

## Syntheses and Structural Characterizations of the First 16-, 17-, and 18-Electron Homoleptic Isocyanide Complexes of Vanadium: Hexakis(2,6-dimethylphenyl isocyanide)vanadium(I, 0, -I)<sup>1</sup>

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There has been considerable interest in exploring the properties of neutral and anionic homoleptic organic isocyanide metal complexes with the hope that these species might prove to be useful in organic, organometallic, and inorganic syntheses, as are analogous metal carbonyls.<sup>1–2</sup> Corresponding isocyanides have received far less attention due to their relative inaccessibility, especially for the very early transition metals. For example, neutral isocyanide complexes of this type are well established for many of the group 6–10 transition metals,<sup>3</sup> but only recently have Cooper and co-workers devised syntheses for the first anionic homoleptic isocyanide complexes of the group 7–9 metals.<sup>4–6</sup> Although neutral (M = V) or anionic (M = V, Nb, Ta) pure carbonyls of the group 5 transition metals have been known for many years, prior attempts to access analogous isocyanide complexes of these elements have been unsuccessful.<sup>7</sup> For example, procedures that work well for the syntheses of other [ML<sub>6</sub>]<sup>–</sup> (M = V, Ta; L = CO, PF<sub>3</sub>),<sup>8</sup> related neutral group 6 metal isocyanides, M(CNR)<sub>6</sub>,<sup>9</sup> or [Co(CNAr)<sub>4</sub>]<sup>–</sup> (Ar = 2,6-dimethylphenyl), the first reported homoleptic isonitrilate,<sup>10</sup> invariably failed with VCl<sub>3</sub>(THF)<sub>3</sub> and CNAr and provided only uncharacterized tarry isocyanide reduction products.<sup>11</sup> We now report on the syntheses, isolation, and structural characterization of the initial vanadium compounds of this class, as well as the previously unknown monocation, [V(CNAr)<sub>6</sub>]<sup>2+</sup> [Z = -1 (**1**), 0 (**2**), and +1 (**3**)]. Compound (**2**) is, perhaps, of most interest in that it is presently the only known stable 17-electron metal(0) isocyanide complex and is thereby analogous to the long-established V(CO)<sub>6</sub>.<sup>12</sup> Compounds **1** and **3** are also the first isocyanide analogues of the stable [V(CO)<sub>6</sub>]<sup>–</sup><sup>13</sup> and exceedingly unstable [V(CO)<sub>6</sub>]<sup>+</sup>,<sup>14</sup> respectively. The only prior example of a

homoleptic isocyanide of vanadium is the dicationic species [V(CN-*t*-Bu)<sub>6</sub>]<sup>2+</sup>.<sup>15</sup>

The recent availability by a conventional route of the highly labile (naphthalene)vanadium(0) complexes, V(η<sup>6</sup>-C<sub>10</sub>H<sub>7</sub>R)<sub>2</sub> (R = H, Me),<sup>16</sup> which function as useful sources of atomic vanadium in chemical reactions,<sup>16b</sup> proved to be of crucial importance in our initial synthesis of **2**, from which **1** and **3** were derived in nearly quantitative yields. In a typical preparation of **2**, a dark red-brown solution of bis(1-methylnaphthalene)vanadium (2.22 g, 6.62 mmol) in heptane/THF (130 mL/130 mL, 0 °C) was mixed with 2,6-dimethylphenyl isocyanide (6.11 g, 46.6 mmol) in heptane/THF (70 mL/30 mL, 0 °C), whereupon a deep purple solution rapidly formed. The reaction mixture was stirred for 12 h, and removal of about 150 mL of the solvent mixture in vacuo gave beautiful dichroic green-purple microcrystals. These were separated by filtration, washed with pentane, dried in vacuo, and recrystallized from THF/heptane to afford 4.50 g (81% yield) of very air-sensitive and golden-purple **2**. Our most efficient conversion of **2** to **1** involved stirring a solution of **2** in THF with a suspension of cesium graphite, CsC<sub>8</sub>,<sup>17</sup> at -50 °C. Following filtration and recrystallization from THF/heptane, an 84% yield of unsolvated cesium salt of **1** was obtained as free flowing and very air-sensitive brown microcrystals. Oxidation of **2** with 1 equiv of [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> in THF at -70 °C gave a deep orange-red solution of **3**. Following solvent removal and recrystallization from THF/heptane, a 92% yield of deep red and moderately air-sensitive, microcrystalline **3**[PF<sub>6</sub>]<sub>2</sub> was isolated as a pure substance.<sup>18</sup>

Spectroscopic and magnetic properties of **1**, **2**, and **3** are fully in accord with their formulations as mononuclear six-coordinate complexes containing low-spin d<sup>6</sup>, d<sup>5</sup>, and d<sup>4</sup> vanadium, respectively. For example, Cs **1** is diamagnetic in solution and the solid state and has <sup>1</sup>H and <sup>13</sup>C NMR spectra for equivalently bound 2,6-dimethylphenyl groups<sup>18</sup> that closely resemble those of Yamamoto's isoelectronic Cr(0) complex.<sup>9</sup> Mineral oil mull infrared spectra in the ν(CN) region show one intense peak with a frequency (1802 cm<sup>-1</sup>) that is very similar to that previously reported for [Co(CNAr)<sub>4</sub>]<sup>–</sup>.<sup>4</sup> Exposure of solutions of **1** to trace amounts of air caused it to be rapidly converted to **2**.

Compound **2** is paramagnetic in THF and in the solid state with μ<sub>eff</sub> = 1.76 μ<sub>B</sub> (298 K), a value that is virtually identical with μ<sub>eff</sub> = 1.78 μ<sub>B</sub> reported for V(CO)<sub>6</sub>.<sup>19</sup> While V(CO)<sub>6</sub> undergoes facile disproportionation in THF<sup>20</sup> and is easily reduced by cobaltocene or decamethylcobaltocene,<sup>21</sup> **2** is unreactive toward these species at room temperature. As in the case of V(CO)<sub>6</sub>,<sup>22</sup> **2** is ESR silent at room temperature. Also, sharp NMR signals are observed for **2** in C<sub>6</sub>D<sub>6</sub>. Both of these features are consistent

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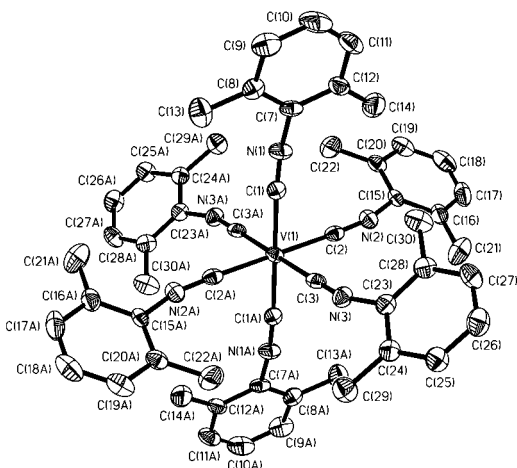
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(18) Satisfactory elemental analyses were obtained for **1–3**. Selected spectral data for Cs **1**: IR ν(CN), (THF) 2028 vw br, 1823 vs br, 1772 sh br cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 25 °C) δ 2.39 (s, 6H, *o*-Me), 6.69 (t, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, 1H, *p*-H), 6.90 (d, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, 2H, *m*-H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>3</sub>CN, 25 °C) 20.3 (CH<sub>3</sub>), 122.9 (*p*-C), 128.5 (*m*-C), 133.2 (*o*-C) ppm. For IR **2**: ν(CN), (mineral oil mull) 2006 w sh, 1929 vs br, 1845 m sh; (THF) 2008 w sh, 1939 vs, 1952 w sh; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ -2.26 (t, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 1H, *p*-H), 9.36 (s, 6H, *o*-Me), 13.84 (d, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, 2H, *m*-H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 23 °C) -4.9 (CH<sub>3</sub>), 101.5 (*m*-C), 176.9 (*p*-C) ppm. For **3** [PF<sub>6</sub>]<sub>2</sub>: IR ν(CN), (THF) 2142 w, 2033 vs, 1995 m sh.

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**Figure 1.** Molecular structure of **2** showing the labeling scheme at 50% probability ellipsoids; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): V–C(1) 2.034(3), V–C(2) 2.022(4), V–C(3) 2.023(4), C(1)–N(1) 1.184(4), C(2)–N(2) 1.183(4), C(3)–N(3) 1.194(4), N(1)–C(7) 1.400(4), N(2)–C(15) 1.408(4), N(3)–C(23) 1.406(4), av ring C–C 1.39(1), av ring C–Me 1.504(5) Å, V–C(1)–N(1) 175.9(3), V–C(2)–N(2) 175.6(3), V–C(3)–N(3) 178.5(3), C(1)–N(1)–C(7) 168.1(3), C(2)–N(2)–C(15) 158.8(3), C(3)–N(3)–C(23) 161.5(3), av cis C–V–C 90(3), trans C–V–C 180.0.

with the very short electron spin relaxation time expected for a homoleptic octahedral low-spin  $d^5$  complex.<sup>23</sup> The  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances<sup>18</sup> show strong paramagnetic shifts that are essentially contact in origin due to the approximately octahedral symmetry of the molecule.<sup>24</sup> HETCOR NMR spectra allowed unambiguous assignments of  $^{13}\text{C}$  NMR resonance positions of the equivalent 2,6-dimethylphenyl groups present in **2**. Solution and mull infrared spectra of **2** are unexceptional and are similar to those reported for the octahedral Cr(0) complex,  $\text{Cr}(\text{CNAr})_6$ .<sup>9</sup> Compound **2** is rapidly oxidized in air to give **3**, which is also air sensitive, but much less so than **1** or **2**.

Compound **3** is paramagnetic in the solid state, with  $\mu_{\text{eff}} = 2.73 \mu_{\text{B}}$  (298 K), which is close to the corresponding value of  $2.75 \mu_{\text{B}}$  reported for the Cr(II) salt,  $[\text{Cr}(\text{CNcyclohexyl})_6][\text{PF}_6]_2$ , also an octahedral low-spin  $d^4$  complex.<sup>25</sup> The IR spectrum of **3**  $[\text{PF}_6]^{18}$  is similar to that reported for the Cr(I) complex,  $[\text{Cr}(\text{CNPh})_6][\text{PF}_6]^{26}$ .

Single-crystal X-ray studies on **1–3** were carried out to confirm their existence and obtain structural data for these novel species.<sup>27</sup> Figure 1 shows the molecular structure of **2**, which contains a vanadium atom on an inversion center resulting in three inde-

pendent  $\text{V}(\text{CN-2,6-xylyl})$  units. Structures for **1** and **3** are qualitatively similar to that of **2**, except the vanadium atoms are in general positions and counterions are present. Substantial scatter is observed in the V–C distances in **1** and **3**, vide infra; however, the inner  $\text{V}(\text{CN})_6$  cores of all three species are best regarded as being essentially octahedral. For example, compounds **1–3** have nearly linear VCN bonds and average cis and trans C–V–C angles that are well within the range of values expected for octahedral structures.<sup>27d</sup> Compound **2** exhibits a possible small tetragonal distortion from a regular octahedron, very similar in magnitude to that observed for  $\text{V}(\text{CO})_6$ .<sup>22c</sup> Average V–C and nitrile C–N distances for **1–3** are 1.98(3), 2.026(7), and 2.07(2) Å and 1.20(2), 1.186(5), and 1.169(6) Å, respectively. The lengthening of the M–C distances and concomitant shortening of the nitrile C–N distances with increasing metal oxidation state in proceeding from **1** to **3** are consistent with the aryl isocyanides functioning as good acceptor ligands<sup>28</sup> and correlate nicely with the aforementioned infrared  $\nu(\text{CN})$  values observed for **1–3**.<sup>18</sup> Exactly the same trends have been observed for the isoelectronic chromium complexes  $[\text{Cr}(\text{CNPh})_6]_Z^{2+}$ , for  $Z = 0$  to  $+2$ , respectively.<sup>26</sup> Also noteworthy is the fact that the average C–N distance for the vanadate **1** is statistically indistinguishable from analogous values of 1.20(2) and 1.20(3) Å previously reported for the other structurally characterized homoleptic isocyanide metalates,  $[\text{Mn}(\text{CNAr})_5]^{-6}$  and  $[\text{Co}(\text{CNAr})_4]^{-10}$  respectively. There is appreciable bending at the isocyanide nitrogens in **1–3** with corresponding CNC angles averaging 158–(10), 163(4), and 173(2)°, respectively. Counterion ( $\text{Cs}^+$ ) perturbation of **1** undoubtedly contributes to the large spread in CNC angles (and to a lesser extent the structural parameters of the  $\text{V}(\text{CN})_6$  core) observed for the vanadate and makes a simple analysis difficult at best.<sup>29</sup> However, the CNC angles observed for **2** and **3**, which are relatively unperturbed by the  $[\text{PF}_6]^-$  counterion, do correlate well with the corresponding V–C and C–N distances and infrared  $\nu(\text{CN})$  values of these species in the expected manner. These data support prior views that  $\eta^1$ -RNC ligands should become increasingly bent as the metal center becomes more electron rich, provided other factors, such as the steric bulk of the ligand, the coordination number of the metal, and so on, remain essentially constant.<sup>28</sup> Ultimately, this nitrile bending may result in reductive coupling of adjacent coordinated isocyanides, which was first observed by Lippard<sup>30</sup> and is now a well-known phenomenon of the early transition metals.<sup>30,31</sup> Whether the bulky nature of the arylisocyanide ligands employed in this study prevents the latter from occurring in **1–3** is an important issue. Also, extension of this research to the group 4 and heavier group 5 elements is currently underway in this laboratory.

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**Supporting Information Available:** Complete crystallographic and additional analytical data for **1–3**, except structure factor tables (22 pages). See any current masthead for ordering and Internet access instructions.

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