2\sigma(I)$) collected at room temperature on a Philips PW1100 diffractometer in the range $6 < 2\theta < 60°$, the current R value is 0.032 (unit weights). At the end of the refinement a residual peak of 1.5 e Å^{-3} in the ΔF map was interpreted as a "partial" vanadium atom (V1B) anchored to the framework provided by the coordinated ligands. This "atom", which defines a V$_2$N$_2$ core perpendicular to that of the "base" molecule, was successfully refined with a site occupation factor of 0.05.

[13] Structure of 4: C$_{50}$H$_{58}$N$_2$V$_2$, M_r = 788.9, monoclinic, space group $C2/c$, a = 15.743(2) Å, b = 17.707(2) Å, c = 16.281(2) Å, β = 96.20(1)°, V = 4512.0(9) Å^3, Z = 4, ρ_{calcd} = 1.161 g cm^{-3}; λ(Mo Kα) = 1.541 78 Å; μ(Mo Kα) = 37.4 cm^{-1}; crystal dimensions 0.20 × 0.35 × 0.55 mm. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and anisotropically refined by full-matrix least squares for all the non-hydrogen atoms. The hydrogen atoms, apart from the two associated with the C27 and C37 methyl carbons, which were ignored, were located from difference Fourier maps and introduced as fixed contributors prior to the last stage of refinement (U_{iso} = 0.038 and 0.13 Å^2 for aromatic and methylic hydrogens, respectively). For 3249 unique observed structure amplitudes ($I > 2\sigma(I)$) collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 140°$ and corrected for absorption, the current R value is 0.056 (unit weights). All calculations were carried out using SHELX76.

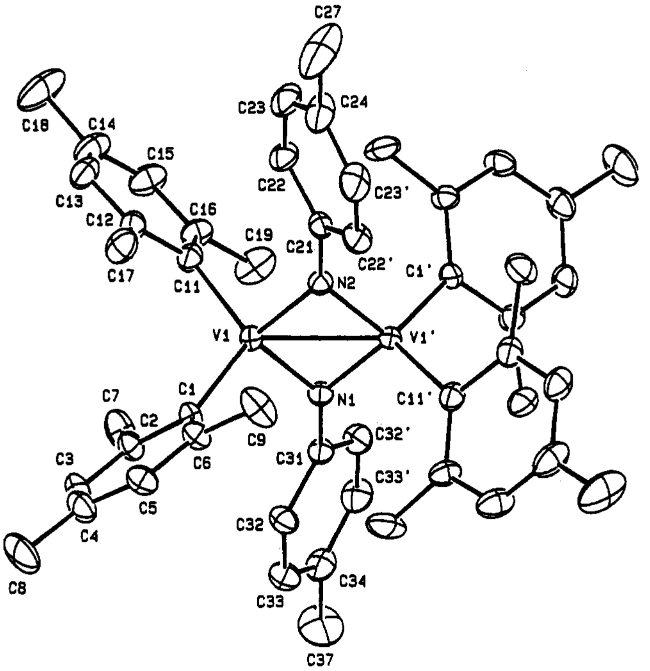

Figure 2. ORTEP drawing (30% probability ellipsoids) of complex 4. Selected bond lengths (Å) and angles (deg): V1—V1′ = 2.487(1), V1—N1 = 1.856(3), V1—N2 = 1.851(3), V1—C1 = 2.056(4), V1—C11 = 2.060(5), N1—C31 = 1.411(6), N2—C21 = 1.420(6); C1—V1—C11 = 115.8(2), N2—V1—C11 = 105.2(1), N2—V1—C1 = 115.4(1), N1—V1—C11 = 117.1(1), N1—V1—C1 = 106.3(1), N1—V1—N2 = 95.7(0), V1—N1—V1′ = 84.1(0), V1—N2—V1′ = 84.0(0). The prime refers to a transformation of $-x$, y, $^1/_2 - z$.

single resonance for the methylene protons (δ 2.43) and methylene carbons (δ 21.84), suggesting equivalency of the methylene groups at this temperature. In contrast, the ^{1}H and ^{13}C NMR spectra at 293 K for 4 are consistent with restricted rotation of the terminal mesityl ligands with three separate signals for respectively the methyl hydrogens (δ 2.28 $\mathrm{Me_{ortho}}$, 2.27 $\mathrm{Me_{ortho'}}$, 1.67 $\mathrm{Me_{para}}$) and methyl carbons (δ 31.2–25.7) of the mesityl groups.

On the basis of some previous limited results[2,4] one can suppose that 3 and 4 form either from a vanadium(V) aryl/alkyl precursor or from a reduction of vanadium(V) followed by its aryl/alkylation, as indicated in pathway B (Scheme 1).

A significant comparison can be made between the properties of the [V_2X_2] dimetallacycle in 3–5. A change in the bridging ligand is observed when the chloride in 5 is replaced by mesityl groups (pathway B in Scheme 1), the imido group becoming the more stable bridging ligand in 4. The structural and magnetic properties are considerably different between 5 and 3 or 4. Complex 5 is slightly antiferromagnetic (μ = 1.70 μ_B at 295 K, J = 30 cm^{-1} in the range 80–300 K), with a rather long V···V distance (3.891(2) Å),[9] while 3 and 4 are diamagnetic with very short V···V distances. Interestingly, treatment of 3 with pyridine results in destruction of the diamagnetic core, whereas no effect is observed when pyridine is added to 4. The diamagnetism of 3 and 4 is in agreement with the existence of core A possessing singlet states only. *Ab initio* calculations performed on (i) the closed shell singlet implying a V—V single bond and on (ii) the open-shell singlet without any V—V bond showed the former electronic configuration as being more stable than the second one by 45 kcal/mol^{-1}.[14] This allows us to report 3 and 4 as having a single metal–metal bond.

Compounds 3 and 4 represent the first entries into a series of tetrahydrocarbyldivanadium(IV) complexes, the chemistry of which is under investigation.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for complexes 3 and 4 and a table of SCF and CI energies and text giving details of the theoretical calculations for the model compound [$V_2N_2H_6$] (12 pages). Ordering information is given on any current masthead page.

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