

B(C₆F₅)₃ Adducts of TCNE– and TCNQ–Vanadium Complexes as New Building Blocks for Molecule-Based Magnets

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Summary: The TCNX ligands TCNE and TCNQ reacted in toluene with Cp₂V in the presence of B(C₆F₅)₃ to yield, depending on the stoichiometry, the divanadium(III) complexes [(Cp₂V)₂{(C₆F₅)₃B·(μ₄-TCNX)·B(C₆F₅)₃}] (X = Q (3), E (4)) or the vanadium(IV) dimers [Cp₂V{(C₆F₅)₃B·(μ₄-TCNX)·B(C₆F₅)₃}]₂ (X = E (5), Q (6)), all containing [TCNX]^{2–} ligands σ-bonded to vanadium through a nitrile nitrogen, as revealed by crystallographic (for 3–5) and magnetic studies (for 3–6).

The discovery in the early 1990s by the group of Miller of the first room-temperature molecule-based magnet, V[TCNE]₂·yCH₂Cl₂ (y ≈ 0.5),¹ from the reaction of V(CO)₆ or V(C₆H₆)₂ with TCNE (TCNE = tetracyanoethylene) in dichloromethane, has stimulated the coordination chemistry of TCNE and related TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) derivatives with various transition metals and coligands.² On the basis of elemental analysis and IR data, the local structure in the V[TCNE]₂ coordination polymers is assumed to consist of 3D networks bridging *cis*-[TCNE]^{•–} ligands between V²⁺ ions;³ however, unambiguous structural information is not available, due to the low solubility of this amorphous material. To obtain insight into the local V coordination geometry of the polymers, we synthesized discrete molecular vanadium species incorporating TCNE ligands that could serve as structural and magnetic model compounds of V[TCNE]₂ magnets.

As part of our long-term interest in the organometallic chemistry of vanadocene (Cp₂V),⁴ we have investigated the

reactivity of Cp₂V with TCNX (X = E, Q). Previously, the vanadium(III) complexes Cp₂VX(η¹-TCNE) (X = Cl, Br, I) have been prepared from the reaction of Cp₂VX and TCNE.⁵ To our knowledge, and although the structure has been only partially solved (X = Br), this represents the only example of a structurally characterized vanadium–TCNE complex supported by Cp ligands. TCNE was also reported to substitute carbon monoxide in Cp₂V(CO) to afford a complex formulated as “Cp₂V(TCNE)” on the basis of analytical and spectroscopic (IR) evidence.⁶ In a somewhat related vein, we have recently demonstrated that Cp₂V reacts with simple nitriles (RCN) when they are activated with a Lewis acid L (L = BCl₃, B(C₆F₅)₃, AlCl₃) to give Lewis acid adducts of vanadium(IV)azirine complexes, [Cp₂V(η²-RC=N·L)].⁷ To extend the scope of this reaction, the reactivity of Cp₂V with TCNE and TCNQ in the presence of the Lewis acid B(C₆F₅)₃ was studied. Here, we present crystallographic evidence for the coordination mode of TCNX ligands to the [Cp₂V] fragment with formation of V^{III} and V^{IV} complexes. The magnetic behavior of these compounds was also determined.

We first investigated the reaction between the nitrile groups of TCNX molecules with the Lewis acid B(C₆F₅)₃, to verify that an adduct similar to that found in simple nitriles could be generated.^{7,8} The addition of 2 equiv of B(C₆F₅)₃ to a toluene solution containing TCNE led to a red solution.⁹ Layering this solution with pentane gave an orange solid identified as the bis-(borane) adduct [TCNE·{B(C₆F₅)₃}]₂ (1). A similar reaction of

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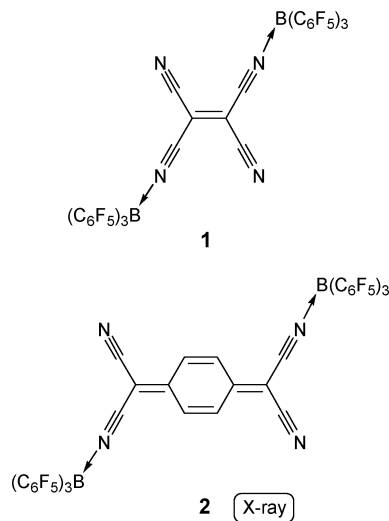
[†] E-mail: lorber@lcc-toulouse.fr.

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B(C₆F₅)₃ with TCNQ in CH₂Cl₂ afforded a red solution from which the orange crystalline product 2 was separated. An X-ray structure determination (see the Supporting Information) on a single crystal clearly confirmed that 2 is the bis(borane) adduct [μ₂-TCNQ·{B(C₆F₅)₃}]₂. The solid-state structure also revealed

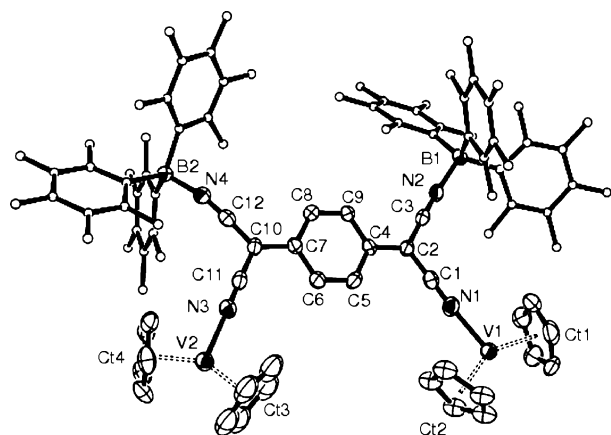
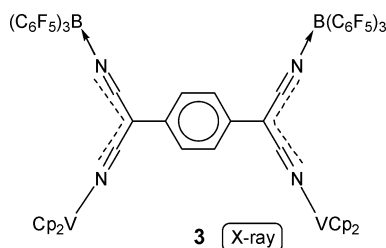


Figure 1. ORTEP drawing of the molecular structure of **3** showing 50% probability ellipsoids and partial atom-labeling schemes. C_6F_5 groups are depicted as spheres, and H atoms are omitted for clarity. Ct denotes the centroid of the cyclopentadienyl ring. Selected interatomic bond distances (Å) and angles (deg): $\text{C}2-\text{C}4 = 1.465(6)$, $\text{C}7-\text{C}10 = 1.475(6)$, $\text{V}1-\text{Ct}1 = 1.993$, $\text{V}1-\text{Ct}2 = 1.982$, $\text{V}1-\text{N}1 = 2.041(5)$, $\text{V}2-\text{Ct}3 = 1.920$, $\text{V}2-\text{Ct}4 = 1.918$, $\text{V}2-\text{N}3 = 2.020(5)$, $\text{B}1-\text{N}2 = 1.564(8)$, $\text{B}2-\text{N}4 = 1.579(8)$, $\text{N}1-\text{C}1 = 1.157(7)$, $\text{N}3-\text{C}11 = 1.150(7)$, $\text{N}2-\text{C}3 = 1.162(7)$, $\text{N}4-\text{C}12 = 1.159(7)$; $\text{Ct}1-\text{V}1-\text{Ct}2 = 144.20^\circ$, $\text{Ct}3-\text{V}2-\text{Ct}4 = 144.10^\circ$.

the attachment of the two $\text{B}(\text{C}_6\text{F}_5)_3$ groups to the nitrogen atom of two CN groups in anti-1,2-positions.

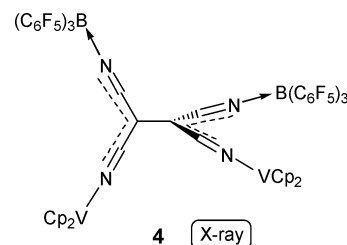
For solubility reasons, the reactivity of Cp_2V was studied with the nonisolated adducts **1** and **2**. The addition of 2 equiv of Cp_2V in toluene to a toluene solution of the adduct **2** (generated in situ from 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ on TCNQ) afforded after suitable workup compound **3** as a crystalline dark precipitate.



Dark red single crystals were obtained from a THF/pentane solution of **3**, which according to single-crystal X-ray analysis were the homobimetallic complex $[(\text{Cp}_2\text{V})_2\{(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{TCNQ} \cdot \text{B}(\text{C}_6\text{F}_5)_3\}]$ (**3**) (Figure 1). The main feature of the solid-state structure of **3** is the presence of two $[\text{Cp}_2\text{V}]$ units σ -bonded in a syn-1,2-positions to the free nitrogen atom of two CN groups of the Lewis acid adduct of the μ_4 -TCNQ group, whereas two $\text{B}(\text{C}_6\text{F}_5)_3$ groups are attached to the two remaining nitrogen atoms of the TCNQ ligand.¹⁰ The V–N distances of 2.041(5) and 2.020(5) Å are longer than those found for compounds

having a V–N single σ bond (1.7–1.8 Å)¹¹ but are in the range of those found in the pseudohalide vanadocene series of complexes Cp_2VX_2 ($\text{X} = \text{NCO}$, N_3 , $\text{N} \equiv \text{CNC} \equiv \text{N}$)¹² (for comparison, in the cationic $[\text{Cp}_2\text{VMe}(\text{N} \equiv \text{CCH}_3)]^+$ the V–N distance is 2.096(4) Å).¹³ All atoms of the TCNQ framework in **3**, as well as the centroids (Ct) of the cyclopentadienyl rings and the boron atoms and the vanadium centers, are roughly contained in the same plane. The V–N $\equiv$ C–C skeleton is essentially linear, and the C $\equiv$ N(V) bond distances are in the same order as the C $\equiv$ N(B) bond distances. The C–C distances in the TCNQ ring are nearly the same (1.376–1.391 Å), leading to a more benzene-like structure, as observed in $[\text{TCNQ}]^{2-}$.¹⁴ Both C–C distances attached to the ring are elongated and are best described as C–C single bonds ($\text{C}2-\text{C}4 = 1.459(7)$ Å, $\text{C}1-\text{C}7 = 1.477(7)$ Å) by comparison to the equivalent distances observed in free TCNQ¹⁵ and in the adduct **1** (1.374(2) and 1.384(9) Å, respectively). The most intriguing feature is the NC–C4–CN and NC–C10–CN carbon chains, in which the formation of a partial double bond (1.356(8)–1.413(8) Å) could be suggested by comparison to the same distances observed in the neutral TCNQ molecule (1.440(4), 1.441(4) Å) and in **2** (1.418(10), 1.435(11) Å). These structural data are consistent with a fully delocalized $[\text{TCNQ}]^{2-}$ system, as suggested in the ruthenium complex $\{(\mu_4\text{-TCNQ})[\text{Ru}(\text{NH}_3)_5]_4\}^{8+}$, for which a crystal structure is not available.¹⁶ The IR spectrum of **2** presents characteristic ν_{CN} bands in the region expected for $[\text{TCNQ}]^{2-}$,¹⁷ but one must keep in mind that the presence of the two coordinated $\text{B}(\text{C}_6\text{F}_5)_3$ groups does not allow a direct comparison with other TCNQ compounds.¹⁸ A magnetic study revealed that the dinuclear complex **3** exhibits an essentially temperature-independent χT vs. T plot. These data are consistent with two independent V^{III} centers ($\chi T_{\text{calcd}} = 2.00$ emu K mol^{−1}, assuming $g = 2$; $\chi T_{300\text{ K}} = 1.98$ emu K mol^{−1}). Therefore, **3** is best described as a $[\text{TCNQ}]^{2-}$ -containing divanadium(III) complex arising from a redox process between two $\text{Cp}_2\text{V}^{\text{II}}$ donors and the TCNQ acceptor.

In a similar way, reacting 2 equiv of Cp_2V with TCNE in the presence of 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene afforded the crystalline dark red complex $[(\text{Cp}_2\text{V})_2\{(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{TCNE} \cdot \text{B}(\text{C}_6\text{F}_5)_3\}]$ (**4**) (Figure 2).¹⁷ Compound **4** crystallized as a toluene solvate,



and its molecular structure was determined by single-crystal

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(9) Note that using 4 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ led to the formation of the same bis-adduct compound.

(10) The μ_4 mode of coordination refers to the 4-fold-coordinated TCNX ligand (see the figures); it is clear in this case that coordination occurs in syn-1,2-positions with two vanadium centers and in syn-1,2-positions with two boron atoms.

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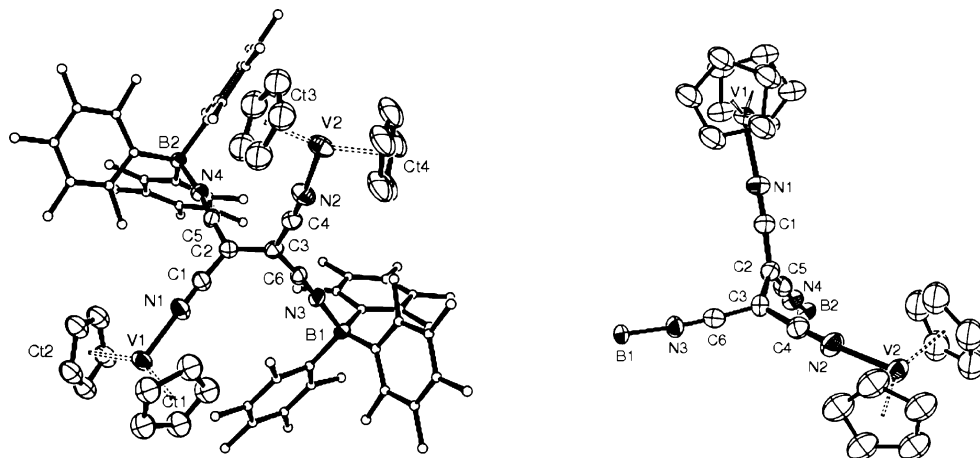


Figure 2. (left) ORTEP drawing of the molecular structure of **4** showing 50% probability ellipsoids and partial atom-labeling schemes. C_6F_5 groups are depicted as spheres, and solvent ($1/2$ THF) and H atoms are omitted for clarity. (right) A different view to show the twist of the TCNE moiety (C_6F_5 groups are omitted). Ct denotes the centroid of the cyclopentadienyl ring. Selected interatomic bond distances (Å) and angles (deg): C2–C3 = 1.459(5), V1–Ct1 = 1.914, V1–Ct2 = 1.928, V1–N1 = 2.041(5), V2–Ct3 = 2.010, V2–Ct4 = 1.994, V2–N3 = 2.020(5), B1–N2 = 1.564(8), B2–N4 = 1.579(8), N1–C1 = 1.157(7), N3–C11 = 1.150(7), N2–C3 = 1.162(7), N4–C12 = 1.159(7); Ct1–V1–Ct2 = 142.30, Ct3–V2–Ct4 = 146.14.

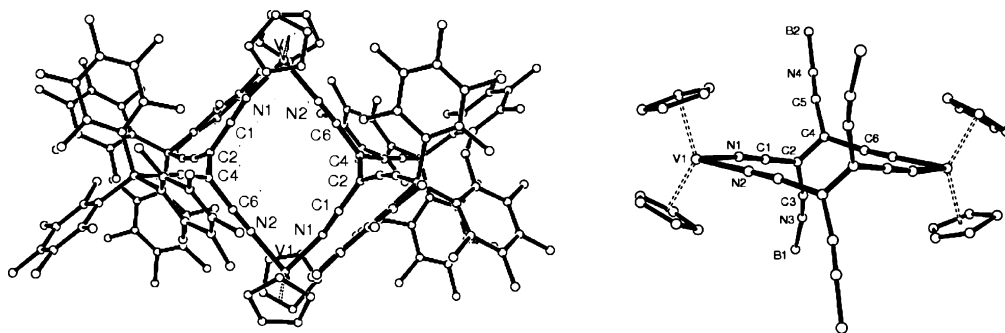


Figure 3. (left) Drawing of the molecular structure of **5** and partial atom-labeling schemes, with all atoms are depicted as spheres. Solvent (2 toluene) and H atoms are omitted for clarity. (right) A different view to show the twist of the TCNE moiety and the 14-atom cyclic arrangement (C_6F_5 groups are omitted for clarity).

X-ray diffraction. Both vanadium centers are σ -bonded to the nitrogen atom of the Lewis acid adduct of μ_2 -TCNE with V–N distances similar to those found in **3** (2.056(3), 2.049(3) Å). The TCNE framework is twisted along the central C–C bond with a dihedral angle of 78.9° . However, the general features (geometrical parameters) of the C–N bonds are comparable to those of **3**. The central C2–C3 bond of the TCNE in **4** (1.459(5) Å) is markedly longer than the analogous C=C in free TCNE (1.344(3) Å)¹⁹ and can be considered as a single bond. The C–C distances in the NCCCN chain (1.380(5)–1.411(5) Å) show the formation of a partial double-bond chain between the nitrogen atom bonded to the vanadium atom and the nitrogen atom bonded to the boron atom. As for **3**, the magnetic properties of complex **4** are characteristic of two independent spin-only V^{III} centers ($\chi T_{300\text{ K}} = 1.98\text{ emu K mol}^{-1}$).

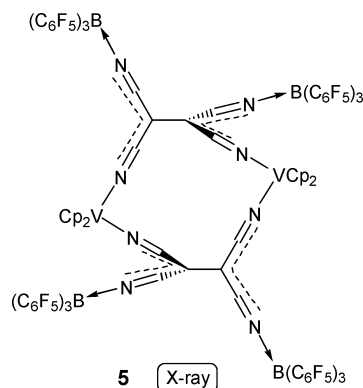
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(17) IR data for all compounds (KBr, cm^{-1}): **1**, $\nu_{\text{CN-B}}$ 2321 (s), ν_{CN} 2234 (w); **2**, $\nu_{\text{CN-B}}$ 2307 (s), ν_{CN} 2224 (w); **3**, $\nu_{\text{CN-B}}$ 2250 (m), ν_{CN} 2201 (w), ν_{CN} 2150 (s); **4**, $\nu_{\text{CN-B}}$ 2254 (m), ν_{CN} 2198 (w), ν_{CN} 2154 (s); **5**, $\nu_{\text{CN-B}}$ 2250 (m), ν_{CN} 2201 (w), ν_{CN} 2150 (s); **6**, $\nu_{\text{CN-B}}$ 2260 (m), ν_{CN} 2196 (w), ν_{CN} 2134 (s). For comparison purposes: TCNE, ν_{CN} 2255 (vs), 2216 (s); TCNQ, ν_{CN} 2228 (s).

(18) For reviews on the assignment of the structure and charge of TCNX-containing compounds on the basis of their ν_{CN} bands, see: (a) Kaim, W.; Moscherosch, M. *Coord. Chem. Rev.* **1994**, 129, 157–193. (b) Miller, J. S. *Angew. Chem., Int. Ed.* **2006**, 45, 2508–2525.

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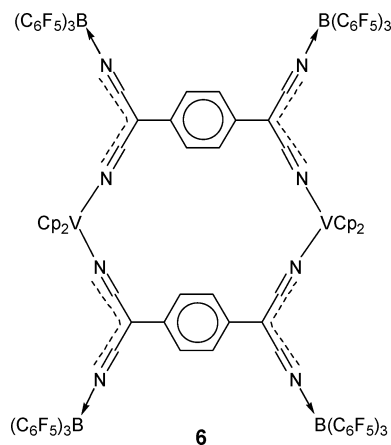
Next, we have studied the effect of a variation of the relative stoichiometry of the reactants by performing the reaction using the ratio $\text{TCNX}:\text{B}(\text{C}_6\text{F}_5)_3:\text{Cp}_2\text{V} = 1:2:1$ (instead of 1:2:2 for the above synthesis of **3** and **4**). For example, the reaction between TCNE, 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, and 1 equiv of Cp_2V was performed in toluene, affording the dark orange complex **5**.¹⁷



Attempts to obtain high-quality crystals of **5** suitable for an X-ray structure determination failed. Nevertheless, the quality of the crystals obtained in THF/pentane was sufficient to establish an overall structure of the atomic connectivity but not to report detailed bond distances and angles. The formation of the dimeric species $[\text{Cp}_2\text{V}\{(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{TCNE}\cdot\text{B}(\text{C}_6\text{F}_5)_3\}]_2$ (**5**) is observed (Figure 3). Each vanadium atom is linked to two

nitrogen atoms of CN groups connected to two twisted $[\text{TCNE} \cdot \{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^{2-}$ molecules, and a 14-atom chairlike cyclic structure is observed. The magnetic susceptibility values determined for **5** are in rather good agreement with two magnetically uncoupled V^{IV} centers ($\chi T_{\text{calcd}} = 0.75 \text{ emu K mol}^{-1}$, assuming $g = 2$; $\chi T_{300 \text{ K}} = 0.70 \text{ emu K mol}^{-1}$).

Similarly, the analogous reaction conducted with TCNQ (instead of TCNE), 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, and 1 equiv of Cp_2V yielded a microcrystalline dark precipitate. We suggest this new compound to be the dimer $[\text{Cp}_2\text{V}\{\{\text{C}_6\text{F}_5\}_3\text{B} \cdot \text{TCNQ} \cdot \text{B}(\text{C}_6\text{F}_5)_3\}]_2$ (**6**) on the basis of its elemental analysis, strong analogy to



spectroscopic data (IR,¹⁷ ^{19}F and ^{11}B NMR) for **5**, and magnetic studies (vide infra). Indeed, the magnetic behavior of **6** is typical of a V^{IV} species, but in contrast to **5**, the magnetic susceptibilities measured for **6** are strongly temperature-dependent ($\chi T_{300 \text{ K}} = 0.90 \text{ emu K mol}^{-1}$). A Bleaney–Bowers treatment²⁰ for **6** renders the following values: exchange constant $J = -55 \text{ cm}^{-1}$ and zero-field splitting $D = -150 \text{ cm}^{-1}$. The previously reported $[\text{V}(\text{C}_5\text{Me}_5)_2\text{Br}]_2(\mu_2\text{-TCNE})$,²¹ in which a V^{IV} center and a $[\text{TCNE}]^{2-}$ ligand are present, was also shown to present a similar temperature-dependent magnetic behavior ($\chi T_{300 \text{ K}} \approx 0.97 \text{ emu K mol}^{-1}$), except with a very distinct coupling constant ($J = -0.6 \text{ cm}^{-1}$, $D = 1.5 \text{ cm}^{-1}$). Figure 4 shows the hysteresis loop for **6** recorded at 2 K (magnetization vs applied magnetic field). We note the absence of saturation for fields up to 50 kOe. However, a coercive field of $H_c \approx 40 \text{ Oe}$ at 2 K is evident,

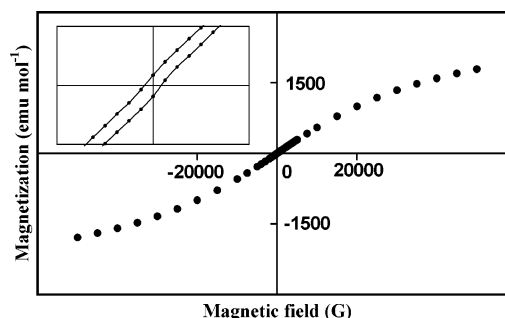


Figure 4. Magnetic behavior for **6** recorded at 2 K (magnetization vs applied magnetic field). The inset represents an enlargement between -600 and $+600 \text{ G}$ and -15 and $+15 \text{ emu mol}^{-1}$.

as shown in the inset in Figure 4. We conclude that magnetic ordering in the sample exists at this temperature. The ferromagnetism of **6** may arise from the planarity of the TCNQ molecule, which may serve as an adequate superexchange mediator between the orbitals of the two metallic ions.^{7b,22}

In conclusion, the reactivity of Cp_2V with $[\text{TCNX} \cdot \{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ is very different from that previously observed with the activated simple nitrile adducts $\text{RCN} \cdot \text{B}(\text{C}_6\text{F}_5)_3$ ⁷ (in which the vanadazirine complexes $[\text{Cp}_2\text{V}(\eta^2(\text{C},\text{N})\text{-RCN} \cdot \text{B}(\text{C}_6\text{F}_5)_3)]$ were obtained). We showed here that $\text{B}(\text{C}_6\text{F}_5)_3$ can be used to block two sites of coordination on the TCNX ligand and to enhance the solubility of the new building block; the magnetic and structural studies suggest a net two-electron reaction with formation of $[\text{TCNX}]^{2-}$ as a consequence of the d^2 (in **3** and **4**) and d^1 (in **5** and **6**) configurations at the metal center. Further efforts will be directed toward studying the redox chemistry of these systems and in the synthesis of new compounds relevant to $[\text{V}(\text{TCNE})_2]$ magnets.

Acknowledgment. We are grateful to the CNRS for financial support.

Supporting Information Available: Text giving a full experimental section for the synthesis of all compounds, a figure detailing a Bleaney–Bowers treatment for **6**, and CIF files and tables of atomic coordinates and bond distances and angles for the X-ray crystal structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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