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Identification of $[M^{II}(Arene)_2]^{2+}$ (M = V, Cr) as the Key Intermediate in the Formation of $V[TCNE]_x{\cdot}y$Solvent Magnets and $Cr[TCNE]_x{\cdot}$Solvent

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Abstract: To elucidate the mechanism of the reaction between $V^0(C_6H_6)_2$ and tetracyanoethylene (TCNE) that leads to the room-temperature magnet $V[TCNE]]_x{\cdot}yCH_2Cl_2$ ($x \sim 2$; $y \sim {}^1/_2$), reactions between bis(arene)-vanadium (arene = 1,3,5-trimethylbenzene, 1,3,5-tri-*tert*-butylbenzene) and its cations and TCNE and its anion were studied. The reaction of $V^o(arene)_2$ with TCNE yields magnets with critical temperatures ranging from 28 to 400 K. Products from the reaction of $[V^I(arene)_2]^+$ with $[TCNE]^{\bullet-}$ were not magnets; however, reaction of $[V^I(arene)_2]^+$ with $[TCNE]^{\bullet-}$ in the presence of TCNE forms a magnetically ordered material. The reaction of $V^0(1,3,5\text{-}C_6H_3Me_3)_2$ with 2 equiv of one-electron oxidant $[Fe^{III}(C_5H_5)_2]^+$, and subsequently with $[TCNE]^{\bullet-}$, also leads to a magnetic material. The results of these investigations suggest that $V^0(arene)_2$ undergoes two one-electron oxidation reactions with TCNE to form sequentially $[V^I(arene)_2]^+$ and "$[V^{II}(arene)_2]^{2+}$", the latter being the key intermediate that reacts with $[TCNE]^{\bullet-}$ to produce the magnetic product. $[V^I(arene)_2]^+$ has been isolated, whereas and "$[V^{II}(arene)_2]^{2+}$" has not. The one-electron oxidation of $V^0[C_6H_3(t\text{-}Bu)_3]_2$ with Ag-$[BPh_4]$ produces $\{V^I[C_6H_3(t\text{-}Bu)_3]_2\}^+[BPh_4]^-$. The stoichiometric reaction of $V^0[C_6H_3(t\text{-}Bu)_3]_2$ with TCNE leads to paramagnetic $\{V^I[1,3,5\text{-}C_6H_3(tBu)_3]_2\}^+[TCNE]^{\bullet-}$. $\{V^I[C_6H_3(t\text{-}Bu)_3]_2\}^+[BPh_4]^-$ and $\{V^I[1,3,5\text{-}C_6H_3\text{-}(tBu)_3]_2\}^+[TCNE]^{\bullet-}$ have been structurally characterized. When $[V^{II}(NCMe)_6]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}_2$ is reacted with $[TCNE]^{\bullet-}$, a route that does not use bis(arene)vanadium complexes, a magnetic precipitate is also produced. As established earlier, the reaction of $Cr^0(arene)_2$ with TCNE forms nonmagnetically ordered $[Cr^I(arene)_2]^{\bullet+}$-$[TCNE]^{\bullet-}$. Reaction of lower oxidation potential Cr^0Np_2 (Np = naphthalene) with TCNE putatively forms "$[Cr^{II}Np_2]^{2+}$" which reacts with $[TCNE]^{\bullet-}$ to form $Cr[TCNE]_x{\cdot}yS$, which was isolated and, unexpectedly, does not magnetically order. Similar results are obtained when $[Cr^{II}(NCMe)_4][BF_4]_2$ or $[Cr^{II}(NCMe)_6][B(3,5\text{-}C_6H_3(CF_3)_2)_4]_2$ is reacted with $[n\text{-}Bu_4N][TCNE]$.

Introduction

The development and understanding of new materials with technologically important properties is a contemporary research area. One aspect is aimed at the development[2] and exploitation[3] of molecule-based materials exhibiting technologically important bulk magnet behavior, e.g., ferro- or ferrimagnetism. The molecule-based magnet with the highest ordering temperature (T_c ~400 K), namely, $V[TCNE]_x{\cdot}yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$), results from the reaction of $V^0(C_6H_6)_2$ (**1**) with tetracyanoethylene (TCNE) in dichloromethane.[4] Variations in x, y, and T_c were observed to be dependent upon reaction conditions.[5] The saturation magnetization for $V[TCNE]_x{\cdot}yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$) is consistent with the presence of antiferromagnetic coupling between $S = {}^3/_2$ V(II) and two $S = {}^1/_2$ $[TCNE]^{\bullet-}$ ligands, forming a ferrimagnet.[2c,4] Despite the unusual magnetic properties of this material, the mechanism of the reaction, as well as the structure of the magnetic product, remains to be elucidated.

In an attempt to address the chemistry and physics associated with for the room-temperature $V[TCNE]_x{\cdot}yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$) magnet, TCNE has been used to synthesize a variety of molecule-based magnets as electron-transfer salts. Examples of structurally characterized TCNE-based molecular magnets include the 1-D chains containing metallocene repeat units, such as $[M^{III}(C_5Me_5)_2]^+[TCNE]^{\bullet-}$ (M = Cr, Fe, Mn)[2c,6] that ferromagnetically order below 8.8 K and the linear chain coordination polymers with $[TCNE]^{\bullet-}$ bridging manganoporphyrins.[2a] TCNE-

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based magnets containing late first-row transition metals (M = Mn, Fe, Co, Ni) have also been prepared and display spontaneous magnetization below 100 K and coercive fields ranging from 300 (M = Ni) to 6500 Oe (M = Co).[7]

Herein we elucidate the mechanism of the reaction between $V^0(arene)_2$ and TCNE that produces V[TCNE]$_x$·yS (S = solvent) magnets using arene = 1,3,5-trimethylbenzene and 1,3,5-tri-*tert*-butylbenzene. Furthermore, we report the structural characterization of $[V^I(C_6H_3(t\text{-}Bu)_3)_2]^+$ as $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$, which represents not only the first characterizations of an early transition metal bis(arene) complex with this bulky ligand but also the first bis(arene)vanadium $[TCNE]^{\bullet-}$ complex. In addition, the preparation and magnetic properties of Cr[TCNE]$_x$·yS, which unexpectedly do not display spontaneous magnetization, is presented.

Experimental Section

All experimental procedures were carried out under inert atmosphere conditions using either Schlenk or glovebox techniques. All solvents used were dried and degassed before use. Tetrahydrofuran (THF), 1,3,5-trimethylbenzene, diethyl ether, toluene, and *n*-hexane were distilled from sodium benzophenone ketyl and dichloromethane was distilled from CaH_2. $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$,[8] $[Fe(C_5H_5)_2]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}$,[9] $[V^{II}(NCMe)_6]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}_2$,[10] Cr^0Np_2 (Np = naphthalene),[11] $[Cr^{II}(NCMe)_4][BF_4]_2$,[12] and $[Cr^{II}(NCMe)_6]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}_2$[10] were synthesized according to previously published procedures. $Ag[BPh_4]$ was obtained from the stoichiometric aqueous reaction of $AgNO_3$ (Johnson-Matthey) and $Na[BPh_4]$ (Strem). Aluminum powder (ACROS), VCl_3 (ACROS), and vanadium foil (Aldrich, 99.7%, 5 × 20 × 0.5 mm) were used as received. $AlCl_3$ (ACROS) was purified by sublimation before use. TCNE[13] and 1,3,5-tri-*tert*-butylbenzene[14] were synthesized according to literature methods and purified by sublimation. Elemental analyses were carried out by Atlantic Microlab Inc. (Norcross, GA). The thermal properties were studied on a TA Instruments model 2050 thermogravimetric analyzer (TGA) equipped with an electron spray mass spectrometer, located in a Vacuum Atmospheres DriLab glovebox under argon. Samples were heated from room temperature to 450 °C at 20 °C/min. Infrared spectra were taken on a BioI-Rad FTS-40 spectrophotometer using Nujol mulls on NaCl plates or as KBr pellets, both prepared in a glovebox. Cyclic voltammetry studies were done in a glovebox under nitrogen using a glassy carbon working electrode, a Ag wire counter electrode, and a Ag/Ag_2O reference electrode. Ferrocene was used as an external standard $\{Fe(C_5H_5)_2/[Fe(C_5H_5)_2]^+$: $E_{1/2} = +0.46$ V vs SCE, $CH_2Cl_2\}$.[15] Scans of **2** and **3** (1 mmol) were done in CH_2Cl_2 at 25 °C at 50 mV/s with supporting electrolyte $[n\text{-}Bu_4N][PF_6]$ (0.1 mol).

Magnetic data were acquired on a Quantum Designs MPMS-5XL SQUID magnetometer as previously described[16] and were corrected for the underlying diamagnetism of the sample from Pascal constants and of the airtight Delrin or nongelatin capsule sample holder. The critical temperature, T_c, is determined as the intersection of the steepest slope of the magnetization curve with the temperature axis, when warming is done under low applied fields. Samples were cooled in zero applied field to 2 K and then warmed under an applied field. Low-field magnetization measurements (3 Oe) were done after degaussing the shield and resetting the magnet. Powder EPR spectra were recorded using a Bruker EMX X-band spectrometer with 1,1-diphenyl-2-picrylhydrazyl (Sigma) as an external standard ($g = 2.0037$).

X-ray crystallography studies were done using a Nonius Kappa CCD diffractometer. The positions of non-hydrogen atoms were obtained by the direct method using SIR-97[17] and were assigned anisotropic thermal parameters. Hydrogen atom positions were determined by isotropic refinement. Structure refinement was done using SHELXL 97[18a] and ORTEP 3.[18b] Structures $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ displayed disorder in the THF solvent molecules. Analysis of crystals of **3** (dark red prisms) revealed a unit cell with $a = 29.1871(6)$ Å, $b = 17.3849(6)$ Å, $c = 9.9041(3)$ Å, $V = 5012.3(3)$ Å^3, and $Z = 6$. The refinement converged to R1 = 0.0895, wR2 = 0.2467, and goodness of fit = 1.079 for 5308 reflections. Axial photographs and systematic absences were consistent with the compound having crystallized in the monoclinic space group *C*2/*m*. There are two disordered molecules of V(1,3,5-tri-*t*-butylbenzene)$_2$ in an asymmetric unit. The first molecule is sitting on a 2/*m* symmetry site while the second molecule is sitting on an *m* symmetry site. The *tert*-butyl groups in both molecules are orientationally disordered, and the second molecule has additional disorder resulting from three different orientations of the complex.

$V^0(1,3,5\text{-}C_6H_3Me_3)_2$ (2). A recently reported procedure[19] was modified as follows. A Schlenk tube was loaded with VCl_3 (1.26 g, 8.01 mmol), $AlCl_3$ (0.343 g, 13.9 mmol), and aluminum powder (0.343 g, 12.7 mmol). 1,3,5-Trimethylbenzene (15 mL, 0.11 mol) was added via syringe, and the tube was heated in an oil bath at 100 °C for 2 h. After cooling to room temperature, 20 mL of THF was added and the reaction mixture was stirred for an additional 72 h. The solvent was removed in vacuo and the residue extracted with hexanes. The solution was then filtered and cooled to 195 K, producing dark red needles (yield: 1.91 g, 82%). IR (KBr, cm^{-1}): 2960−2872 (s), 1655−1596 (m), 1450 (m), 1372 (s), 1146 (m), 1028 (s), 986 (s), 812 (m), 444 (vs). Anal. Calcd for $V(1,3,5\text{-}C_6H_3Me_3)_2\cdot 0.75(C_4H_8O)$, $C_{21}H_{30}O_{0.75}V$: C, 73.02; H, 8.75. Found: C, 72.75; H, 8.41. EPR (9.785 GHz): $\langle g\rangle_{300\,K} = 1.989$; $\langle A^{51V}\rangle_{300\,K} = 6.10$ mT.

$[V^I(1,3,5\text{-}C_6H_3Me_3)_2]^+[BPh_4]^-$, $\mathbf{2}^+[BPh_4]^-$. A slurry of $Ag[BPh_4]$ (30 mg, 0.70 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C, a 20-mL CH_2Cl_2 solution of **2** (0.141 g, 0.484 mmol) was added dropwise, and the reaction mixture was stirred for 1 h, then warmed slowly to room temperature, and stirred for an additional 18 h. The reaction mixture was filtered through Celite on a medium frit and the solid washed with CH_2Cl_2. The filtrate was then concentrated to ∼10 mL and layered with hexanes (20 mL), which produced orange/red microcrystals (yield: 0.177 g, 60%). IR (KBr, cm^{-1}): 3048−2921 (s), 1580 (m), 1479 (s), 1453 (s), 1427 (s), 1379 (s), 1030 (s), 742 (vs), 731 (vs), 709 (vs), 603 (s). Anal. Calcd for $[V(1,3,5\text{-}C_6H_3Me_3)_2][BPh_4]\cdot 1.15CH_2Cl_2$, $C_{43.15}H_{46.3}BCl_{2.26}V$: C, 73.18; H, 6.59. Found: C, 73.10; H, 6.62.

Reaction of 2 with TCNE (1:1) (CH_2Cl_2, 25 °C) (4). A solution of **2** (53.5 mg, 0.184 mmol) dissolved in CH_2Cl_2 (15 mL) was added to a 15-mL CH_2Cl_2 solution of TCNE (23.9 mg, 0.187 mmol), which immediately formed a black precipitate (yield: 46.5 mg). The reaction mixture was stirred for an additional 24 h and then filtered, washed with CH_2Cl_2, and dried in vacuo. IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2197 (m), 2097 (s, br). $T_c = 160$ K.

Reaction of 2 with TCNE (1:2) (toluene, −78 °C) (5). A solution of **2** (58 mg, 0.20 mmol) dissolved in toluene (15 mL) was added to a

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5-mL CH_2Cl_2 solution of TCNE (33.4 mg, 0.261 mmol), which immediately formed a precipitate. The reaction mixture was stirred for 1 h, warmed to room temperature, then filtered, washed with toluene, and dried in vacuo, producing a blue/black powder (yield: 68.4 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2190 (m), 2147 (s), 2101 (w). $T_c = 260$ K.

Reaction of 2 with TCNE (1:2) (CH_2Cl_2, −25 °C) (6). A solution of 2 (30.8 mg, 0.106 mmol) dissolved in CH_2Cl_2 (15 mL) was added to a cooled (−25 °C) 15-mL CH_2Cl_2 solution of TCNE (44.7 mg, 0.349 mmol), which immediately formed a fine blue/black precipitate. The reaction mixture was then warmed to room temperature, filtered, washed with CH_2Cl_2, and dried in vacuo (yield: 23.0 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2218 (m), 2152 (s,br). $T_c = 138$ K.

Reaction of $2^+[BPh_4]^-$ with TCNE (1:1) (CH_2Cl_2, 25 °C) (7). A 5-mL CH_2Cl_2 solution of $\mathbf{2}^+[BPh_4]^-$ (27.5 mg, 0.045 mmol) was added to a 5-mL CH_2Cl_2 solution of TCNE (5.6 mg, 0.044 mmol), which immediately formed a black precipitate. The reaction mixture was stirred for 24 h, then the solid was filtered and dried in vacuo (yield: 15.6 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2200 (m), 2104 (s, br). $T_c = 28$ K.

Reaction of $2^+[BPh_4]^-$ with $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$ (1:1) (CH_2Cl_2, 25 °C) (8). A 15-mL CH_2Cl_2 solution of $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$ (19.4 mg, 0.052 mmol) was added to a 15-mL CH_2Cl_2 solution of $\mathbf{2}^+[BPh_4]^-$ (30.9 mg, 0.051 mmol), which immediately formed a black precipitate. The reaction mixture was then stirred at room temperature for an additional 60 min, filtered, washed with CH_2Cl_2, and dried in vacuo (yield: 11.2 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2201 (m), 2146 (m), 2110 (s). TGA/MS, $m/z+$: 71 (BuN^+), 57 (Bu^+), 56 (BuN^+ -Me), 42 (BuN^+ -Et), no observed solvent loss. $\theta = -28$ K ($T > 100$ K) and $\theta = -570$ K ($200 < T < 300$ K).

Reaction of $2^+[BPh_4]^-$ with (1:1) $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$ and TCNE (CH_2Cl_2, 25 °C) (9). A solution of $\mathbf{2}^+[BPh_4]^-$ (14.7 mg, 0.025 mmol) dissolved in CH_2Cl_2 (5 mL) was added to a 5-mL CH_2Cl_2 solution containing TCNE (3.4 mg, 0.027 mmol) and $[n\text{-}Bu_4N][TCNE]$ (9.9 mg, 0.027 mmol), which immediately formed a blue/black precipitate. The reaction mixture was stirred for 15 min, and then the solid was filtered and dried in vacuo (yield: 6.8 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2188 (m), 2146 (m), 2101 (w). $T_c = 265$ K.

Reaction of 2 with $[Fe^{III}(C_5H_5)_2]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}$ and $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$ (10). A 20-mL CH_2Cl_2 solution of $[Fe(C_5H_5)_2]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}$ (109.8 mg, 0.105 mmol) was added dropwise to a 15-mL CH_2Cl_2 solution of **2** (15.2 mg, 0.052 mmol) at −78 °C. The reaction mixture was stirred for 40 min, changing color from dark red to green. A −78 °C solution of $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$ (39.6 mg, 0.107 mmol) dissolved in 10 mL of CH_2Cl_2 was added to the above solution, immediately forming a dark blue precipitate. The reaction mixture was stirred at this temperature for 9 h and then warmed to room temperature, filtered, and dried in vacuo (yield: 14.2 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2212 (m), 2192 (m), 2146 (s, br), 2100 (sh). $T_c = 200$ K.

$V^0[C_6H_3(t\text{-}Bu)_3]_2$ (3). Vanadium vapor was co-condensed with 1,3,5-tri-*tert*-butylbenzene (∼5 g) at 77 K by resistively heating vanadium foil at 125 A and 3.3 V for 40 min. After being warmed to room temperature under an argon atmosphere, the product was extracted with hexanes and the resulting solution filtered through Celite on a sintered frit. Solvent was removed in vacuo, and the excess ligand was removed by sublimation (50 °C, 10^{-3} Torr). The residue was redissolved in hexanes, filtered, and crystallized by slow evaporation of the solvent under argon, producing red/black prisms (yield: 120 mg, ∼10% based on evaporated V). IR (KBr, cm^{-1}): 3088 (w), 2956−2863 (s, br), 1478 (s), 1457 (s), 1389 (m), 1358 (s), 1287 (m), 1240 (s), 1135 (s), 993 (s), 876 (m), 814 (m). ^1H NMR (300 MHz, C_6D_6) δ: 4.25 (s, 54H), ring protons not observed. Anal. Calcd for $C_{36}H_{60}V$: C, 79.51; H, 11.12. Found: C, 79.35; H, 11.06. EPR (9.785 GHz): $\langle g \rangle_{300\,K} = 1.988$; $\langle A^{51V} \rangle_{300\,K} = 6.72$ mT.

$\{V^I[C_6H_3(t\text{-}Bu)_3]_2\}^+[BPh_4]^-$, $3^+[BPh_4]^-$. Both **3** (27 mg, 0.050 mmol) and $Ag[BPh_4]$ (44 mg, 0.10 mmol) were combined in a Schlenk flask, cooled to −78 °C, and to this was added 20 mL of toluene. The reaction mixture was stirred for 1 h, then slowly warmed to ambient temperature, and stirred for 14 h. The reaction mixture was filtered through Celite on a medium frit and the collected solid washed with toluene and dried in vacuo. The solid was extracted with CH_2Cl_2, producing a cherry-red solution, and the solvent was removed in vacuo. The resulting product was redissolved in 3 mL of THF, and vapor diffusion of hexane into the solution at 220 K for 3 days resulted in formation of dark red crystals (yield: 37 mg, 87%). Single crystals (plates) of $\mathbf{3}^+[BPh_4]^-$ suitable for X-ray crystallography were obtained by crystallization at −35 °C from a THF/hexanes (1:1) solution. IR (KBr, cm^{-1}): 3124 (w), 3057−2873 (s), 1581 (m), 1480 (s), 1461 (m), 1366 (s), 1240 (s), 1136 (m), 993 (w), 878 (w), 732 (s), 703 (vs). μ_{eff}(300K) = 2.85 μ_B. Anal. Calcdd for $C_{60}H_{80}BV$: C, 83.50; H, 9.34. Found: C, 83.52; H, 9.32.

$\{V^I[C_6H_3(t\text{-}Bu)_3]_2\}^+[TCNE]^{\bullet-}$, $3^+[TCNE]^{\bullet-}$. A solution of TCNE (5.2 mg, 0.041 mmol) dissolved in THF (15 mL, −78 °C) was added dropwise to a solution of **3** (23.0 mg, 0.042 mmol) in THF (15 mL, −78 °C). The reaction mixture was stirred at −78 °C for 4 h, then slowly warmed to room temperature, and concentrated under vacuum to ∼15 mL. The suspension was then filtered, and the orange powder washed with THF and dried in vacuo (yield: 20 mg, 73%). Vapor diffusion of *n*-hexane into a THF solution at −35 °C over several days produced red prisms suitable for single-crystal X-ray crystallographic analysis. IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2185 (s), 2146 (s).

Reaction of 3 with Excess TCNE (11). A solution of **3** (17 mg, 0.031 mmol) dissolved in 5 mL of CH_2Cl_2 was added to a 5-mL CH_2Cl_2 solution of TCNE (10 mg, 0.078 mmol) in CH_2Cl_2 at room temperature, producing a dark blue precipitate within a few minutes. The solution was stirred for 18 h, and the precipitate was then filtered and dried under vacuum (yield: 2.5 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2218 (m), 2194 (m), 2155 (s), 2100 (sh). $T_c = 203$ K.

Attempts to make $\mathbf{3}^{2+}[BPh_4^-]_2$. A 15-mL solution of **3** (34 mg, 0.063 mmol) in THF was added dropwise to a cooled (−78 °C) slurry of $Ag[BPh_4]$ (87 mg, 0.204 mmol) in 15 mL of THF. The reaction mixture was stirred for 1 h, warmed to room temperature over 3 h, and then filtered through Celite, producing an orange/red solution that was subsequently pumped to dryness and redissolved in 1 mL of THF, layered with diethyl ether (2 mL), and placed in the freezer (−40 °C). After several days, red needles were isolated (yield: 31.0 mg); however, magnetic measurements and elemental analysis characterization confirmed this material to be $\mathbf{3}^+[BPh_4]^-$.

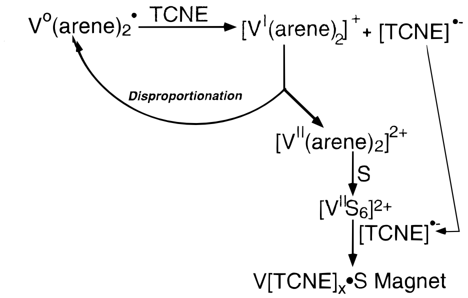
Thermolysis of $3^+[TCNE]^{\bullet}$ (12). $\mathbf{3}^+[TCNE]^{\bullet-}$ (7.8 mg, 0.012 mmol) was refluxed in toluene (15 mL) for 14 h producing a black precipitate that was filtered, washed with hexanes (yield: 0.4 mg), and dried in vacuo. IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2205 (m), 2122 (s).

Reaction of $3^+[BPh_4]^-$ with TCNE and $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$ (CH_2Cl_2, 25 °C) (13). A solution of $\mathbf{3}^+[BPh_4]^-$ (7.9 mg, 0.0091 mmol) dissolved in CH_2Cl_2 (8 mL) was added to an 8-mL CH_2Cl_2 solution containing TCNE (1.1 mg, 0.0085 mmol) and $[n\text{-}Bu_4N]^+[TCNE]^{\bullet-}$ (3.9 mg, 0.010 mmol), which immediately formed a dark precipitate. The reaction mixture was stirred for 3 h, filtered, washed with CH_2Cl_2, and dried in vacuo, producing a dark blue powder (Yield: 3.4 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2193 (m), 2159 (m), 2034 (w, br). $T_c = 258$ K.

Reaction of $[V^{II}(NCMe)_6][B(3,5\text{-}C_6H_3(CF_3)_2)_4]_2$ with $[n\text{-}Bu_4N][TCNE]$ (14). A solution of $[V^{II}(NCMe)_6]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}_2$ (56.2 mg, 0.0277 mmol) in CH_2Cl_2 (15 mL) was added to a stirring solution of $[n\text{-}Bu_4N][TCNE]$ (20.2 mg, 0.0545 mmol) in CH_2Cl_2 (15 mL), immediately forming a black solution. The reaction mixture was left stirring at room temperature for an additional 2.5 h after which the solution was filtered, and the precipitate was washed with CH_2Cl_2 and then dried in vacuo (yield: 12.9 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2212 (w), 2192 (m), 2154 (s), 2041 (m, br). $T_c = 188$ K.

Reaction of Cr^0Np_2 with TCNE (Toluene, 25 °C) (15). A solution of Cr^0Np_2 (52.0 mg, 0.169 mmol) dissolved in toluene (15 mL) was added dropwise to a stirring solution of TCNE (56.0 mg, 0.438 mmol) dissolved in 15 mL of toluene and immediately formed a black precipitate. The reaction mixture was left stirring at room temperature for an addition 20 h after which the solution was filtered and the precipitate washed with toluene and then dried in vacuo (yield: 51.0 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2213 (m), 2110 (s). No absorptions assignable to υ_{CH} were observed. TGA/MS: 13% weight loss between 50 and 225 °C; $m/z+$: 92 ($PhMe^+$). Elemental Anal. Found: C, 44.48; H, 2.29; N, 26.74. $\theta = -75$ K ($T > 80$ K).

Scheme 1



Reaction of [Cr^{II}(NCMe)$_4$][BF$_4$]$_2$ with [*n*-Bu$_4$N]$^+$[TCNE]$^{•-}$ (MeCN, 25 °C) (16). A solution of [Cr^{II}(NCMe)$_4$][BF$_4$]$_2$ (78.0 mg, 0.020 mmol) dissolved in 8 mL of MeCN was added to a stirring 8-mL MeCN solution of [*n*-Bu$_4$N]$^+$[TCNE]$^{•-}$ (185.0 mg, 0.50 mmol), immediately forming a dark precipitate. The reaction mixture was left stirring at room temperature for an addition 6 h after which the solution was filtered, and the precipitate washed with MeCN and then dried in vacuo (yield: 55.4 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2300 (vw), 2214 (m), 2111 (s) No absorptions assignable to υ_{CH} were observed. TGA/MS: 20% weight loss between 50 and 300 °C; *m*/*z*+: 41 (MeCN$^+$). Elemental Anal. Found: C, 45.74; H, 3.13; N, 25.07. $\theta = -70$ K ($T > 80$ K).

Reaction of [Cr^{II}(NCMe)$_6$]{B[3,5-C$_6$H$_3$(CF$_3$)$_2$]$_4$}$_2$ with [*n*-Bu$_4$N]$^+$[TCNE]$^{•-}$ (CH$_2$Cl$_2$, 25 °C) (17). A solution of [Cr^{II}(NCMe)$_6$]{B[3,5-C$_6$H$_3$(CF$_3$)$_2$]$_4$}$_2$ (71.3 mg, 0.035 mmol) dissolved in 8 mL of CH$_2$Cl$_2$ was added to a stirring 8-mL CH$_2$Cl$_2$ solution of [*n*-Bu$_4$N]$^+$[TCNE]$^{•-}$ (25.1 mg, 0.068 mmol), immediately forming a dark precipitate. The reaction mixture was left stirring at room temperature for an addition 30 min after which the solution was filtered, and the dark brown precipitate was washed with CH$_2$Cl$_2$ and then dried in vacuo (yield: 12.6 mg). IR (NaCl/Nujol, cm^{-1}) $\nu_{C\equiv N}$: 2298 (vw), 2212 (m), 2098 (s). TGA/MS: 22% weight loss between 50 and 325 °C; *m*/*z*+: 41 (MeCN$^+$), no CH$_2$Cl$_2$ solvent observed. Elemental Anal. Found: C, 41.85; H, 1.87; N, 23.15. $\theta = -42$ K ($T > 80$ K).

Results and Discussion

Mechanistic investigations of the reaction of V^0(C$_6$H$_6$)$_2$ with TCNE centered on the hypothesis that the first step was an electron-transfer reaction forming [V^I(C$_6$H$_6$)$_2$]$^+$ and [TCNE]$^{•-}$, eq 1, Scheme 1.

$$\mathrm{V^0(arene)_2 + TCNE \rightarrow [V^I(arene)_2]^+ + [TCNE]^{\bullet-}} \quad (1)$$

$$\mathrm{2[V^I(arene)_2]^+ \rightarrow V^0(arene_6)_2 + [V^{II}(arene)_2]^{2+}} \quad (2)$$

$$\mathrm{[V^{II}(arene)_2]^{2+} + 6S \rightarrow [V^{II}S_6]^{2+} + 2arene} \quad (3)$$

$$\mathrm{[V^{II}(arene)_2]^{2+} + 2[TCNE]^{\bullet-} \rightarrow [TCNE]_{\mathit{x}}{\cdot}\mathit{y}S\ magnet} \quad (4a)$$

$$\mathrm{[V^{II}S_6]^{2+} + 2[TCNE]^{\bullet-} \rightarrow [TCNE]_{\mathit{x}}{\cdot}\mathit{y}S\ magnet} \quad (4b)$$

This reaction was immediately followed by the disproportionation of [V^I(C$_6$H$_6$)$_2$]$^+$ to [V^{II}(C$_6$H$_6$)$_2$]$^{2+}$ and re-forming V^0(C$_6$H$_6$)$_2$, eq 2. [V^{II}S$_6$]$^{2+}$ (S = THF, MeCN) via the solvation of [V^{II}(C$_6$H$_6$)$_2$]$^{2+}$, eq 3, has been established to form from the disproportionation of [V^I(arene)$_2$]$^+$ in the presence of nucleophiles, e.g., THF, P(OMe)$_3$, MeCN, and 1,2-dimethoxyethane.[20] Either dication would be subsequently attacked by [TCNE]$^{•-}$ to form the magnetic product, eq 4, Scheme 1. Furthermore, the reaction of [V^{II}(NCMe)$_6$]$^{2+}$ with [TCNE]$^{•-}$, eq 4b, independently has been reported to form the V[TCNE]$_x$·*y*S magnet.[21]

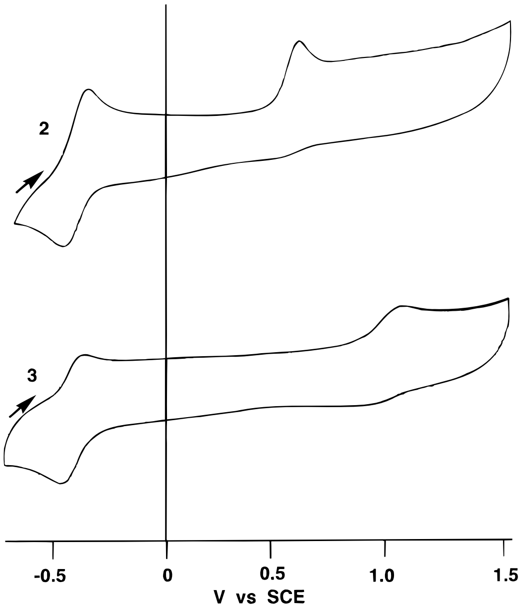


Figure 1. Cyclic voltammograms of **2** and **3** in CH$_2$Cl$_2$ at 25 °C, with 0.1 M [*n*-Bu$_4$N][PF$_6$] at a glassy carbon electrode versus SCE. **2**: $E_{1/2} = -0.37$ V reversible; $\Delta E_p = 100$ mV; $E_{pa} = +1.09$ V irreversible. $E_{1/2} = -0.29$ V reversible; $\Delta E_p = 105$ mV; $E_{pa} = +0.66$ V irreversible.

It was anticipated from the work of Cloke et al.[22] that sterically demanding arene ligands would increase the stability of electron-deficient bis(arene)vanadium complexes and aid in the isolation of the mono- and dication complexes. Stabilization of an electron-deficient metal center in a sandwich complex by a bulky arene ligand was demonstrated with the report of [Ti^I(1,3,5-triisopropylbenzene)$_2$]$^+$.[23]

To test this hypothesis, the reactions of V^0(arene)$_2$ and [V^I(arene)$_2$]$^+$ [arene = 1,3,5-trimethylbenzene (**2** and **2**$^+$), 1,3,5-tri-*tert*-butylbenzene (**3** and **3**$^+$)] with TCNE and [TCNE]$^{•-}$ were studied. **2**$^+$ and **3**$^+$ as the [BPh$_4$]$^-$ salts were isolated from the reaction of **2** and **3** with Ag[BPh$_4$], and the latter was crystallographically characterized (vide infra) and is the first report of the structure of a transition metal sandwich complex with this bulky 1,3,5-tri-*tert*-butylbenzene ligand. The reversible one-electron reduction potential for **1**$^+$, **2**$^+$, and **3**$^+$ vs SCE are $E_{1/2} = -0.36$ (dimethoxyethane),[24] -0.29, and -0.37 V (CH$_2$Cl$_2$), Figure 1, respectively. Furthermore, these compounds exhibit irreversible oxidations to the 2+ state at $E_{pa} = +0.24$,[25] $+0.66$, and $+1.09$ V, respectively. Hence, **1**, **2**, and **3** will reduce TCNE [$E^{-/0} = +0.25$; $E^{2-/-} = -0.83$ V (CH$_2$Cl$_2$)][26] to [TCNE]$^{•-}$, but not [TCNE]$^{2-}$.

The reaction of either **1** or **2** with TCNE leads to the rapid formation of the V[TCNE]$_x$·*y*S magnets. The mechanism of this reaction is the focus of the research reported herein. In contrast,

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Table 1. Crystal and Experimental Data for $\{V^{I}[C_6H_3(t\text{-}Bu)_3]_2\}[BPh_4]\cdot THF$, $\mathbf{3}^+[BPh_4]^-$ and $\{V^{I}[C_6H_3(t\text{-}Bu)_3]_2\}[TCNE]\cdot{}^3/_2THF$, $\mathbf{3}^+[[TCNE]^{\bullet-}$

	$\mathbf{3}^+[BPh_4]^-\cdot THF$	$\mathbf{3}^+[TCNE]^{\bullet-}\cdot{}^3/_2THF$
empirical formula	$C_{64}H_{84}BOV$	$C_{48}H_{72}N_4O_{1.5}V$
formula weight	931.06	780.04
temperature (K)	200.0(1)	200.0(1)
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	11.2396(1)	11.0332(3)
b (Å)	20.2835(4)	18.03389(5)
c (Å)	26.6935(4)	22.7485(7)
β (deg)	94.6430(10)	92.8691(16)
V (Å^3)	6065.57(16)	4597.1(2)
Z	4	4
density calc (Mg/m^3)	1.020	1.127
goodness of fit on F^2 [a]	1.063	1.046
final R indices	$R1^b = 0.0638$ $wR2^c = 0.1750$	$R1^b = 0.0733$ $wR2^c = 0.1717$

[a] Goodness of fit $= [\Sigma(w(F_o^2 - F_c^2)/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters refined. [b] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $wR2 = [\Sigma(w(F_o^2 - F_c^2)2)/\Sigma(F_o^2)^2]^{1/2}$.

the 1:1 stoichiometric reaction of the easier-to-oxidize **3** with TCNE led to the isolation of $\mathbf{3}^+[TCNE]^{\bullet-}$. When this reaction is undertaken in the presence of excess TCNE, then a magnetic product, and not the electron-transfer salt, is obtained. $\mathbf{3}^+[TCNE]^{\bullet-}$ is stable in solution with non-Lewis base solvents or in the solid state (−78 °C) for extended periods of time but is only moderately stable in solvents such as THF at room temperature. Hence, the bulky 1,3,5-tri-*tert*-butylbenzene ligand imparts an increased stability on $\mathbf{3}^+$ with respect to nucleophilic attack enabling the isolation and subsequent characterization of $\mathbf{3}^+[TCNE]^{\bullet-}$.

Structures of $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$. The structures of both $\mathbf{3}^+[BPh4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ were determined by single-crystal X-ray analyses, Table 1, Figure 2. Although $M^0[C_6H_3(t\text{-}Bu)_3]_2$ (M = Y, Ti, Zr, Hf, V, Nb, Cr, W) have been synthesized via the co-condensation of early transition metal vapor with the arene ring,[22] structures of these complexes have not been reported. Selected bond lengths and bond angles of $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ are listed in Table 2. Both $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ display near-parallel planar rings with angles between mean ring planes of only 1.3 and 0.35°, respectively. The average VC bond distance in $\mathbf{3}^+[BPh_4]^-$ is 2.301(3) Å and in $\mathbf{3}^+[TCNE]^{\bullet-}$ is 2.297(3) Å, and both are significantly larger than the average VC bond distance reported for $\mathbf{2}^+$ [2.231(10) Å].[27] This is consistent with the presence of increased steric repulsion between rings for the $\mathbf{3}^+$ cations, due to the bulkier *t*-Bu groups with respect to Me groups. The arene rings in $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ are puckered. For $\mathbf{3}^+[BPh_4]^-$, the VC_{Bu} bond distances to vary between 2.299(3) and 2.341(3) Å while the VC_H bond distances range from 2.288(3) to 2.340(3) Å. For $\mathbf{3}^+[TCNE]^{\bullet-}$, the VC_{Bu} bond distances to vary between 2.263(3) and 2.299(3) Å while the VC_H bond distances range from 2.257(3) to 2.295(3) Å, Table 2. The *t*-Bu groups of $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ are eclipsed, and the *t*-Bu carbon atoms deviate from the mean plane of the ring by 0.259(4)−0.349(4) and 0.308(5)−0.391(5) Å, respectively, and therefore lie bent away from the metal center by approximately 14.5 ± 0.5° in relation to the mean ring plane. In comparison, the *t*-Bu groups of $Gd^0[C_6H_3(t\text{-}Bu)_3]_2$ are bent out of the plane of the arene ring by 6−10°.[28] This distortion from planarity of the arene ring in $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ is presumed to be due to interannular repulsion driven by the presence of the bulky *t*-Bu groups. The puckered C_6 ring in $\mathbf{3}^+[BPh_4]^-$ and $\mathbf{3}^+[TCNE]^{\bullet-}$ has also been noted to a lesser degree for $Gd^0[C_6H_3(t\text{-}Bu)_3]_2$, which has a significantly larger metal center allowing for greater separation between the rings [average Gd−C_{ring} bond distance is 2.630(4) Å].[28]

The $[TCNE]^{\bullet-}$ anion of $\mathbf{3}^+[TCNE]^{\bullet-}$ is slightly twisted about the central C═C bond creating a dihedral angle of 5.7(2)°. The C═C bond length is 1.389 Å, the C−C bond lengths vary between 1.426 and 1.450 Å, and the CN bond lengths vary between 1.119 and 1.129 Å. These bond lengths are very similar those found in the unbound anion of $[Cr^{I}(benzene)_2][TCNE]^{\bullet-}$ with reported CC, C−CN, and CN average bond lengths of 1.436, 1.414, and 1.140 Å,[29] respectively, and $[Fe^{III}(C_5Me_5)_2][TCNE]^{\bullet-}$ with reported CC, C−CN, and CN average bond lengths of 1.3926, 1.417, and 1.140 Å,[6b] respectively,

Magnetic Properties. The 2−300 K magnetic susceptibilities, χ, of **2**, **3**, $\mathbf{2}^+[BPh_4]^-$, $\mathbf{3}^+[BPh_4]^-$, and $\mathbf{3}^+[TCNE]^-$ have been measured, Figure 3. The $S = {}^1/_2$ V(0) complexes **2** and **3** obey the Curie−Weiss law, $\chi \propto (T - \theta)^{-1}$, above 150 K with $\theta = -0.40$ and 1.2 K, and temperature-independent paramagnetism (TIP) values of 200×10^{-6} and 300×10^{-6} emu/mol, respectively. The 300 K effective moments, μ_{eff} [$\equiv (8\chi T)^{1/2}$], are 1.81 and 1.74 μ_B, respectively, which are slightly higher than that reported for **1** (1.68 μ_B),[30] but are very close to the spin-only value of 1.73 μ_B expected for a $S = {}^1/_2$ complex. The $S = 1$ V(I) monocations $\mathbf{2}^+[BPh_4]^-$ and $\mathbf{3}^+[BPh_4]^-$ also obey the Curie−Weiss law with $\theta = 3.9$ and −5.9 K and TIP values of 200×10^{-6} and 220×10^{-6} emu/mol, respectively. The 300 K μ_{eff} are 2.91 and 2.83 μ_B, respectively, in agreement with a previously reported $\mathbf{2}^+[AlCl_4]^-$ (2.80 μ_B)[30] and the spin-only value of 2.83 μ_B expected for a $S = 1$ complex. Due to the paucity of variable-temperature magnetic studies of bis(arene)-vanadium complexes, θ and TIP values are generally unavailable, but temperature-dependent moments characteristic of having TIPs have been reported for low-spin d^4 and d^5 compounds.[31] The slight increase in μ_{eff} below 10 K for both **2** and $\mathbf{2}^+[BPh_4]^-$ requires further study.

The susceptibility of $\mathbf{3}^+[TCNE]^{\bullet-}$ above 100 K obeys the Curie−Weiss law with $\theta = -0.7$ K and a TIP of 200×10^{-6} emu/mol and has a 240 K[32] μ_{eff} of 3.28 μ_B, Figure 3. This moment is consistent with the expected spin-only moment of 3.32 μ_B for an independent $S = {}^1/_2$ plus $S = 1$ spin system.

The magnetically ordered $V[TCNE]_x\cdot yS$ materials, prepared from the reaction of (a) $V^0(arene)_2$ with TCNE, (b) $[V^{I}(arene)_2]^+$ with 1:1 $TCNE/[TCNE]^{\bullet-}$, (c) 1:2 $V^0(arene)_2/[Fe^{III}(C_5H_5)_2]^{\bullet+}$ with $[TCNE]^{\bullet-}$, (d) or $[V^{II}(NCMe)_6][B(3,5\text{-}C_6H_3(CF_3)_2)_4]_2$ with $[TCNE]^{\bullet-}$, display the presence of spontaneous magnetization below a critical temperature, T_c. T_c is determined as the intersection of the steepest slope of the magnetization curve with the temperature axis, when the sample is cooled in the absence of a field and warming is done under low applied fields. From the field dependence of the magnetization it is known that these $V[TCNE]_x\cdot yS$ materials are bulk ferrimagnets whereby antiferromagnetic interactions between the metal and ligand lead

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[32] This material was only measured up to 240 K due to instrumental difficulties.

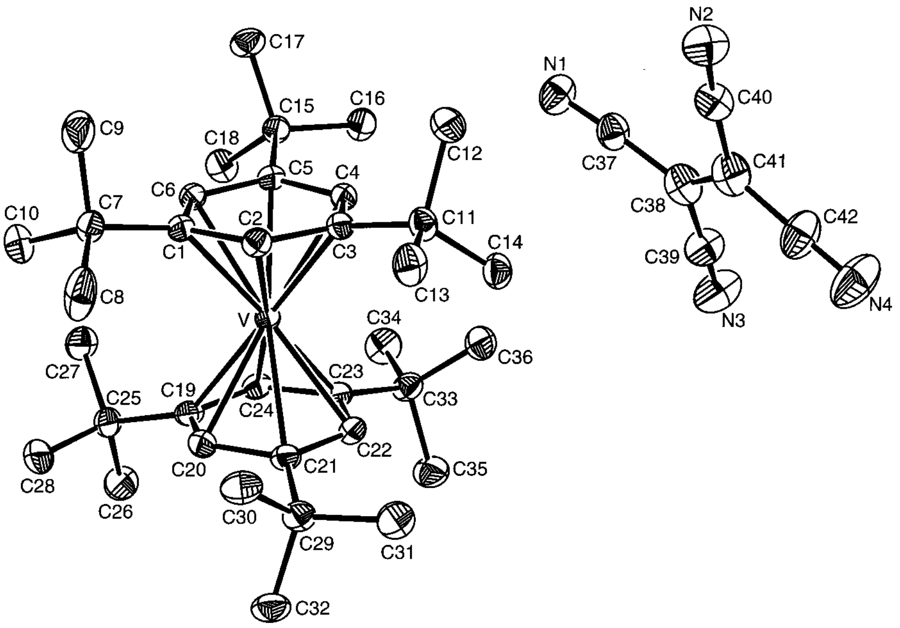

Figure 2. ORTEP (ellipsoids at 30% probability) and atom-labeling diagram for $\{V^I[C_6H_3(t\text{-}Bu)_3]_2\}[TCNE]$, $\mathbf{3}^+[TCNE]^{\bullet-}$. The same cation labeling scheme is used for $\mathbf{3}^+[BPh_4]^-$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{V^I[C_6H_3(t\text{-}Bu)_3]_2\}[BPh_4]\cdot THF$, $\mathbf{3}^+[BPh_4]^-$, and $\{V^I[C_6H_3(t\text{-}Bu)_3]_2\}[TCNE]\cdot{}^3/_2THF$, $\mathbf{3}^+[TCNE]^{\bullet-}$

	$\mathbf{3}^+[BhPh_4]^-$	$\mathbf{3}^+[TCNE]^{\bullet-}$
Bond Distances		
$V-C_{phenyl}$ (1−6)	2.277(3)−2.341(3)	2.272(3)−2.340(3)
$V-C_{phenyl}$ (19−24)	2.263(3)−2.329(3)	2.257(3)−2.339(3)
$C_{phenyl}-C_{phenyl}$	1.402(4)−1.428(4)	1.406(4)−1.423(4)
$C_{phenyl}(1)-C_{butyl}(7)$	1.531(4)	1.532(4)
$C_{phenyl}(3)-C_{butyl}(11)$	1.543(4)	1.538(4)
$C_{phenyl}(5)-C_{butyl}(15)$	1.537(4)	1.542(4)
$C_{butyl}(7)-C_{methyl}(8-10)$	1.516(5)−1.545(5)	1.516(5)−1.529(5)
$C_{butyl}(11)-C_{methyl}(12-14)$	1.530(4)−1.535(4)	1.530(5)−1.541(5)
$C_{butyl}(15)-C_{methyl}(16-18)$	1.522(4)−1.537(4)	1.528(5)−1.534(5)
Bond Angles		
$C_{phenyl}-C_{phenyl}-C_{phenyl}$	116.4(3)−122.9(3)	117.4(3)−122.5(3)
$C_{phenyl}(1)-C_{butyl}(7)-C_{methyl}(10)$	106.5(3)	113.0(3)
$C_{phenyl}(3)-C_{butyl}(11)-C_{methyl}(14)$	105.9(2)	109.1(3)
$C_{phenyl}(5)-C_{butyl}(15)-C_{methyl}(16)$	111.5(2)	112.6(3)

to uncompensated spin.[2a,c,4,21,33] **8** formed from the reaction between $\mathbf{2}^+$ and $[TCNE]^{\bullet-}$ neither orders magnetically nor simply obeys the Curie−Weiss law. The data can be fit to the Curie−Weiss expression with $\theta = -28$ K ($T > 100$ K) and $\theta = -570$ K ($200 < T < 300$ K).

Infrared Spectra. All magnetically ordered V[TCNE]$_x$·yS precipitates display a complex, nominal three-absorption peak pattern for υ_{CN} stretching modes as previously reported, Table 3, Figure 4.[4] TCNE^0 has υ_{CN} absorption bands that occur above 2200 cm^{-1}.[34] The $[TCNE]^{2-}$ υ_{CN} absorption bands are found at 2139 (m) and 2057 (s) cm^{-1} [34,35a] and at 2176 (m) and 2097 (s) cm^{-1} for bound μ-$[TCNE]^{2-}$.[35b] The υ_{CN} absorption bands for coordinated and noncoordinated $[TCNE]^{\bullet-}$ occur between these values.[34] Therefore, from the υ_{CN} stretching frequencies of the magnetic precipitates, typically around 2210(m), 2190(m) and 2146(s), it is concluded that $[TCNE]^{\bullet-}$ is present as coordinated $[TCNE]^{\bullet-}$. Two bands are expected for either isolated or trans-μ bonded $[TCNE]^n$ ($n = 0$, 1-, 2). The presence of the additional bands suggest the presence of μ_3-, and μ_4-$[TCNE]^n$, as reported for $[Mn(C_5Me_5)(CO)_2]_3[TCNE]$,[36a] $[Mn(C_5Me_5)(CO)_2]_4[TCNE]$,[36a] and $[Ru(NH_3)_5]_4[TCNE][PF_6]_8$.[36b] Additionally, cis-μ bridging may be present and lead to additional absorptions. Furthermore, the complex and broad nature of the absorptions suggest that mixtures of bonding motifs are present. Similar absorptions have been reported for V[TCNE]$_x$.yS prepared from $V(CO)_6$.[21] The nonmagnetic product **8** from the reaction of $\mathbf{2}^+$ with $[TCNE]^{\bullet-}$ displays a very different υ_{CN} absorption band pattern [2201(m), 2146(m), 2110(s)]. The thermolysis of $\mathbf{3}^+[TCNE]^{\bullet-}$ (**12**), which presumably forms a material of nominal $V^+[TCNE]^{\bullet-}$ composition, has υ_{CN} bands [2205(m), 2122(s)] that do not resemble that for **8**. Nonetheless, like **8**, **12** lacks the υ_{CN} absorption at ~2150 cm^{-1} present for all V[TCNE]$_x$·yS magnets, and its 2122(s) is close to the 2110(s) band for **8**. The relationship between this spectrum and the magnetic properties of the material has yet to be established.

All V[TCNE]$_x$·yS precipitates, magnetic or not, do not have an absorption at ~1000 cm^{-1} assignable to $\upsilon_{V=O}$, indicating that the material has not undergone accidental oxidation during manipulation. In addition, a $\upsilon_{C=C}$ band is not observed for these materials. Such a band (~1400 cm^{-1}) either may be obscured by intense Nujol absorption in this area or may be absent due to the TCNE adopting binding modes that lead to IR-inactive C=C vibrations.

The only V-containing sample that does not display this three-banded pattern is $\mathbf{3}^+[TCNE]^{\bullet-}$, which possesses υ_{CN} absorptions at 2185 (s) and 2146 (s) cm^{-1}, diagnostic of isolated unbound $[TCNE]^{\bullet-}$.[6b,34] These bands are very similar to the υ_{CN} absorp-

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[33] The magnetically ordered products of the reactions with $\mathbf{2}^n$ and $\mathbf{3}^n$ ($n = 0$, 1+) display significant variation in T_c, dependent upon reaction temperature, solvent, and complex oxidation state, as reported earlier.[4,5] The synthetic procedure that favors the formation of such a binding mode that leads both to strongly coupled V^{II} and $[TCNE]^{\bullet-}$ radicals and to a 3-D network will be the one that leads to the product with the highest T_c. As the synthetic procedure used to produced these materials suffers from the shortcoming that all solids immediately precipitate from solution, it becomes clear that a controlled and reproducible method for magnet formation is required in order to consistently yield the desired magnetic properties. This is currently under further investigation in this laboratory.

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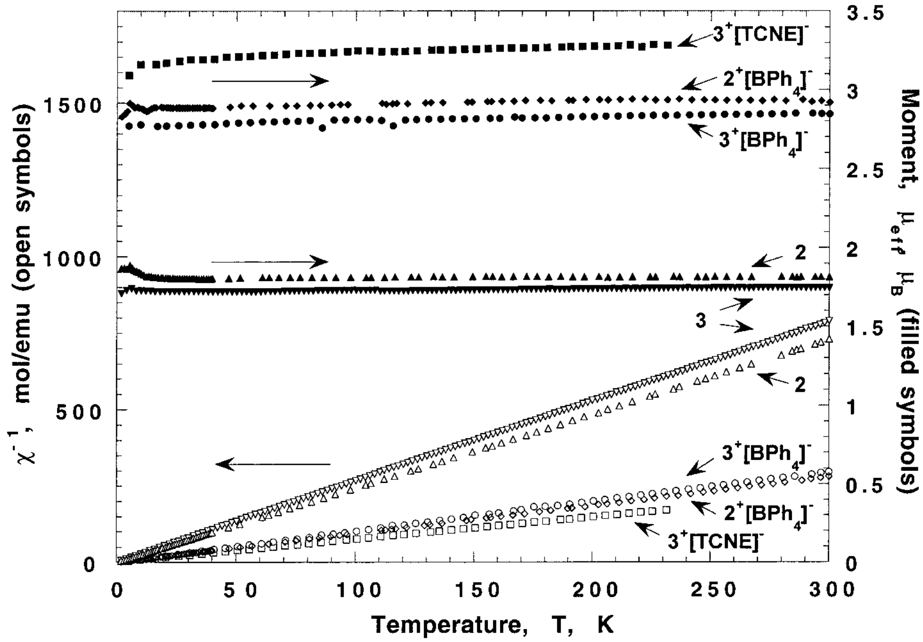


Figure 3. Magnetic moment and reciprocal susceptibility of **2** (▲, △), **3** (▼, ▽), **2**$^+$[BPh$_4$]$^-$ (◆, ◇), **3**$^+$[BPh$_4$]$^-$ (●, ○), and **3**$^+$[TCNE]$^{•-}$ (■, □).

Table 3. Summary of the υ_{CN} IR Absorption Data

compd	υ_{CN}, cm^{-1}
4	2197 (m), 2097 (s, br)
5	2190 (m), 2147 (s), 2101 (w)
6	2218 (m), 2152 (s,br)
7	2200 (m), 2104 (s, br)
8	2201 (m), 2146 (m), 2110 (s)
9	2188 (m), 2146 (m), 2101 (w)
10	2212 (m), 2192 (m), 2146 (s, br), 2100 (sh)
3$^+$[TCNE]$^{•-}$	2185 (s), 2146 (s)
11	2218 (m), 2194 (m), 2155 (s), 2100 (sh)
12	2205 (m), 2122 (s)
13	2193 (m), 2159 (m), 2034 (w, br)
14	2212 (w), 2192 (m), 2154 (s), 2041 (m, br)
15	2213 (m), 2110 (s)
16	2300 (vw), 2214 (m), 2111 (s)
17	2298 (vw), 2212 (m), 2098 (s)

tions at 2183 and 2144 cm^{-1} reported for, e.g., [n-Bu$_4$N]$^+$[TCNE]$^{•-}$ [8] and [Fe^{III}(C$_5$Me$_5$)$_2$]$^+$[TCNE]$^{•-}$,[6b] confirming that isolated [TCNE]$^{•-}$ is present.

V^{II} Identified as the Key Intermediate. As noted for **1**,[4] the reactions of **2** and **3** with TCNE lead to the rapid formation of black insoluble precipitates **5** and **11** that magnetically order at ~260 and ~205 K, respectively. These T_c's are lower than that reported from the reaction with **1** with a T_c ~400 K,[4] but as noted for the reactions with **1**, the T_c's are highly sensitive to reaction conditions (temperature and solvent), ranging from ~28 to ~400 K.[4,5,33] These differences are attributed to a variation in [TCNE]$^{•-}$ bonding motifs leading to different connectivities, which directly affects the magnetic coupling between metal centers as well as the υ_{CN} absorptions.

The determination of a viable mechanism, either the disproportionation reaction (Scheme 1) or the electron-transfer reaction (Scheme 2) (vide infra), for the formation of the V(TCNE)$_x$ magnet is the question that the following reactions address. Central to this issue is the importance of the presence of a V^{II} species, which the results support as being the key intermediate toward magnet formation. Once produced, the [V^{II}(arene)$_2$]$^{2+}$ species reacts with either (a) [TCNE]$^{•-}$, producing the magnetic product, or (b) a coordinating solvent (S) to form the well-known [V^{II}S$_6$]$^{2+}$, which reacts with [TCNE]$^{•-}$ to form the magnetic product. It will be demonstrated that the disproportionation reaction is not a kinetically important mechanism. The oxidation of [V^I(arene)$_2$]$^+$ by TCNE will be discussed as the likely path for formation of the magnet. It is important to note that as the

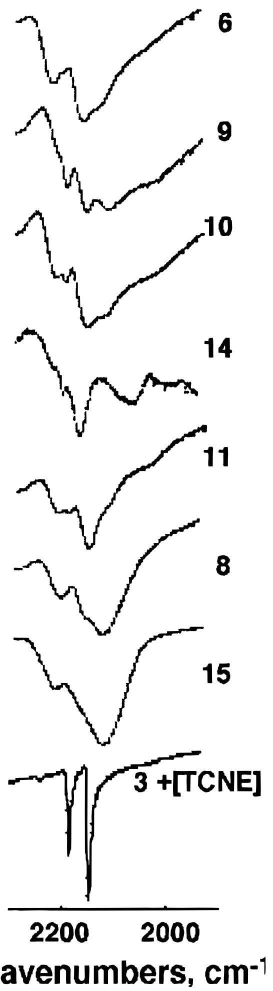
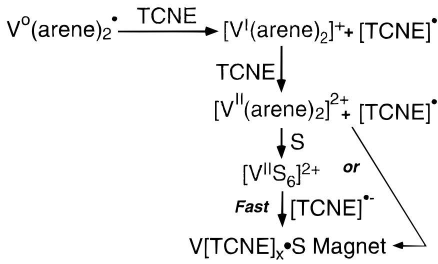


Figure 4. υ_{CN} IR absorptions for representative V[TCNE]$_x$•yS materials.

Scheme 2



V(TCNE)$_x$ product precipitates from solution, the oxidation reactions that form the V^{2+} species must be considered as irreversible. The product insolubility can therefore drive the oxidation reaction to completeness despite the formal reduction potential of TCNE having more negative potentials than the oxidation potential of [V^I(arene)$_2$]$^+$.[15]

The reactions of [V^I(arene)$_2$]$^+$ with [TCNE]$^{•-}$ directly address the importance of the disproportionation mechanistic step in the formation of a magnetic precipitate and would suggest that the formation of a "[V^{II}(arene)$_2$]$^{2+}$" species in situ has occurred. Attempts to isolate [V^{II}(arene)$_2$]$^{2+}$ as the [BPh$_4$]$^-$ salt were unsuccessful. Importantly, there is no reaction observed nor precipitate produced from the stoichiometric reaction between **3**$^+$[BPh$_4$]$^-$ and [n-Bu$_4$N]$^+$[TCNE]$^{•-}$ either at −78 °C or at room temperature for one week in CH$_2$Cl$_2$. Redox chemistry was not anticipated to occur between **2**$^+$ or **3**$^+$ and [TCNE]$^{•-}$. This demonstrates the stability of the **3**$^+$ cation under these conditions toward decomposition in the presence of nucleophiles such as [TCNE]$^{•-}$. In contrast to this reaction, the reaction of **2**$^+$[BPh$_4$]$^-$ with [n-Bu$_4$N]$^+$[TCNE]$^{•-}$ leads to the immediate formation of black insoluble precipitate **8**, which does not exhibit a spontaneous magnetization. This result is consistent with the rapid decomposition of the cation **2**$^+$ in the presence of the nucleophile [TCNE]$^{•-}$, leading to the precipitate, but not the V[TCNE]$_x$·yS magnet as an oxidant to oxidize V^I to V^{II} is not present. The presence of a magnetic product would only be expected should the disproportionation of the monocation be sufficiently rapid to produce [V^{II}(arene)$_2$]$^{2+}$ before precipitate formation, and this does not occur. Therefore, since the IR spectrum for this material does not display aromatic υ_{CH} bands (∼3060 cm^{-1}) and the υ_{CN} bands [2201 (m), 2146 (m), 2110 (s)] are consistent with μ_n ($n > 2$) bound [TCNE]$^{•-}$,[36] we attribute this insoluble material as a [n-Bu$_4$N]$_{x-1}$V^I[TCNE]$_x^{•-}$·yS-containing polymeric material. As **8** does not display magnetic ordering, it was not studied in greater detail.

In contrast, addition of 1 equiv of both TCNE and [n-Bu$_4$N]$^+$[TCNE]$^{•-}$ to the reaction with either **2**$^+$[BPh$_4$]$^-$ or **3**$^+$[BPh$_4$]$^-$ leads to the rapid formation of magnetically ordered **13** and **9**, respectively. Likewise, addition of 2 equiv of the one-electron oxidant, [Fe^{III}(C$_5$H$_5$)$_2$]$^+$, to **2** and the immediate reaction of this product with [n-Bu$_4$N]$^+$[TCNE]$^{•-}$ leads to the formation of magnetically ordered **10**. The production of magnetic product in the former reaction is attributed to the oxidation of **2**$^+$ or **3**$^+$ by TCNE, confirming that [TCNE]$^{•-}$ is an insufficient oxidant to oxidize V^I to V^{II}. The magnetic product from the latter reaction is attributed to the oxidation of **2**$^+$ or **3**$^+$ by [Fe^{III}(C$_5$H$_5$)$_2$]$^+$, further confirming that [TCNE]$^{•-}$ is an insufficient to oxidize V^I to V^{II}.

Since **3**$^+$[TCNE]$^{•-}$ is readily isolated, the results from the above reactions are inconsistent with the initial hypothesis that the disproportionation reaction is a key step, Scheme 1, toward the formation of a V^{II} species. Thus, the kinetics of the disproportionation of **3**$^+$[BPh$_4$]$^-$ or **3**$^+$[TCNE]$^{•-}$ is not sufficiently rapid to observe the formation of a magnetic precipitate. For complexes containing less hindered arene rings, such as **2**$^+$I$^-$ and **2**$^+$[AlBr$_4$]$^-$, this reaction has been reported as very rapid and plays an important role in the formation of a V^{II} species.[20b] Since a magnetic product is not obtained from the reaction between **2**$^+$[BPh$_4$]$^-$ and [TCNE]$^{•-}$, this reaction does not appear to play an important role in the reaction of less hindered arenes, including the reaction of **1** that leads to the room-temperature V[TCNE]$_x$·yS magnet.

Due to V^0(arene)$_2$ being redox active in the presence of TCNE, we hypothesize that the V^{II} species could alternatively be formed from a second one-electron oxidation with another TCNE molecule, Scheme 2, eq 5.

$$[\mathrm{V^I(arene)_2}]^+ + \mathrm{TCNE} \rightarrow [\mathrm{V^{II}(arene)_2}]^{2+} + [\mathrm{TCNE}]^{\bullet-} \quad (5)$$

$$[\mathrm{V^I(arene)_2}]^+ + [\mathrm{TCNE}]^{\bullet-} \rightarrow [\mathrm{V^{II}(arene)_2}]^{2+} + [\mathrm{TCNE}]^{2-} \quad (6)$$

$$[\mathrm{V^I(arene)_2}]^+ + [\mathrm{TCNE}]^{\bullet-} \rightarrow [\mathrm{V^I(arene)_2}]^+[\mathrm{TCNE}]^{\bullet-} \quad (7)$$

As previously discussed, [TCNE]$^{•-}$ is too weak of an oxidant to oxidize [V^I(arene)$_2$]$^+$ to '[V^{II}(arene)$_2$]$^{2+}$', which reduces [TCNE]$^{•-}$ to [TCNE]$^{2-}$, eq 6. The reaction of [V^I(arene)$_2$]$^+$ and [TCNE]$^{•-}$, eq 7, does not produce a magnetic material, but leads either to the stable **3**$^+$[TCNE]$^{•-}$ or to the nonmagnetic precipitate, of putative [n-Bu$_4$N]$_{1-x}$V^I[TCNE]$_x$·yS composition when 1,3,5-trimethylbenzene is used as the ligand. Therefore "[V^{II}(arene)$_2$]$^{2+}$" is hypothesized to be the key intermediate in the formation of the V[TCNE]$_x$·yS magnet from the reaction of bis(arene)vanadiums and TCNE, Scheme 2. However, its formation may additionally include the kinetically slower disproportionation of [V^I(arene)$_2$]$^+$.

Scheme 2 is consistent with all the reactions between V−arene complexes and TCNE and correctly predicts which reactions lead to magnetically ordered or nonordered products. The magnetic behavior of several representative compounds is shown in Figure 5. As reported for **1**,[4] reactions between the V^0(arene)$_2$ complexes, **2** or **3**, and TCNE both lead to magnetic materials, **5** and **11**, respectively. For these reactions, the excess TCNE serves to doubly oxidize V^0(arene)$_2$, and form the V[TCNE]$_x$·solvent magnets. Recall that it is the irreversible reaction from eq 5 that drives this electron-transfer reaction. As with **1**,[4] the stoichiometric (1:1) reaction between **2** and TCNE also yields a magnet (**7**), whereas unlike for **1**,[4] the same reaction between **3** and TCNE yields the stable salt **3**$^+$[TCNE]$^{•-}$. This is attributed to the kinetic stabilization of **3**$^+$ with respect to **1**$^+$ and **2**$^+$ due to the bulkier arene ligand. **7**, however, may include material in which spontaneous moment does not occur, since vanadium in oxidation states lower than two may be present.

Material that does not display a spontaneous magnetization (**8**), likely of nominal [n-Bu$_4$N]$_{x-1}$V^I[TCNE]$_x$·yS composition, was produced from the reaction between **2**$^+$ and [TCNE]$^{•-}$. This result is consistent with the inability of [TCNE]$^{•-}$ to oxidize **2**$^+$ to **2**$^{2+}$. However, when this same reaction between **2**$^+$ and [TCNE]$^{•-}$ is done in the presence of TCNE, the magnetic precipitate **9** is formed, indicating that TCNE is a sufficiently strong oxidant to oxidize **2**$^+$. The direct reaction of [V^{II}(NCMe)$_6$]{B[3,5-C$_6$H$_3$(CF$_3$)$_2$]$_4$}$_2$ and [n-Bu$_4$N][TCNE], as expected, leads to the magnetic product **14**. Similar results were obtained from the reaction between [V^{II}(NCMe)$_6$][BPh$_4$]$_2$ and [n-Bu$_4$N][TCNE].[21] All of these reactions are consistent with both V^{II} and [TCNE]$^{•-}$ being required in order to produce a final product that displays magnetic ordering.

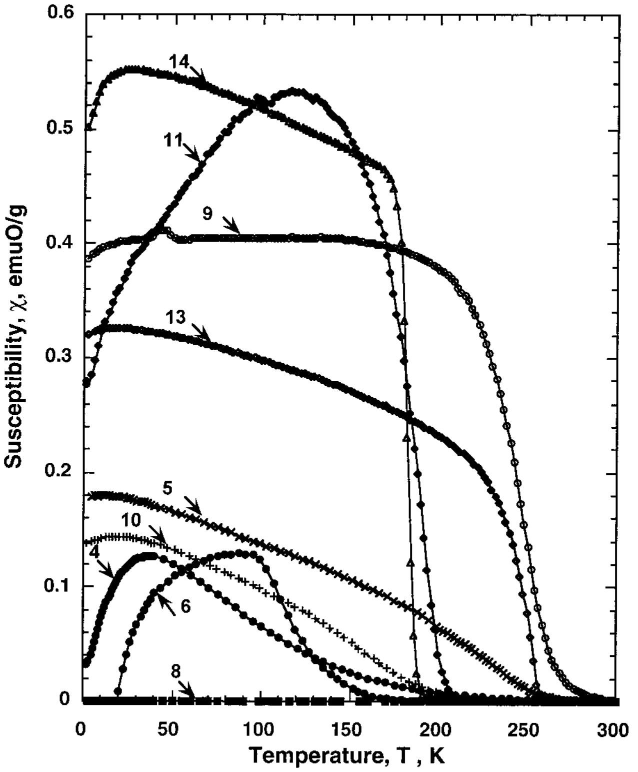


Figure 5. Temperature dependence of the susceptibility, $\chi(T)$, for representative V[TCNE]$_x$·yS materials.

Cr[TCNE]$_x$·ySolvent. In contrast to the reaction of V^0(arene)$_2$ and TCNE to form magnetically ordered materials of nominal V[TCNE]$_x$·yS composition, the reaction of Cr^0(arene)$_2$ and TCNE forms $[Cr^I(arene)_2]^+[TCNE]^{•-}$,[29] which does not magnetically order. Alternatively, reaction of $M^{II}I_2$·xMeCN (M = Mn, Fe, Co, Ni) with TCNE forms M[TCNE]$_x$·yS[7] magnets displaying reduced T_c's with respect to M = V. Due to the greater covalency of $Cr^{II}I_2$, Cr[TCNE]$_x$·yS has yet to be prepared and was targeted for preparation.

The key intermediate in the mechanism outlined in Scheme 2 is $[M^{II}(arene)_2]^{2+}$, formed from two one-electron oxidation reactions with TCNE. This suggests that $[Cr^{II}(arene)_2]^{2+}$ also needs to be generated in order to form the desired Cr[TCNE]$_x$·yS. Cr^0(arene)$_2$ complexes are harder to oxidize than the corresponding V^0(arene)$_2$ complexes, e. g., $Cr^0(C_6H_6)_2$: $E_{1/2}{}^{+/0} = -0.69$ V (vs SCE; DME).[24] As the reaction of Cr^0(arene)$_2$ with TCNE leads to $[Cr^I(arene)_2]^+[TCNE]^{•-}$,[29] a more labile arene ligand was sought. Cr^0Np_2 (Np = naphthalene) [$E_{1/2}{}^{+/0} = -1.19$; $E_{1/2}{}^{2+/+} = +0.20$ V (vs Ag/AgNO$_3$; THF)][37] was identified and targeted to react with TCNE. Cr^0Np_2 can be readily oxidized to the dication due to the appropriate reduction potential for TCNE,[26] and the Np ligand is more labile than benzene-based arene ligands.[38] Furthermore, these potentials render the production of either $[TCNE]^{2-}$ or a Cr^{III} metal center unlikely.

As expected, a black precipitate **15** was immediately produced upon reacting Cr^0Np_2 with TCNE in toluene. In addition to supporting the proposed mechanism (Scheme 2), Cr[TCNE]$_x$·yPhMe was available for study. Unexpectedly, Cr[TCNE]$_x$·yPhMe does not magnetically order above 2 K (vide infra). Cr[TCNE]$_x$·yS was also prepared from the reactions of $[Cr^{II}(NCMe)_4][BF_4]_2$ and $[Cr^{II}(NCMe)_6][B(3,5\text{-}C_6H_3(CF_3)_2)_4]_2$ with [n-Bu$_4$N][TCNE], **16** and **17**, respectively, and exhibits similar spectral and magnetic properties, Figure 6.

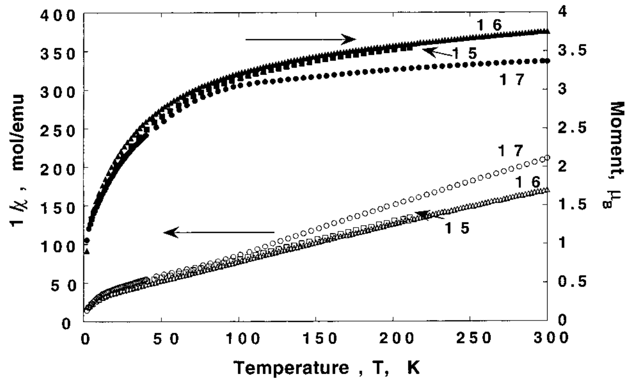


Figure 6. Magnetic moment (filled symbols) and reciprocal susceptibility (open symbols) of Cr[TCNE]$_x$· formed from the reaction of Cr^0Np_2 and TCNE (**15**; □, ■) and from the reaction of $[Cr^{II}(NCMe)_4][BF_4]_2$ (**16**; △, ▲) and $[Cr^{II}(NCMe)_6][B(3,5\text{-}C_6H_3(CF_3)_2)_4]_2$ (**17**; ○, ●) with [n-Bu$_4$N] [TCNE].

The solvent content in the nonmagnetic Cr-containing reaction products was determined by TGA/MS, assuming Cr[TCNE]$_2$, as results from elemental analysis were not readily interpretable, possibly due to oxygen contamination. This led to the following composition for **15**, **16**, and **17**: Cr[TCNE]$_2$·0.5PhMe, Cr[TCNE]$_2$·1.9MeCN, and Cr[TCNE]$_2$·2MeCN, respectively.

The 2−300 K magnetic susceptibility of **15**, prepared from the reaction of Cr^0Np_2 and TCNE, can be fit to the Curie−Weiss expression above 50 K with $\theta = -75$ K. The 300 K μ_{eff} is 3.54 μ_B, Figure 6. Similar results are noted for **16** and **17**, i.e., $\theta = -70$ K, $\mu_{eff}(210\ K) = 3.75\ \mu_B$ and $\theta = -42$ K, μ_{eff} (300 K) = 3.37 μ_B, respectively. Assuming a Cr(TCNE)$_2$·yS composition, this independent $S = 2, {}^1/_2, {}^1/_2$ system should have a moment of 5.47 μ_B. Strong antiferromagnetic coupling, as evidenced by the θ values of <-42 K should lead to reduced values of the moment, as observed. Variations between the high-temperature μ_{eff} values may be due to residual solvent not accounted for by TGA/MS.

For these materials, the large negative θ value characterizes the magnetic interaction between spin centers as strongly antiferromagnetic, as observed for materials composed of M = V, Mn, Fe, Co, Ni metal centers.[7] Surprisingly, however, magnetic ordering, e.g., antiferro- ferri-, metamagnetic ordering is not observed above 2 K. This is in sharp contrast with the magnetic behavior observed for M = V, Mn, Fe, Co, Ni materials, which all order as ferrimagnets with T_c's of >44 K.[7] The surprising lack of magnetic ordering is not understood at the present time and is the subject of ongoing studies.

The IR spectra of the Cr[TCNE]$_x$·yS materials display υ_{CN} absorption bands that do not appear for the magnetically ordering V[TCNE]$_x$ materials. **15**, **16**, and **17** exhibit υ_{CN} absorptions at 2213 (m), 2110 (s); 2300 (vw), 2214 (m), 2111 (s); and 2298 (vw), 2212 (m), 2098(s) cm^{-1}, respectively. The lowest energy bands at ~2100 cm^{-1} are not characteristic of the spectra observed for the magnetically ordering M[TCNE]$_x$·yS (M = V, Mn, Fe, Co, Ni) class of materials.[4,7] It is interesting to note that a υ_{CN} band at 2110 cm^{-1} was also observed for **8** from the reaction between $\mathbf{2}^+[BPh_4]^-$ with $[n\text{-}Bu_4N]^+[TCNE]^{•-}$ that is a nonmagnetic black precipitate. Although these υ_{CN} bands cannot be assigned to a particular $[TCNE]^{•-}$ binding mode, it is clear that a correlation exists between the observation of these bands and the presence of strongly antiferromagnetic coupling

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and no magnetic ordering in the sample; however, the relationship between the metal center electronic state and $[\mathrm{TCNE}]^{\bullet-}$ binding mode that leads to this magnetic behavior remains unclear.

Conclusion

The reactions between $[\mathrm{V(arene)_2}]^n$ ($n = 0, 1+, 2+$) and $[\mathrm{TCNE}]^y$ ($y = 0, 1-$), as well as the reactions between $[\mathrm{V^{II}(NCH)_6}]^{2+}$ and $[\mathrm{TCNE}]^{\bullet-}$, indicate that V^{2+} is a key intermediate toward the formation of the room-temperature $\mathrm{V[TCNE]}_x\cdot y\mathrm{S}$ magnet. The data presented support the reaction mechanism in which two independent one-electron-transfer reactions occur with TCNE as the oxidant, while reactions probing the possible presence of a disproportionation reaction with $[\mathrm{V^I(arene)_2}]^+$ did not lead to the magnetic product. The variation in magnetic properties and IR spectra of the $\mathrm{V[TCNE]}_x$ magnets from different routes clearly demonstrates that control over the structure of the magnetic precipitate is required in order to obtain consistent material properties. Exploitation of this mechanism, which requires formation of $\mathrm{M^{II}}$, leads to formation of previously unreported $\mathrm{Cr(TCNE)}_x$. In contrast to the magnetic nature of the $\mathrm{M(TCNE)}_x$ (M = V, Mn, Fe, Co, Ni) materials, the reactions done with Cr do not follow this trend.

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Supporting Information Available: Crystallographic data including bond distances and angles and final positional and thermal parameters for $\mathbf{3}^+[\mathrm{BPh_4}]^-$ and $\mathbf{3}^+[\mathrm{TCNE}]^{\bullet-}$ are provided in PDF and CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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