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Reaction of $V(C_6H_6)_2$ with the Borane Adducts of Malononitrile $[(C_6F_5)_3B{\cdot}NCCH_2CN{\cdot}B(C_6F_5)_3]$ and Water $[H_2O{\cdot}B(C_6F_5)_3]$

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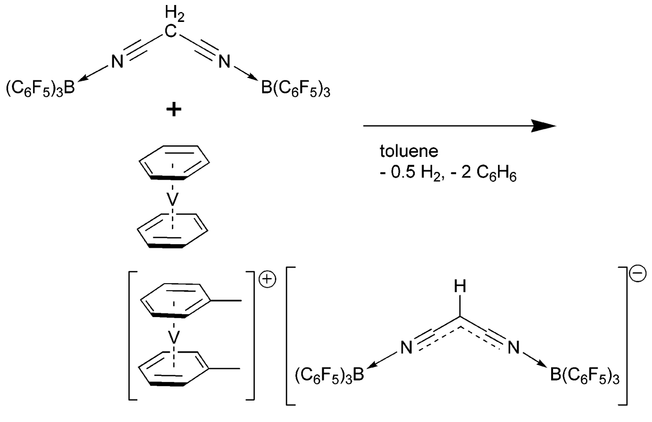
Summary: Reaction of malononitrile, $NCCH_2CN$, with $V(C_6H_6)_2$ in toluene in the presence of 2 equiv of $B(C_6F_5)_3$ afforded the vanadium(I) complex $[V(C_6H_5Me)_2][(F_5C_6)_3B{\cdot}NCCHCN{\cdot}B(C_6F_5)_3]$, in which deprotonation of the malononitrile ligand and arene exchange at the vanadium center have occurred. In the absence of malononitrile, a redox reaction was observed between $V(C_6H_6)_2$ and the water adduct $H_2O{\cdot}B(C_6F_5)_3$, which gave the vanadium(I) complex $[V(C_6H_6)_2][(F_5C_6)_3BOB(C_6F_5)_2]$.

The reactivity of the bis(benzene) vanadium with polynitriles is an active subject of research since the discovery of the exceptional room-temperature magnet $V(TCNE)_x$ prepared from $V(C_6H_6)_2$ and TCNE, by Miller et al.[1,2] Recently, we reported a new nitrile platform ligand based on the tris(perfluorophenyl)borane adduct of various nitriles. A recent exploration of the tris(perfluorophenyl)borane adduct of TCNX (X = E (tetracyanoethylene), Q (7,7,8,8-tetracyano-*p*-quinodimethane)) with Cp_2V has showed that the $[TCNX]^{2-}$ ligand is σ bonded to vanadium(III) or vanadium(IV) centers through a nitrile nitrogen atom such as in $[(Cp_2V)_2\{(F_5C_6)_3B{\cdot}(\mu_4\text{-TCNX}){\cdot}B(C_6F_5)_3\}]$.[3] We have also studied the reactivity of the metallocene complexes Cp_2V and $Cp_2Ti(CO)_2$ toward different Lewis acid (LA) adducts of nitriles $RCN{\cdot}B(C_6F_5)_3$. The behavior of the nitrile bond, when $RCN{\cdot}B(C_6F_5)_3$ was used as an "activated nitrile, was exemplified by the formation of M(IV)azirine complexes (M = Ti, V) such as $[Cp_2M(\eta^2\text{-C,N-RCN}{\cdot}B(C_6F_5)_3)]$.[4]

Starting from the idea that a LA adduct of a nitrile could be a useful tool to give a structural model for molecule-based magnets, we proposed to initiate the study of the reactivity of $V(C_6H_6)_2$ toward LA adducts of various nitriles. Herein we present our first results obtained with malononitrile in which two CN moieties are attached to two tris(pentafluorophenyl)boranes, $(C_6F_5)_3B{\cdot}NCCH_2CN{\cdot}B(C_6F_5)_3$.

Scheme 1. Synthesis of 1



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As depicted in Scheme 1, the reaction of $V(C_6H_6)_2$ with the in-situ-prepared $B(C_6F_5)_3$ adduct of the malonotritrile in toluene at room temperature gives a yellow product. Single-crystal X-ray structure analysis revealed that the compound is the salt $[V(C_6H_5CH_3)_2][(C_6F_5)_3B{\cdot}NCCHCN{\cdot}B(C_6F_5)_3]$, **1**, which crystallizes with two molecules of toluene. As revealed by the structure, two important features were observed. First the benzene ligand was exchanged with the toluene solvent in the vanadium cationic moiety to give the bis(toluene) vanadium cation, in which both rings have methyl groups in eclipsed position.[5] Second, the abstraction of one hydrogen atom on the malononitrile is evidenced by the sp^2 configuration at the central C2 atom (119.5(3)°). The data were of sufficiently high quality that we were able to locate the hydrogen atom on the carbon C2. Bond distances within the carbanion are also affected, as evidenced by comparison of the metric parameters in **1** with that of the bis-borane adduct of malononitrile, $[(C_6F_5)_3B{\cdot}NCCH_2CN{\cdot}BC_6F_5)_3]$ (**2**) (which was synthesized and characterized by X-ray structure determination for this purpose; see Figure 2). Indeed, the C−C bond distances in **1** (1.377(3) Å) are significantly shorter that in **2** (av 1.455 Å). The magnetic moment of **1**, which is nearly equivalent to two unpaired electrons (3.08 μ_B), supports the formation of a cationic $[V^I]$ species. Attempts to follow the reaction by NMR spectroscopy (^1H, ^{19}F) were unsuccessful due to the paramagnetism present in the solution. We note that in the absence of $V(C_6H_6)_2$ the malononitrile led to the sole formation of **2** when reacted with a large excess of $B(C_6F_5)_3$ (2−5 equiv).

Strong bases such as alkali metals are known to promote deprotonation of the acidic proton of malononitrile (or aceto-

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10.1021/om070052y CCC: $37.00

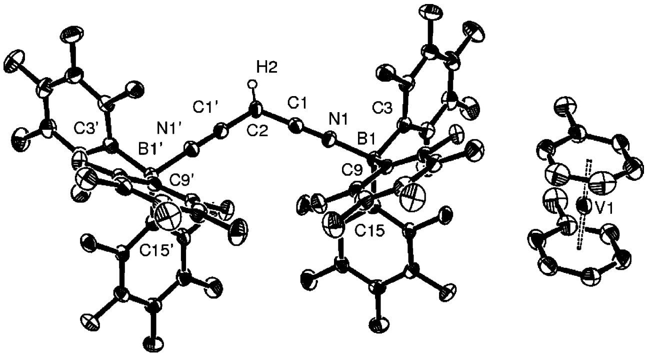


Figure 1. ORTEP drawing of the molecular structure of **1** showing 50% probability ellipsoids and partial atom-labeling scheme. H atoms are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg): V−C av 2.24, N1−C1 1.145(3), C1−C2 1.377(3), N1−B1 1.548(3), N1−C1−C2 179.2(3), C1−C2−C1 119.5(3).

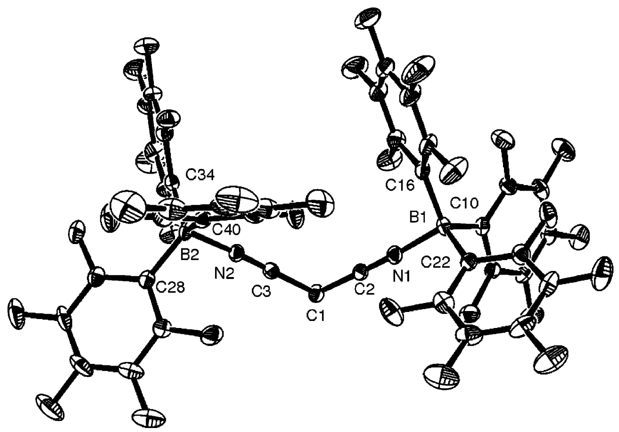


Figure 2. ORTEP drawing of the molecular structure of **2** showing 50% probability ellipsoids and partial atom-labeling scheme. H atoms are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg): C1−C2 1.459(5), C1−C3 1.452(5), N1−C1 1.125(4), N1−B1 1.603(5), N2−C3 1.125(4), N2−B2 1.610(5), C3−C1−C2 109.9(3), C2−N1−B1 175.4(4), C3−N2−B2 175.2(4).

nitrile), and a few examples of metal complexes were also reported in the literature to induce such reaction.[6,7] In this context, deprotonation of malononitrile by the electron-rich bis(benzene)vanadium would also be favored by the enhanced electrophilicity at the activated methylene carbon atom due to coordination of two $B(C_6F_5)_3$. A transient (17 electrons) cationic vanadium hydride species $[HV(C_6H_6)_2]^+$ may be involved in the formation of **1**.[8]

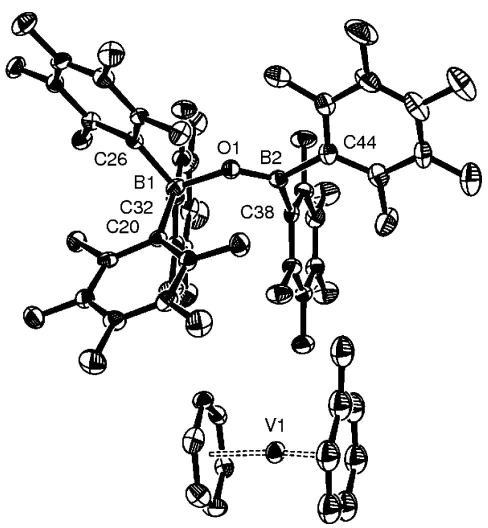
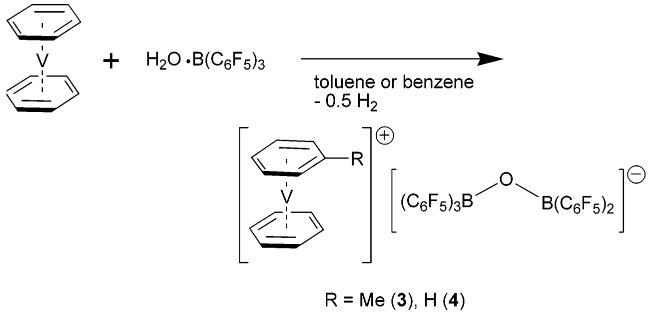


Figure 3. ORTEP drawing of the molecular structure of **3** showing 50% probability ellipsoids and partial atom-labeling scheme. H atoms are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg): V−C av 2.22, B1−O1 1.503(6), B1−O2 1.300(6), B1−O1−B2 137.5(4).

Scheme 2. Synthesis of Complexes 3 and 4



Crystals of another compound, **3** (different from **1**), were obtained from the filtrate solution during the synthesis of **1**. The crystallographic analysis of **3** reveals that **3** is the cationic vanadium species $[V(C_6H_6)(C_6H_5CH_3)][(C_6F_5)_3BOB(C_6F_5)_2]$ (**3**) (Figure 3). The presence of an oxygen atom in the anionic part of **3** is certainly due to some adventitious water in our synthesis (Scheme 2). In our hands, no reaction was observed between $V(C_6H_6)_2$ and H_2O in toluene or benzene.[9] By contrast, immediate evolution of H_2 gas was observed when $B(C_6F_5)_3$ was added to a wet toluene solution of $V(C_6H_6)_2$. In order to reproduce the formation of **3** and to better control the amount of added water in the reaction, the solid water adduct $H_2O \cdot B(C_6F_5)_3$ was used. The reaction with $V(C_6H_6)_2$ was performed in benzene to avoid ligand exchange reaction with toluene. The ionic complex **4**, composed of a cationic vanadium species $[V(C_6H_6)_2]^+$ associated with the anion $[(C_6F_5)_3BOB(C_6F_5)_2]^-$, was fully characterized by X-ray structure determination (Figure 4). Complexes **3** and **4** are paramagnetic with two unpaired electrons, which supports the formation of a cationic $[V^I]$ species. The crystal structures of the cationic vanadium moieties of **3** and **4** do not show any special features. The anionic part was also already structurally characterized as the salt $[NEt_3H][(C_6F_5)_3BOB(C_6F_5)_2]$.[10] The B−O−B angles observed in **3** and **4** (141.0(3)° and 137.5(4)°, respectively) are significantly

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(8) An example of a V−H bond obtained by redox and disproportionation reactions was recently reported in our group. It consisted of a two-electron reduction of water, mediated by Cp_2V in the presence of $B(C_6F_5)_3$ and resulted in the formation of a V^{III} hydride complex. Choukroun, R.; Lorber, C.; Vendier, L.; Lepetit, C. *Organometallics* **2006**, *25*, 1551−1553.

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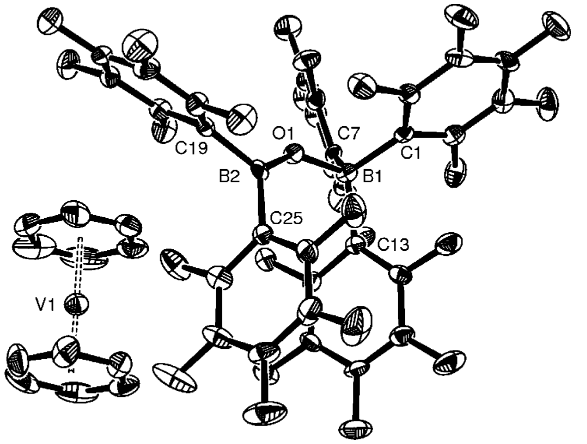

Figure 4. ORTEP drawing of the molecular structure of **4** showing 50% probability ellipsoids and partial atom-labeling schemes. H atoms are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg): V−C av 2.22, B1−O1 1.494(4), B1−O2 1.294(4), B1−O1−B2 141.0(3).

different from that observed in the salt $[NEt_3H][(C_6F_5)_3BOB(C_6F_5)_2]$ (134.07(13)°). It is worth noting that the salt $[NEt_3H][(C_6F_5)_3BOB(C_6F_5)_2]$ was synthesized by treating an equimolar mixture of $B(C_6F_5)_3$ and the bis(pentafluorophenyl)boronic acid $(F_5C_6)_2BOH$ in the presence of NEt_3.[10] The above suggested mechanism based on the intermediate formation of $(F_5C_6)_2BO^-$ could be operative in our system, but our attempts to prepare **3** (or **4**) from an equimolar ratio of $V(C_6H_6)_2$, $B(C_6F_5)_3$, and $(F_5C_6)_2BOH$ gave only untractable oils.

Moreover when the reaction between $V(C_6H_6)_2$ and $H_2O\cdot B(C_6F_5)_3$ is performed in deuterated benzene, the presence of C_6F_5H and H_2 was detected by NMR (^1H and ^{19}F), which implies a redox reaction with $V(C_6H_6)_2$ and the possible formation of a vanadium hydride.[8] Unfortunately, ^{19}F NMR spectroscopic studies of **3** or **4** in a polar solvent (THF-d_8, CD_3CN or CD_2Cl_2 in which **3** and **4** are soluble) did not show the characteristic peaks of the anionic part of the borinatoborate moiety as for $[NEt_3H][(C_6F_5)_3BOB(C_6F_5)_2]$. Instead, the spectra revealed the presence of THF or acetonitrile adducts of $B(C_6F_5)_3$ along with peaks arising from the decomposition of **3** or **4**, probably through disproportionation of vanadium(I) to $V(C_6H_6)_2$ and vanadium(II) complexes (coordinative solvents are known to initiate disproportionation of vanadium(I) complexes).[13]

All the ionic complexes reported in this paper showed easy substitution of the arene ligand during the redox V^0-V^I reaction with the bis(benzene)vanadium. Arene exchange is usually observed in late transition metals.[11] Nevertheless, an example of arene exchange in bis(benzene)vanadium has, to our knowledge, never been observed, except in the reaction of laser-vaporized vanadium atoms with arene vapor.[12] In the present work, the benzene for toluene exchange probably resulted from the presence of a large excess of toluene, which is also a better electron donor than benzene. The cationic species $[V(C_6H_6)_2]^+$ is generally known for its tendency to disproportionate to neutral $[V(C_6H_6)_2]$, V^{II}, and V^{III} compounds,[13] whereas in the present study the vanadium(I) center is stabilized in hydrocarbon solvents by a noncoordinating counteranion. Furthermore, since deprotonation of nitriles has already been observed with the formation of a metal hydride bond, we suggest in the present bis(benzene)vanadium system the formation of a transient vanadium hydride species via the formation of a vanada(IV)-azirine complex, $[(arene)_2V(\eta^2\text{-C,N-}(F_5C_6)_3B\cdot NCH_2N\cdot B(C_6F_5)_3]$.

Experimental Section

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon, collected by distillation, and stored in a drybox over activated 4 Å molecular sieves. Deuterated solvents were degassed and dried over activated 4 Å molecular sieves. Elemental analyses (C, H, N) were performed at the Laboratoire de Chimie de Coordination (Toulouse, France). $V(C_6H_6)_2$,[9,14] $B(C_6F_5)_3$,[15] and $H_2O\cdot B(C_6F_5)_3$[16] were prepared according to the literature. We were unable to obtain satisfactory elemental analysis for **1**, **3**, and **4**, probably because of their high air and moisture sensitivity. Single crystals, suitable for X-ray structure determination, of all compounds were obtained directly from the reactions.

$[V(C_6H_5CH_3)_2][(C_6F_5)_3B\cdot NCCHCN\cdot B(C_6F_5)_3]$ (1). To $NCCH_2CN$ (7 mg, 0.1 mmol) dissolved in 2 mL of toluene was added $B(C_6F_5)_3$ (102 mg, 0.2 mmol) in 2 mL of toluene. After 1 h stirring, $V(C_6H_6)_2$ (21 mg, 0.1 mmol) dissolved in toluene (10 mL) was added. The resulting red solution was left for 2−3 days at room temperature to give yellow crystals of **1**. Yield: 60 mg (40%). Anal. Calcd for **1**·(2 toluene), $C_{67}H_{33}B_2F_{30}N_2V$ (1508.51): C 53.35, H 2.20, N 1.86. Found: C 52.75, H 2.05, N 1.70.

$[(C_6F_5)_3B\cdot NCCH_2CN\cdot B(C_6F_5)_3]$ (2). To $NCCH_2CN$ (13 mg, 02 mmol) dissolved in 5 mL of C_6H_6 was added $B(C_6F_5)_3$ (205 mg, 0.4 mmol) in 5 mL of C_6H_6. After 10 min of stirring, the solution was left 1 day and a yellow microcrystalline solid was filtered as **2**. Yield: 120 mg (55%). Anal. Calcd for **2** (2 C_6H_6): $C_{51}H_{14}B2F_{30}N_2$ (1246.24): C 49.15, H 1.13, N 2.25. Found: C 49.23, H 1.25, N 2.22.

$[V(C_6H_6)(C_6H_5CH_3)][(C_6F_5)_3BOB(C_6F_5)_2]$ (3) and $[V(C_6H_6)_2][(C_6F_5)_3BOB(C_6F_5)_2]$ (4). Both compounds were prepared by a similar procedure from $V(C_6H_6)_2$ (20 mg, 0.1 mmol) and $H_2O\cdot B(C_6F_5)_3$ (53 mg, 0.1 mmol) in toluene or benzene solvent, respectively. For **4**: a benzene solution (10 mL) of $V(C_6H_6)_2$ was quickly added to a benzene solution (10 mL) containing $H_2O\cdot B(C_6F_5)_3$ under stirring. Then the stirring was immediately stopped and the solution left 3−4 days until the appearance of crystalline **4**. The use of 2 equiv of $B(C_6F_5)_3$ in the reaction does not improve appreciably the yield of **3** or **4**. For **3**: yield 42 mg (38%). Anal. Calcd for $C_{43}H_{14}B_2F_{25}OV$ (1094.09): C 47.20, H 1.29. Found: C 46.33, H 1.05. For **4**: yield 35 mg (33%). Anal. Calcd for $C_{42}H_{12}B_2F_{25}OV$ (1080.07): C 46.71, H 1.12. Found: C 45.93, H 1.35.

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Supporting Information Available: Tables of atomic coordinates, 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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