$B(C_6F_5)_3$ Adducts of TCNE− and TCNQ−Vanadium Complexes as New Building Blocks for Molecule-Based Magnets

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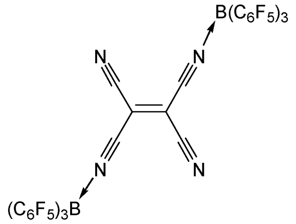
*Summary: The TCNX ligands TCNE and TCNQ reacted in toluene with Cp_2V in the presence of $B(C_6F_5)_3$ to yield, depending on the stoichiometry, the divanadium(III) complexes $[(Cp_2V)_2\{(C_6F_5)_3B\cdot(\mu_4\text{-TCNX})\cdot B(C_6F_5)_3\}]$ (X = Q (**3**), E (**4**)) or the vanadium(IV) dimers $[Cp_2V\{(C_6F_5)_3B\cdot(\mu_4\text{-TCNX})\cdot B(C_6F_5)_3\}]_2$ (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, $V[TCNE]_2\cdot yCH_2Cl_2$ ($y \approx 0.5$),[1] from the reaction of $V(CO)_6$ or $V(C_6H_6)_2$ 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*-$[TCNE]^{\bullet-}$ ligands between V^{2+} 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 (Cp_2V),[4] we have investigated the reactivity of Cp_2V with TCNX (X = E, Q). Previously, the vanadium(III) complexes $Cp_2VX(\eta^1\text{-TCNE})$ (X = Cl, Br, I) have been prepared from the reaction of Cp_2VX 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 $Cp_2V(CO)$ to afford a complex formulated as "$Cp_2V(TCNE)$" on the basis of analytical and spectroscopic (IR) evidence.[6] In a somewhat related vein, we have recently demonstrated that Cp_2V reacts with simple nitriles (RCN) when they are activated with a Lewis acid L (L = BCl_3, $B(C_6F_5)_3$, $AlCl_3$) to give Lewis acid adducts of vanada(IV)azirine complexes, $[Cp_2V(\eta^2\text{-RC}{=}N\cdot L)]$.[7] To extend the scope of this reaction, the reactivity of Cp_2V with TCNE and TCNQ in the presence of the Lewis acid $B(C_6F_5)_3$ was studied. Here, we present crystallographic evidence for the coordination mode of TCNX ligands to the $[Cp_2V]$ 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 $B(C_6F_5)_3$, to verify that an adduct similar to that found in simple nitriles could be generated.[7,8] The addition of 2 equiv of $B(C_6F_5)_3$ 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 $[TCNE\cdot\{B(C_6F_5)_3\}_2]$ (**1**). A similar reaction of $B(C_6F_5)_3$ with TCNQ in CH_2Cl_2 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 $[\mu_2\text{-TCNQ}\cdot\{B(C_6F_5)_3\}_2]$. The solid-state structure also revealed



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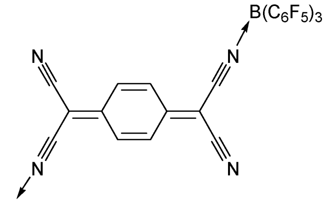

2 X-ray

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[†] E-mail: lorber@lcc-toulouse.fr.

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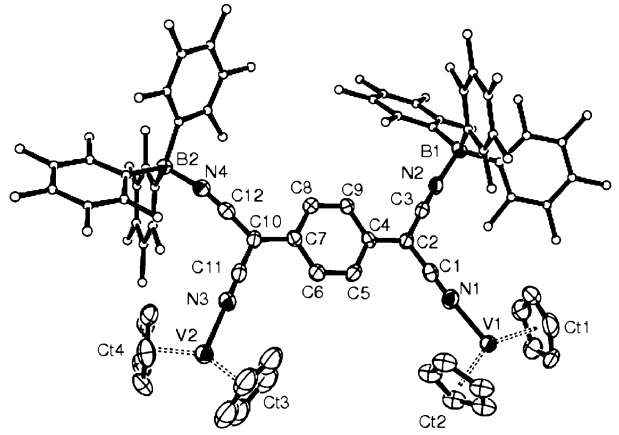
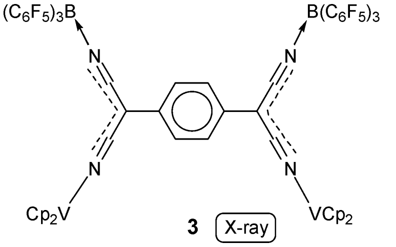


Figure 1. ORTEP drawing of the molecular structure of **3** showing 50% probability ellipsoids and partial atom-labeling schemes. C_6F_5 groups are depicted as spheres, and H atoms are omitted for clarity. Ct denotes the centroid of the cyclopentadienyl ring. Selected interatomic bond distances (Å) and angles (deg): C2−C4 = 1.465(6), C7−C10 = 1.475(6), V1−Ct1 = 1.993, V1−Ct2 = 1.982, V1−N1 = 2.041(5), V2−Ct3 = 1.920, V2−Ct4 = 1.918, 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 = 144.20 Ct3−V2−Ct4 = 144.10.

the attachment of the two $B(C_6F_5)_3$ groups to the nitrogen atom of two CN groups in anti-1,2-positions.

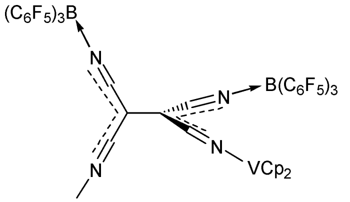
For solubility reasons, the reactivity of Cp_2V was studied with the nonisolated adducts **1** and **2**. The addition of 2 equiv of Cp_2V in toluene to a toluene solution of the adduct **2** (generated in situ from 2 equiv of $B(C_6F_5)_3$ on TCNQ) afforded after suitable workup compound **3** as a crystalline dark precipitate.



3 X-ray

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 $[(Cp_2V)_2\{(C_6F_5)_3B\cdot TCNQ\cdot B(C_6F_5)_3\}]$ (**3**) (Figure 1). The main feature of the solid-state structure of **3** is the presence of two $[Cp_2V]$ 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 $B(C_6F_5)_3$ 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 (X = NCO, N_3, N≡CNC≡N)[12] (for comparison, in the cationic $[Cp_2VMe(N{\equiv}CCH_3)]^+$ 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≡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 $[TCNQ]^{2-}$.[14] Both C−C distances attached to the ring are elongated and are best described as C−C single bonds (C2−C4 = 1.459(7) Å, C1−C7 = 1.477(7) Å) by comparison to the equivalent distances observed in free TCNQ[15] 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 $[TCNQ]^{2-}$ system, as suggested in the ruthenium complex $\{(\mu_4\text{-TCNQ})[Ru(NH_3)_5]_4\}^{8+}$, for which a crystal structure is not available.[16] The IR spectrum of **2** presents characteristic ν_{CN} bands in the region expected for $[TCNQ]^{2-}$,[17] but one must keep in mind that the presence of the two coordinated $B(C_6F_5)_3$ 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 ($\chi T_{calcd} = 2.00$ emu K mol^{-1}, assuming $g = 2$; $\chi T_{300\,K} = 1.98$ emu K mol^{-1}). Therefore, **3** is best described as a $[TCNQ]^{2-}$-containing divanadium(III) complex arising from a redox process between two Cp_2V^{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 $B(C_6F_5)_3$ in toluene afforded the crystalline dark red complex $[(Cp_2V)_2\{(C_6F_5)_3B\cdot TCNE\cdot B(C_6F_5)_3\}]$ (**4**) (Figure 2).[17] Compound **4** crystallized as a toluene solvate,



4 X-ray

and its molecular structure was determined by single-crystal

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(7) (a) Choukroun, R.; Lorber, C.; Donnadieu, B. *Chem. Eur. J.* **2002**, *8*, 2700−2704. (b) Choukroun, R.; Lorber, C.; Vendier, L.; Donnadieu, B. *Organometallics* **2004**, *23*, 5488−5492.

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(9) Note that using 4 equiv of $B(C_6F_5)_3$ 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.

(11) Selected examples of V−N amido bonds: (a) Choukroun, R.; Moumboko, P.; Chevalier, S.; Etienne, M.; Donnadieu, B. *Angew. Chem., Int. Ed.* **1998**, *37*, 3169−3172. (b) Lorber, C.; Choukroun, R.; Donnadieu, B. *Inorg. Chem.* **2002**, *41*, 4217−4226.

(12) (a) Honzicek, J.; Erben, M.; Cisarova, I.; Vinklarek, J. *Appl. Organomet. Chem.* **2005**, *19*, 100−101. (b) Honzicek, J.; Erben, M.; Cisarova, I.; Vinklarek, J. *Appl. Organomet. Chem.* **2005**, *19*, 102−103. Honzicek, J.; Erben, M.; Cisarova, I.; Vinklarek, J. *Inorg. Chim. Acta* **2005**, *358*, 814−819.

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(14) Miller, J. S.; Zhang, J. H.; Reiff, W. M.; Dixon, D. A.; Preston, L. D.; Reis, A. H., Jr.; Gebert, E.; Extine, M.; Troup, J.; Epstein, A. J.; Ward, M. D. *J. Phys. Chem.* **1987**, *91*, 4344−4360.

(15) Long, R. E.; Sparks, R. A.; Trueblood, K. *Acta Crystallogr.* **1965**, *18*, 932−939.

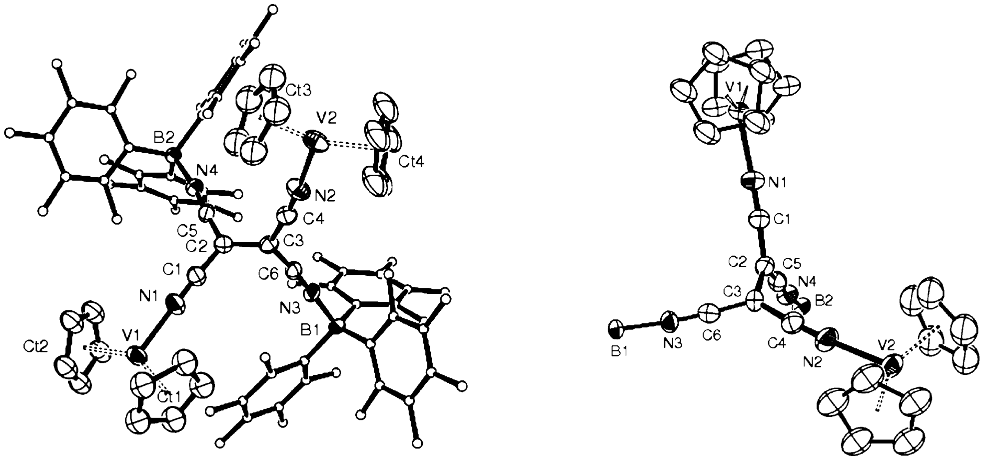


Figure 2. (left) ORTEP drawing of the molecular structure of **4** showing 50% probability ellipsoids and partial atom-labeling schemes. C_6F_5 groups are depicted as spheres, and solvent ($^1/_2$ THF) and H atoms are omitted for clarity. (right) A different view to show the twist of the TCNE moiety (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.

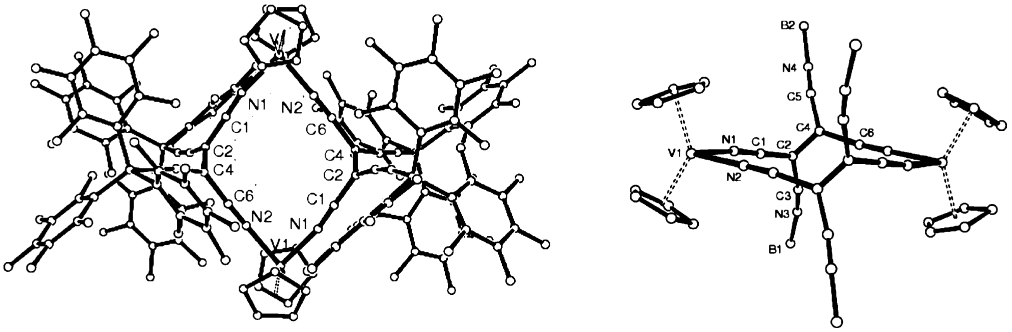
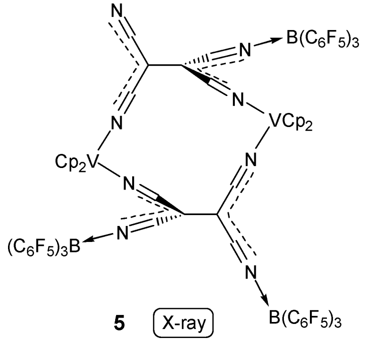


Figure 3. (left) Drawing of the molecular structure of **5** and partial atom-labeling schemes, with all atoms are depicted as spheres. Solvent (2 toluene) and H atoms are omitted for clarity. (right) A different view to show the twist of the TCNE moiety and the 14-atom cyclic arrangement (C_6F_5 groups 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 ($\chi T_{300\ K}$ = 1.98 emu K mol^{-1}).

Next, we have studied the effect of a variation of the relative stoichiometry of the reactants by performing the reaction using the ratio TCNX:$B(C_6F_5)_3$:Cp_2V = 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 $B(C_6F_5)_3$, and 1 equiv of Cp_2V was performed in toluene, affording the dark orange complex **5**.[17]



5 X-ray

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 $[Cp_2V\{(C_6F_5)_3B{\cdot}TCNE{\cdot}B(C_6F_5)_3\}]_2$ (**5**) is observed (Figure 3). Each vanadium atom is linked to two

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(16) Moscherosch, M.; Kaim, W. *Inorg. Chim. Acta* **1993**, *206*, 229−230.

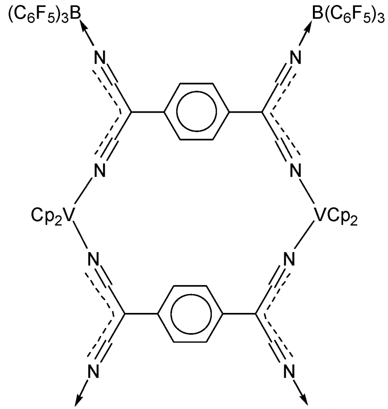
(17) IR data for all compounds (KBr, cm^{-1}): **1**, $\nu_{CN{\cdot}B}$ 2321 (s), ν_{CN} 2234 (w); **2**, $\nu_{CN{\cdot}B}$ 2307 (s), ν_{CN} 2224 (w); **3**, $\nu_{CN{\cdot}B}$ 2250 (m), ν_{CN} 2201 (w), ν_{CN} 2150 (s); **4**: $\nu_{CN{\cdot}B}$ 2254 (m), ν_{CN} 2198 (w), ν_{CN} 2154 (s); **5**: $\nu_{CN{\cdot}B}$ 2250 (m), ν_{CN} 2201 (w), ν_{CN} 2150 (s); **6**: $\nu_{CN{\cdot}B}$ 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.

(19) (a) Little, R. G.; Pauther, D.; Coppens, P. *Acta Crystallogr.* **1971**, *B27*, 1493−1499. (b) Chaplot, S. L.; Mierzejewski, A.; Pawley, G. S. *Acta Crystallogr.* **1984**, *C40*, 663−666.

nitrogen atoms of CN groups connected to two twisted [TCNE$\cdot$\{B(C_6F_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 ($\chi T_{calcd} = 0.75$ emu K mol^{-1}, assuming $g = 2$; $\chi T_{300\,K} = 0.70$ emu K mol^{-1}).

Similarly, the analogous reaction conducted with TCNQ (instead of TCNE), 2 equiv of B(C_6F_5)$_3$, and 1 equiv of Cp_2V yielded a microcrystalline dark precipitate. We suggest this new compound to be the dimer [Cp_2V\{(C_6F_5)$_3$B$\cdot$TCNQ$\cdot$B(C_6F_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 susceptibilites measured for **6** are strongly temperature-dependent ($\chi T_{300\,K} =$ 0.90 emu K mol^{-1}). A Bleany−Bowers treatment[20] for **6** renders the following values: exchange constant $J = -55$ cm^{-1} and zero-field splitting $D = -150$ cm^{-1}. The previously reported [V(C_5Me_5)$_2$Br]$_2$(μ_2-TCNE),[21] in which a V^{IV} center and a [TCNE]$^{2-}$ ligand are present, was also shown to present a similar temperature-dependent magnetic behavior ($\chi T_{300\,K} \approx$ 0.97 emu K mol^{-1}), except with a very distinct coupling constant ($J = -0.6$ cm^{-1}, $D = 1.5$ 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 $H_c \approx 40$ Oe at 2 K is evident, 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]



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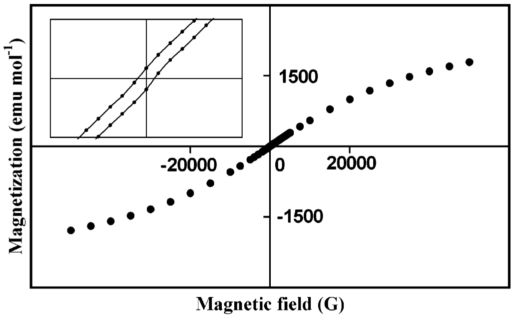

Figure 4. Magnetic behavior for **6** recorded at 2 K (magnetization vs applied magnetic field). The inset represents an enlargement between −600 and +600 G and −15 and +15 emu mol^{-1}.

In conclusion, the reactivity of Cp_2V with [TCNX$\cdot$\{B(C_6F_5)$_3$\}$_2$] is very different from that previously observed with the activated simple nitrile adducts RCN$\cdot$B(C_6F_5)$_3$[7] (in which the vanadaazirine complexes [Cp_2V(η^2(*C*,*N*)-RCN$\cdot$B(C_6F_5)$_3$)] were obtained). We showed here that B(C_6F_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 [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 [V(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 Bleany−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.

OM060433W

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