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Vanadium(II) Complexes

Reactivity Studies of a Masked Three-Coordinate Vanadium(II) Complex**

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Dedicated to Professor Herbert W. Roesky

The ability of vanadium to exist in various oxidation states renders this ion ideal for multielectron reactions, and therefore, a suitable metal for incorporation into novel ligand frameworks. An archetypal example of a low-valent vanadium species is vanadocene, $[\mathrm{V(Cp)_2}]$ ($\mathrm{Cp^-} = \eta^5\text{-}\mathrm{C_5H_5}$),[1] and its hindered relative decamethylvanadocene, $[\mathrm{V(Cp^*)_2}]$ ($\mathrm{Cp^{*-}} = \eta^5\text{-}\mathrm{C_5Me_5}$).[2] Despite these complexes being known for quite some time, and being $S = 3/2$ systems, their reactivity is often restricted given the coordinatively saturated metal ion. Prototypical among mononuclear $\mathrm{V^{II}}$ species are other coordinatively saturated complexes, $[\mathrm{VCl_2(L)_2}]$ ($\mathrm{L} = \mathrm{Me_2XCH_2CH_2XMe_2}$, X = N or P)[3] as well as complexes with a three-legged piano stool geometry such as $[\mathrm{V(Cp)(dmpe)(X)}]$ (dmpe = $\mathrm{Me_2PCH_2CH_2PMe_2}$, X = monoanionic ligand).[4] However, one approach to preparing a more reactive, low-valent metal fragment is by masking its coordination sphere with an arene, analogous to that of Rothwell et al. 15 years ago.[5] Reminiscent of this strategy are other masked, low-valent arene complexes having metals such as Zr, V, Fe, Ni, Co, Cu, Cr, and U.[6] Of these examples, the work by Tsai et al. has demonstrated facile access to monovalent vanadium through the isolation of an inverted sandwich divanadium(I) species supported by the ubiquitous nacnac ligand ($\mathrm{nacnac^-} = [\mathrm{Ar}]\mathrm{NC(Me)CHC(Me)N}[\mathrm{Ar}]$, Ar = 2,6-$\mathrm{(CHMe_2)_2C_6H_3}$).[6f] What is striking about this system is the presence of a highly reducing metal center supported by an innocent nacnac scaffold. The innocence of the nacnac ligand is atypical in the context of electron-rich early transition metals given the vulnerability of the imine functionality of nacnac to engage in two-electron reductive cleavage.[7] The stability of this low-valent vanadium nacnac scaffold suggested that hemilabile arenes, in combination with an appropriate ligand, could mask low-coordinate and thus reactive vanadium fragments.

Described herein is the isolation and characterization of a masked three-coordinate vanadium(II) complex, whereby a tethered arene moiety protects the unsaturated and highly reducing metal center. We investigate the electronic structure of the $\mathrm{V^{II}}$ complex and through a series of reactivity studies, we demonstrate it to be a suitable three-coordinate template for two- and three-electron chemistry including the formation of the first *cyclo*-$\mathrm{P_3}$ complex of vanadium.

We reasoned that direct reduction of the $\mathrm{V^{III}}$ complex, $[\mathrm{(nacnac)VCl(Ntol_2)}]$ (**1**),[8] should provide access to a mononuclear vanadium(II) species, given the unique ability of nacnac in stabilizing vanadium(I) and (II) complexes.[6e,9,10] Electrochemical studies of $[\mathrm{(nacnac)VCl(Ntol_2)}]$ showed irreversible anodic and reversible cathodic waves at +0.47 and −1.30 V, respectively (referenced vs. $[\mathrm{Fe(Cp_2)}]^{0/+}$ couple at 0.0 V in THF).[10] Chemical reduction of **1** with $\mathrm{KC_8}$ or 0.5 % Na/Hg in benzene produced dark red solids obtained in 54 % yield after crystallization from *n*-pentane at −37 °C (Scheme 1). ^{1}H NMR spectroscopic data revealed extremely shifted and broadened resonances consistent with a paramagnetic metal center, while single crystal X-ray diffraction (XRD) measurements confirmed loss of chloride ligand concurrent with formation of the $\mathrm{V^{II}}$ complex, $[\mathrm{(nacnac)V(Ntol_2)}]$ (**2**) (Figure 1).[10] Taking into account only the nitrogen interactions, the vanadium center in the molecular structure of **2** adopts a distorted trigonal geometry in which the V center lies 0.47 Å above the $\mathrm{N_3}$ plane. However, the most salient structural feature is the presence of V−C(*ipso*) (2.505(6) Å) and V−C(*ortho*) interactions (2.441(5) Å) with one of the aryl moieties of the $\mathrm{Ntol_2}$ ligand. Similar η^3 bonding interactions are commonly observed for the benzyl ligand and have been structurally observed with bulky anilide ligands coordinated to three-coordinate Ti, V, and U complexes.[11] Solid-state magnetization measurements (SQUID) of two independently prepared samples of **2** over a 2–300 K temper-

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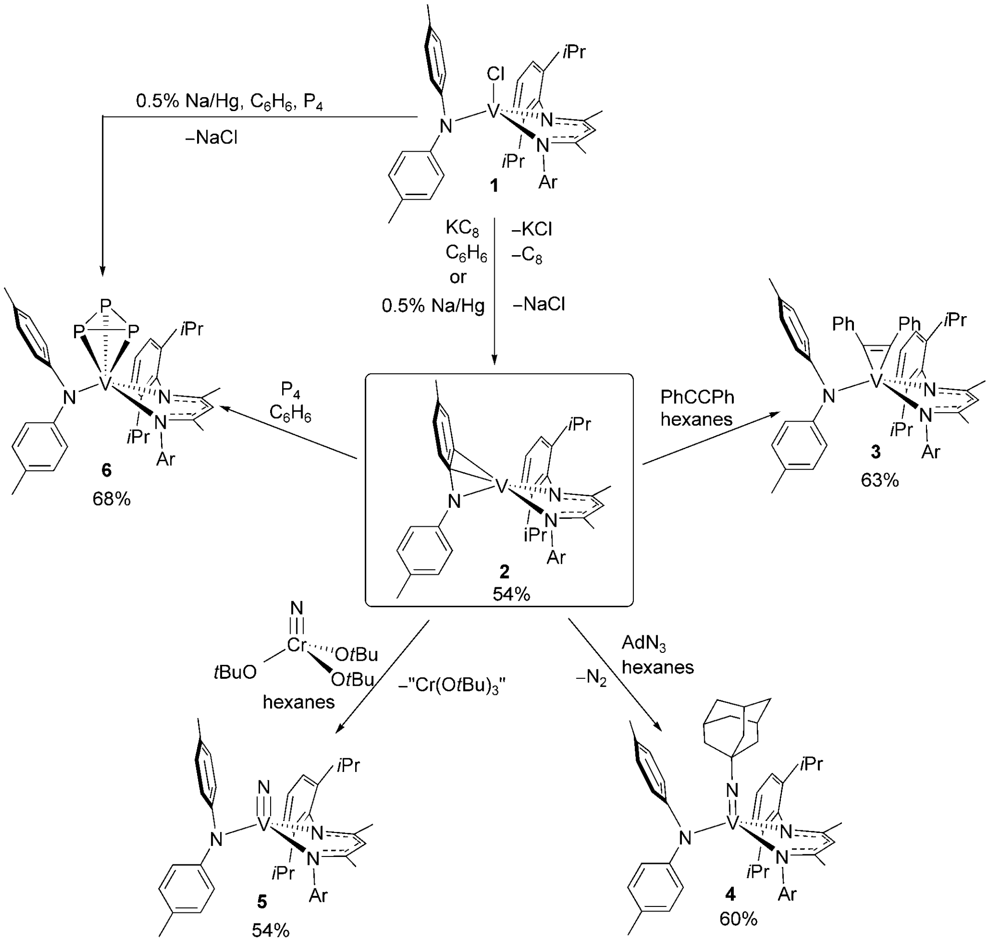

Scheme 1. Synthesis of complexes **2**–**6**.

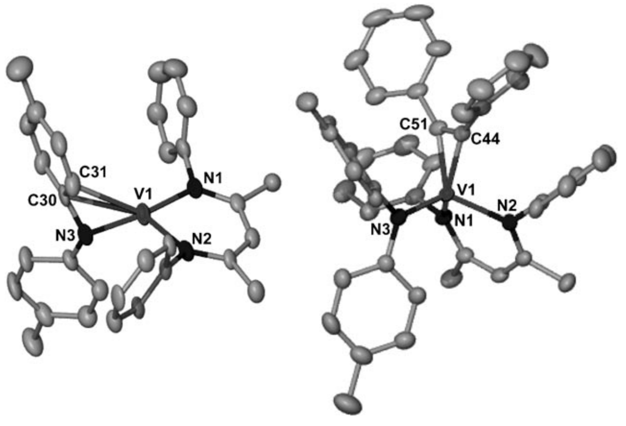

Figure 1. The molecular structures of [(nacnac)V(Ntol$_2$)] (**2**) and [(nacnac)V(η^2-C$_2$Ph$_2$)(Ntol$_2$)] (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and isopropyl groups on the nacnac ligand have been excluded for clarity. Selected bond lengths [Å] and angles [°] for **2**: V1–N1 2.016(5), V1–N2 1.999(4), V1–N3 1.980(4), V1–C30 2.441(4), V1–C31 2.505(6); N3-V1-N2 127.0(2), N3-V1-N1 125.18(19), N2-V1-N1 90.47(19), N3-V1-C30 34.67(18), N2-V1-C30 144.2(2), N1-V1-V1-C30 125.35(19), N3-V1-C31 62.52(19), N2-V1-C31 119.63(19), N1-V1-C31 136.4(2), C30-V1-C31 33.67(17). For **3**: V1–N1 2.0378(15), V1–N2 2.0468(15), V1–N3 1.9169(16), V1–C44 2.0009(19), V1–C51 2.0063(18); N1-V1-N4 99.47(10), N1-V1-N2 91.89(8), N1-V1-N3 128.00(8), N3-V1-N4 105.62(9).

ature range confirmed the presence of a V$^{\mathrm{II}}$ ion with three unpaired electrons (Figure 2).[10] The average magnetic moment of μ_{eff} (3.76 μ_{B}) is invariable over the range 20–250 K. There is a slight decrease above 250 K, which at this point we cannot fit or explain. Below 20 K, the magnetic moment sharply decreases in accord with zero-field splitting (zfs) effects. Fitting of the magnetization data using a standard spin Hamiltonian for $S = 3/2$ with axial zfs ($D \neq 0$, $E = 0$) and an isotropic g value yielded $g_{\mathrm{iso}} = 1.94(4)$ and $|D| = 2.9(5)\ \mathrm{cm}^{-1}$ (Figure 2). Additionally, room temperature magnetic susceptibility measurement (300 K) of **2** in C$_6$D$_6$ by the Evans method ($\mu_{\mathrm{eff}} = 4.05\ \mu_{\mathrm{B}}$) is consistent with an $S = 3/2$ system in solution. Despite the fact that **2** is EPR silent at 298 K in an X-band EPR experiment (9 GHz, perpendicular mode), and which was also the case for [Cp$_2$V],[1f] high-frequency and -field EPR (HFEPR) measurements of polycrystalline samples over the temperature range 10–50 K at 208 GHz were also consistent with a mononuclear complex having a quartet ground state (Figure 2).[12] Simulations of the HFEPR spectra of **2** yielded the following spin Hamiltonian parameters: $g_{\mathrm{iso}} = 1.98(1)$, $D = +2.99(2)$, $E = +0.11(2)\ \mathrm{cm}^{-1}$. The absolute value of D is in excellent agreement with magnetometry, while its positive sign (determined by comparing the relative amplitudes of particular turning points with simulations) and the value of the rhombic component E could be established thanks to superiority of a resonance technique over a bulk measurement. The zfs for **2**, determined here by two independent methods, is significantly larger than that reported for mononuclear V$^{\mathrm{II}}$ complexes, with the closest being vanadocene, for which the zfs was indirectly determined by X- and Q-band EPR to be $|D| = 2.3\ \mathrm{cm}^{-1}$.[1f] The zfs of V(II) has been reported for a number of systems in which the ion is coordinated in homoleptic, six-coordinate environments with N,[12a] O,[12b] or halide[12c] donors. In these highly symmetric cases, $|D| < 0.2\ \mathrm{cm}^{-1}$, and is often $< 0.01\ \mathrm{cm}^{-1}$, which allowed its facile measurement by X-band EPR. Of greater relevance to **2**, we note two V$^{\mathrm{II}}$ molecular complexes of lower symmetry: *trans*-[VCl$_2$(dmpe)$_2$], for which $D \approx 0.46\ \mathrm{cm}^{-1}$,[13a] and an organovanadium(II) complex,

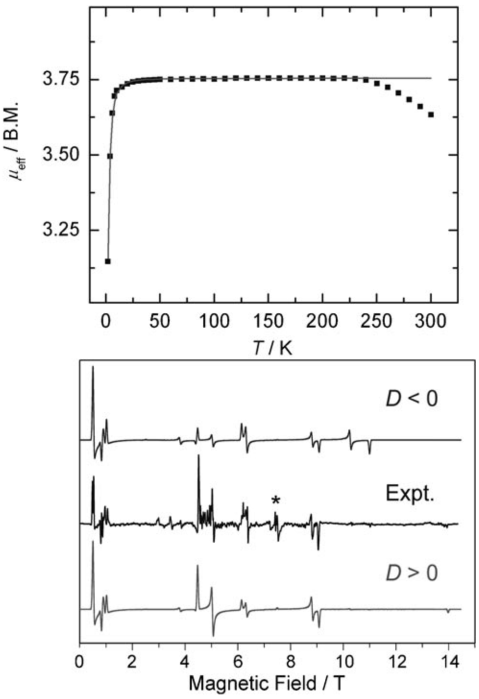

Figure 2. Upper: DC susceptibility of a powder of **2** measured at 1 T (squares) with a simulation (black line) based on a best fit of the data points in the range 2–200 K, and using the following parameters: $S=3/2$, $g_{iso}=1.938$, $|D|=2.934\ cm^{-1}$, TIP $=145\times10^{-6}$ emu. Lower: HFEPR spectra of a polycrystalline sample of **2** recorded at 10 K and 208 GHz (middle trace). Simulated traces are given above and below, employing the parameters: $S=3/2$, $|D|=2.99$, $|E|=0.11\ cm^{-1}$, $g_{iso}=1.98$, $\Delta B_{iso}=250$ G; for the upper trace, $(D, E)<0$ was used; for the lower trace, $(D, E)>0$ was used. The asterisk indicates a minor V^{IV} impurity which is not simulated.

$[V(dipp)_4]^{2-}$ (dipp = 2,6-diisopropylphenylate), with approximate square-planar geometry, which exhibits a rhombic EPR spectrum at X-band and 77 K that is indicative of $D \gg h\nu$ ($>0.3\ cm^{-1}$).[13b] HFEPR of this complex (and of vanadocene) would be instructive by allowing direct measurement of zfs (sign as well as magnitude) for comparison with **2**.[13c]

Compound **2** is a $[V^{II}\{N_2N'\}]$ template for two- and three-electron reactions, since the arene interaction of the anilide is readily disrupted upon treatment with various small molecules. Accordingly, mixing of diphenylacetylene with **2** results in two-electron reduction of the acetylene C−C triple bond to afford the metallacyclopropene complex, [(nacnac)V-(η^2-C_2Ph_2)($Ntol_2$)] (**3**), in 63% isolated yield. Solution susceptibility measurement (300 K, Evans method, $\mu_{eff}=1.92\ \mu_B$) is consistent with oxidation to V^{IV} ($S=1/2$) as result of two-electron reduction of the alkyne moiety. The presence of a V^{IV} ion is further corroborated by the room temperature X-band EPR spectrum in toluene solution ($g_{iso}=1.97$), which reveals an eight line pattern arising from hyperfine coupling to ^{51}V ($I=7/2$; 99.6%) of $A_{iso}=166$ MHz,[10] and in the range reported for $[V(Cp)_2]^{2+}$ complexes ($A_{iso}=120$–210 MHz).[1e] Furthermore, XRD studies unambiguously reveal formation of a metallacyclopropene (V−C44, 2.0009(19) Å; V−C51, 2.0063(18) Å; C51V−C44, 38.10(8)°) moiety derived from two-electron reduction of the alkyne (Figure 1). This reaction of **2** with an alkyne is reminiscent of the reaction of vanadocene and diphenylacetylene.[1e]

In an analogous two-electron reaction, treating **1** with an equivalent of N_3Ad (Ad = 1-adamantyl) at room temperature leads to rapid extrusion of N_2 with concomitant formation of [(nacnac)V=NAd($Ntol_2$)] (**4**) in 60% isolated yield from recrystallization in diethyl ether at −37 °C (Scheme 1). Formation of V^{IV} in **4** is again confirmed by room temperature susceptibility (Evans method, $\mu_{eff}=1.84\ \mu_B$) as well as X-band EPR ($g_{iso}=1.97$ and $A_{iso}(^{51}V)=74$ MHz).[10] This hyperfine coupling value is low compared to that of $[V(Cp)_2]^{2+}$ complexes[1e] and may reflect greater delocalization of the unpaired electron onto the imido ligand. XRD studies reveal formation of a terminal imido (V=N, 1.654(2) Å, V=N−C, 177.4(2)°). Complex **4** resembles reported tetrahedral V^V imido complexes.[14] As with **3**, and in contrast to **2**, no arene interactions are observed in the molecular structure of **4** (Figure 3).

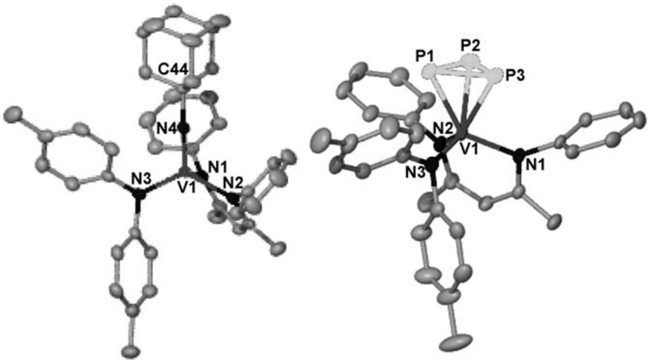

Figure 3. The molecular structures of [(nacnac)V(=NAd)($Ntol_2$)] (**4**) (left) and [(nacnac)V(*cyclo*-P_3)($Ntol_2$)] (**6**) (right) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and isopropyl groups on the nacnac ligand have been excluded for clarity. Selected bond lengths [Å] and angles [°] for **4**: V1−N1 2.047(2), V1−N2 2.054(2), V1−N3 1.956(2), V1−N4 1.654(2); N1-V1-N4 106.99(10), N1-V1-N2 88.30(9), N1-V1-N3 120.64(10), N3-V1-N4 107.64(11). For **6**: V1−N1 1.988(2), V1−N2 2.030(2), V1−N3 1.911(2), V1−P1 2.4300(9), V1−P2 2.4388(9), V1−P3 2.4328(9); P1-V1-P2 52.07(3), P1-V1-P3 51.80(3), N1-V-N2 96.17(9), N1-V-N3 112.7(1), P1-V1-N1 138.43(7), P1-V1-N3 87.07(7).

Complex **2** can also promote three-electron reactions. For example, the reaction of **2** and [(tBuO)$_3$Cr≡N][15] in hexanes at room temperature over 3 h results in complete intermetal N-atom transfer with quantitative conversion to the recently reported V^V nitride [(nacnac)V≡N($Ntol_2$)][8] (**5**). This result is based on comparison of ^1H NMR and FT-IR spectra of **5** to authentic samples (Scheme 1).[10] To our knowledge, formation of **5** from **2** and [(tBuO)$_3$Cr≡N] represents the first example of complete intermetal N-atom transfer involving a group 5 metal.[16] The fact that **2** can engage in three-electron reactions prompted the pursuit of other substrates that could form unusual ligand frameworks on the [(nacnac)V($Ntol_2$)] scaffold.

When complex **2** is treated with 1 equivalent of P_4 at room temperature, the first *cyclo*-P_3 complex of vanadium, namely diamagnetic [(nacnac)V(*cyclo*-P_3)($Ntol_2$)] (**6**), is isolated as a golden brown solid in 68% yield subsequent to recrystallization (Scheme 1). Moreover, **6** can also be generated independently, and in a one-pot synthesis, through the reduction of **1** with 0.5% Na/Hg in the presence of 1 equivalent of P_4 in 40% isolated yield. The other reaction products, which presumably would give the fate of the fourth equivalent of P from P_4, have not yet been characterized. XRD studies of the major product unambiguously revealed the formation of **6**.[17] The molecular structure of **6** is shown in Figure 3 and features a *cyclo*-P_3 moiety coordinated in a η^3 coordination mode to render a tetrahedral vanadium(V) center with a V–P_3 centroid distance of 2.10 Å. The average V–P distance of **6** at 2.44 Å coupled with the internuclear P–P distances (≈2.13 Å) is consistent with a *cyclo*-P_3^{3-} ligand. Complex **6** can thus be viewed both as a P_3V core where the vanadium center represents one vertex of the tetrahedron, or as a pseudo tetrahedral vanadium center with three N donors where the *cyclo*-P_3^{3-} ligand occupies the fourth site. Solution state $^{31}P\{^1H\}$ NMR spectroscopic measurements at room temperature of this diamagnetic complex revealed a broad resonance at $\delta = 85.0$ ppm ($\Delta\nu_{1/2} = 234$ Hz), which is significantly downfield shifted compared to related heavier congeners.[18] ^1H NMR spectroscopic data of compound **6** indicates C_s symmetry in solution as all four *i*Pr methyl resonances associated with the nacnac ligand are well-resolved doublets ($J_{HH} = 7.0$ Hz). However, the resonance associated with the methyl groups on the ditolylamide ligand is broad ($\Delta\nu_{1/2} = 63.0$ Hz) suggesting dynamic behavior of complex **6** at room temperature.[10] Variable-temperature ^1H NMR spectroscopy (25 to −60 °C) was performed on **6** in [D$_8$]toluene to gain insight into this fluxionality, and spectra reveal two well-resolved singlets at $\delta = 2.29$ and 1.92 ppm for the tolyl methyls as well as inequivalent aryltolyl environments.[10] In contrast, the $^{31}P\{^1H\}$ spectrum of **6** at −60 °C still evinces a rapidly rotating P_3^{3-} framework with a broad singlet shifted upfield at $\delta = 76$ ppm ($\Delta\nu_{1/2} = 123$ Hz). ^{51}V NMR spectrum of **6** recorded in [D$_8$]toluene at 25 °C revealed a broad resonance extremely downfielded at $\delta = 2798$ ppm ($\Delta\nu_{1/2} = 596$ Hz).

In summary, we have demonstrated that combining a monoanionic bidentate ligand (nacnac) with a sterically demanding ditolylamide results in formation of a reactive $[V^{II}\{N_2N'\}]$ scaffold reminiscent of the masked three-coordinate complex, $[(H)Mo(\eta^2\text{-}i\text{PrC=NAr})\{N(i\text{Pr})Ar\}_2]$ reported by Cummins et al. in 1998.[16g] Although there is a diagonal relationship between V and Mo, complex **2** fails to activate and split N_2 under normal conditions therefore hinting that the aryl interaction might be inhibiting such a process. This behavior is in contrast to work by Cloke et al.[19] in which a V^{II} complex generated in situ from V^{III} cleaves N_2 to give a nitrido-bridged dimer. We are currently trying to understand these significant differences by both experimental and theoretical approaches. In particular, the large zfs of **2**, in contrast to that found for six-coordinate V^{II} complexes,[12] needs to be investigated computationally, as has been done for certain V^{III} complexes of less common geometry.[20]

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[10] See the Supporting Information. CCDC 787159–787162 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.)

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[12] HFEPR spectra were also recorded for **2** in toluene frozen solution. The majority signal was due to the same species as seen in the solid state. Minority signals from two uncharacterized decomposition products (one of V^{IV} and one possibly of V^{III}) were also observed, which is inevitable given the sensitivity of **2**; a) C. J. H. Jacobsen, E. Pedersen, J. Villadsen, H. Weihe, *Inorg. Chem.* **1993**, *32*, 1216; b) N. Laurance, J. Lambe, *Phys. Rev.* **1963**, *132*, 1029; c) K. K. Chan, L. Shields, *J. Chem. Soc. A* **1970**, 2700.

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