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Mono- and Homobimetallic Vanadium Complexes: Borane Adducts of Vanada(IV)azirine Complexes

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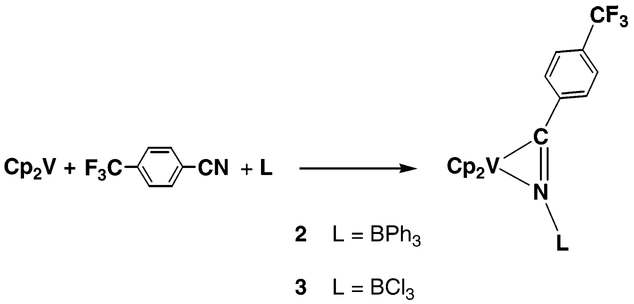
The reaction between [VCp_2], BPh_3, or BCl_3 and the nitrile $F_3CC_6H_4C{\equiv}N$ gives the borane adduct of vanada(IV)azirine complex [$VCp_2\{\eta^2$:C,N-$F_3CC_6H_4C{=}N{\cdot}BR_3\}$] (R = Ph (**2**), Cl (**3**)). Using $B(C_6F_5)_3$ and dicyano compounds such as 1,4-benzene dicarbonitrile $N{\equiv}C(C_6H_4)C{\equiv}N$ and adiponitrile $N{\equiv}C(CH_2)_4C{\equiv}N$, an access to homobimetallic vanadium complexes was obtained and complexes [$(VCp_2)_2\{\eta^2$:C,N-$(C_6F_5)_3B{\cdot}N{=}C(C_6H_4)C{=}N{\cdot}B(C_6F_5)_3\}$] (**6**) and [$(VCp_2)_2\{\eta^2$:C,N-$(C_6F_5)_3B{\cdot}N{=}C(CH_2)_4C{=}N{\cdot}B(C_6F_5)_3\}$] (**8**) are formed. Malononitrile $N{\equiv}CCH_2C{\equiv}N$ in the presence of 2 equiv of $B(C_6F_5)_3$ and 1 or 2 equiv of [VCp_2] gave the monometallic complex [$(VCp_2)\{\eta^2$:C,N-$(C_6F_5)_3B{\cdot}N{=}CCH_2C{\equiv}N{\cdot}B(C_6F_5)_3\}$] (**7**). Complexes **2**, **3**, **7**, and **8** were characterized by X-ray structure determination. All these complexes are paramagnetic to one electron per vanadium.

Introduction

Adducts of nitrile RCN with Lewis acid have been reported for a long time and widely studied.[1] Recently, we demonstrated that the coordination of a Lewis acid to a nitrile modifies the reactivity of the $-C{\equiv}N$ bond, and the adduct $RC{\equiv}N{\cdot}$Lewis acid is now considered as being a ligand containing an "activated" $-C{\equiv}N$ bond. The Lewis acid-activated nitrile was used as a reagent to facilitate η^2:C,N interaction with the vanadocene [VCp_2] to give a borane adduct of vanada(IV)azirine complexes [$Cp_2V\{\eta^2$:C,N-$RC{=}N{\cdot}B(C_6F_5)_3\}$] (R = CH_3, $F_3CC_6H_4$),[2] for which EPR spectra provide evidence of a C−F···V intramolecular interaction. Similarly, the titanocene [$Cp_2Ti(CO)_2$] was shown to give a borane adduct of titana(IV)azirine complex [$Cp_2Ti\{\eta^2$:C,N-$RC{=}N{\cdot}B(C_6F_5)_3\}$] (R = $F_3CC_6H_4$).[3]

Herein, we will describe an extension of this work by using different boranes such as BCl_3 and the less acidic borane $B(C_6H_5)_3$ on trifluoro-*p*-tolunitrile $F_3CC_6H_4C{\equiv}N$. We shall also extend the reactivity of $B(C_6F_5)_3$ to nitrile ligands containing two $-C{\equiv}N$ nitrile functions in order to synthesize binuclear vanadium(IV) complexes in which d^1−d^1 interaction could be potentially present.

Scheme 1



Results and Discussion

Reactivity of [VCp_2], Borane BR_3 (R = Ph, Cl), and Nitrile $F_3CC_6H_4C{\equiv}N$. Our precedent studies on BR_3 (R = C_6F_5, 2,6-$F_2C_6H_3$, and 3,4,5-$F_3C_6H_2$) with $R^1C{\equiv}N$ (R^1 = CH_3, $F_3CC_6H_4$) and [VCp_2] (**1**) demonstrate the facile formation of borane adducts of vanada(IV)azirine complexes [$VCp_2\{\eta^2$:C,N-$R^1C{=}N{\cdot}BR_3\}$] and, via EPR spectroscopy, that complexes having an *ortho*-fluorine atom in the borane group exhibit a V···F interaction between the vanadium center and the fluorine atom in *ortho*-position (R = C_6F_5, 2,6- $F_2C_6H_3$).[2] We extended this work on BPh_3 and BCl_3 assuming that we could prepare other varieties of borane adducts of vanada(IV)azirine complexes and to confirm that no EPR interaction is observed between the vanadium center and the hydrogen atom of the borane in the case of R = C_6H_5 as was observed in the case of R = 3,4,5-$F_3C_6H_2$.

A 1:1 molar mixture of BPh_3 and $F_3CC_6H_4C{\equiv}N$ in pentane is added to a pentane solution of **1** and left 2 days at room temperature; purple crystals of [$VCp_2\{\eta^2$:C,N-$F_3CC_6H_4C{=}N{\cdot}BPh_3\}$] (**2**) appear (Scheme 1), supported by an X-ray structure determination (Figure 1). It is remarkable that the nitrile $RC{\equiv}N$ could react with the borane BPh_3, in the presence of **1**. It is well known that the presence of a phenyl group attached to

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[1] (a) Shriver, D. F.; Swanson, B. *Inorg. Chem.* **1971**, *10*, 1354–1365. (b) Swanson B.; Shriver, D. F. *Inorg. Chem.* **1969**, *8*, 6–1416. (c) Hoard, J. L.; Owen, T. B.; Buzzell, A.; Salmon, N. O. *Acta Crystallogr.* **1950**, *3*, 130–137. (d) Hoard, J. L.; Geller, S.; Owen, T. B. *Acta Crystallogr.* **1951**, *4*, 405–407. (e) Li, L.; Marks, T. J. *Organometallics* **1998**, *17*, 3996–4003. (f) Tornieporth-Oetting, I. C.; Klapötke, T. M.; Cameron, T. S.; Vallonen, J.; Rademacher, P.; Kowski, K. *J. Chem. Soc., Dalton Trans.* **1992**, 537–541. (g) Hoti, R.; Mihalic, Z.; Vancik, H. *Croatica Chem. Acta* **1995**, *2*, 359–371. (h) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724–1735. (i) Vei, I. C.; Pascu, S. I.; Green, M. L. H.; Green, J. C.; Schilling, R. E; Anderson, G. D. W.; Rees, L. H. *Dalton Trans.* **2003**, 2550–2557.

[2] Choukroun, R.; Lorber, C.; Donnadieu B. *Chem. Eur. J.* **2002**, *8*, 2700–2704.

[3] Choukroun, R.; Lorber, C.; Vendier, L. *Eur. J. Inorg. Chem.* **2004**, 317–321.

10.1021/om049488t CCC: \$27.50

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2, 3, 4, and 5

$[VCp_2\{\eta^2\text{-}F_3CC_6H_4C{=}N{\cdot}L\}]$	**2** L = BPh_3	**3** L = BCl_3	**4** $[F_3CC_6H_4C{\equiv}N{\cdot}B(C_6F_5)_3]$ $[F_3CC_6H_4C{\equiv}N]^a$	$\mathbf{5}^b$ L = $B(C_6F_5)_3$
V−N(1)	2.096(4)	2.071(3)		2.0922(17)
V−C(1)	2.033(5)	2.049(3)		2.032(2)
N(1)−C(1)	1.237(5)	1.248(4)	1.15(2) [1.1482(14)]	1.236(3)
N(1)−B(1)	1.622(6)	1.525(5)	1.59(2)	1.586(3)
C(1)−C(2)	1.471(6)	1.459(5)	1.45(3) [1.4500(13)]	
C(1)−V(1)−N(1)	34.83(15)	35.25(12)		34.83(7)
N(1)−C(1)−C(2)	139.3(5)	136.7(3)	177(2) [179.59(12)]	137.9(2)
C(1)−N(1)−B(1)	145.7(4)	142.6(3)	174(2)	138.52(18)

[a] The main distances and angles of the trifluoro-*p*-tolunitrile are reported in brackets.[10] [b] See ref 2.

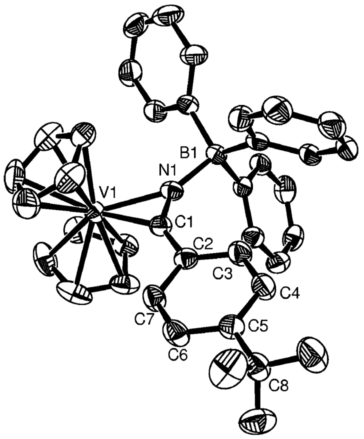

Figure 1. Molecular structure of **2** with partial atom labeling. Hydrogen atoms are omitted for clarity.

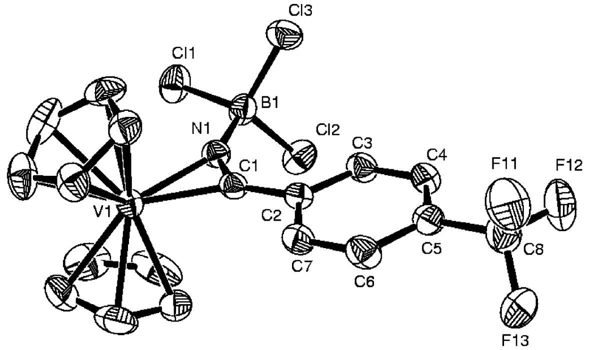

Figure 2. Molecular structure of **3** with partial atom labeling. Hydrogen atoms are omitted for clarity.

the boron atom decreases the boron-donor bond strength.[4] In the absence of $[VCp_2]$, IR spectra in toluene of a mixture of nitrile $F_3CC_6H_4C{\equiv}N$ and BPh_3 (1:1 or 1:5 ratio) do not show any change in the position of the ν_{CN} (2234 cm^{-1}) due to an eventual formation of the borane·Lewis acid adduct (some rare examples of BPh_3·Lewis base adducts are known with amine NR_3 and pyridine but to our knowledge not with nitrile). Nevertheless, it is clear that an undetectable small amount of the adduct is formed, which allows the formation of **3**. A fast reaction was also observed between **1**, trifluoro-*p*-tolunitrile, and BCl_3. By mixing a hexane solution of BCl_3 and $F_3CC_6H_4C{\equiv}N$ in toluene, followed by the addition of **1** in toluene, blue-violet crystals were formed and identified as $[Cp_2V\{\eta^2\text{:C,N-}F_3CC_6H_4C{=}N{\cdot}BCl_3\}]$ (**3**) (Scheme 1) by an X-ray structure determination (Figure 2). All the structural details of bonds and angles of **2** and **3** and for comparison those obtained from the X-ray structure of the borane adduct $F_3CC_6H_4C{\equiv}N{\cdot}B(C_6F_5)_3$ (**4**)[5] (although the crystals obtained were of poor quality) and from the previously reported $[Cp_2V\{\eta^2\text{:C,N-}F_3CC_6H_4C{=}N{\cdot}B(C_6F_5)_3\}]^2$ (**5**) are collected in Table 1. Changing the $B(C_6F_5)_3$ by $B(C_6H_5)_3$ or BCl_3 in the borane adduct of vanada(IV)azirine complex shows slight differences for the VNC cycle moiety in which a C=N double bond is now formed. In contrast, B−N distances are modified according to the expected Lewis acidity strength of the borane, $BCl_3 > B(C_6F_5)_3 > BPh_3$, and in agreement with the $\nu_{C=N}$ frequencies observed for these complexes (**2**, 1752 cm^{-1}; **5**, 1731 cm^{-1}; **3**, 1725 cm^{-1}).

Both **2** and **3** are paramagnetic to one electron as V^{IV} species (μ_{eff} = 1.81 and 1.65 μB, respectively). EPR studies of **2** and **3** were carried out in THF. For **2** and **3**, the formation of an octet was observed, due to the coupling of the unpaired electron of the vanadium atom with the ^{51}V (I = 7/2) nucleus (**2**, g = 1.997, $a(^{51}V)$ 42.0 G; **3**, g = 1.999, $a(^{51}V)$ 41.0 G). Variable-temperature experiments from −60 to +90 °C do not show any change. No additional hyperfine coupling of the unpaired electron of the vanadium atom with the hydrogen atom of the borane BPh_3 was observed for **2**. This result confirms our previous results on $[VCp_2\{\eta^2\text{:C,N-}F_3CC_6H_4C{=}N{\cdot}B(3,4,5\text{-}F_3C_6H_2)_3\}]$ in which the absence of a fluorine atom in the *ortho*-position of the borane $B(3,4,5\text{-}F_3C_6H_2)_3$ gives the octet EPR spectrum. In contrast, **5** or $[VCp_2\{\eta^2\text{:C,N-}F_3CC_6H_4C{=}N{\cdot}B(2,6\text{-}F_2C_6H_3)_3\}]$, in which two fluorine atoms are in *ortho*-position of the phenyl rings, give a doublet of octets due to a C−F···V interaction and subsequent hyperfine coupling $a(^{19}F)$.[2]

Reactivity of $[VCp_2]$, Borane $B(C_6F_5)_3$, and Dinitrile N≡C−(X)−C≡N (X = C_6H_4, CH_2, $(CH_2)_4$). In attempts to synthesize a bimetallic vanadium d^1−d^1 complex with a potential magnetic interaction between the two centers,[6] the choice of the ligand was first reported on 1,4-benzene dicarbonitrile N≡C−(C_6H_4)−C≡N, an aromatic unit between two nitrile groups. Following the same experimental procedure as above, 2 equiv of **1** was reacted in a mixture of N≡C−(C_6H_4)−C≡N in the presence of 2 equiv of $B(C_6F_5)_3$ in a toluene

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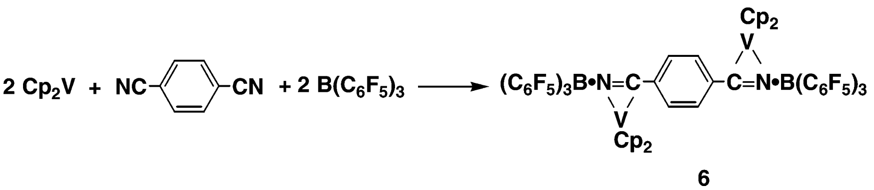
(4) Onak, T. *Organoborane Chemistry*; Organometallic Chemistry Series; Academic Press: New York, 1975.

(5) The related borane adduct $H_3CC_6H_4CN{\cdot}B((C_6F_5)_3$ was recently isolated and characterised by Erker and colleagues.[1h]

(6) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431−509.

Scheme 2

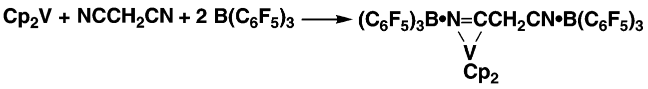


6

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7, 8, and 9

7		8		9	
V(1)–N(1)	2.114(3)	V(1)–N(1)	2.098(4)		
		V(2)–N(2)	2.107(4)		
V–C(1)	2.022(4)	V(1)–C(1)	2.031(5)		
		V(2)–C(6)	2.042(5)		
N(1)–C(1)	1.236(5)	N(1)–C(1)	1.244(6)	N(1)–C(1)	1.130(5)
N(2)–C(3)	1.133(4)	N(2)–C(6)	1.253(6)	N(2)–C(3)	1.131(6)
N(1)–B(1)	1.596(5)	N(1)–B(1)	1.581(7)	N(1)–B(1)	1.605(5)
N(2)–B(2)	1.598(5)	N(2)–B(2)	1.594(7)		
C(1)–V(1)–N(1)	34.68(13)	C(1)–V(1)–N(1)	35.02(17)		
		C(6)–V(2)–N(2)	35.11(17)		
N(1)–C(1)–C(2)	131.7(4)	N(1)–C(1)–C(2)	137.0(4)		
C(2)–C(3)–N(2)	178.0(4)				
		N(2)–C(6)–C(5)	135.1(5)		
C(1)–N(1)–B(1)	141.5(3)	C(1)–N(1)B(1)	139.1(4)	C(1)–N(1)–B(1)	178.2(4)
C(3)–N(2)–B(2)	177.2(4)	C(6)–N(2)–B(2)	138.3(4)		

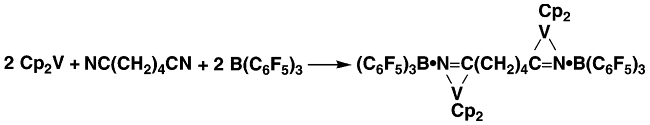
Scheme 3



$$Cp_2V + NCCH_2CN + 2\,B(C_6F_5)_3 \longrightarrow (C_6F_5)_3B{\bullet}\underset{\underset{Cp_2}{V}}{N{=}C}CH_2CN{\bullet}B(C_6F_5)_3$$

7

Scheme 4



$$2\,Cp_2V + NC(CH_2)_4CN + 2\,B(C_6F_5)_3 \longrightarrow (C_6F_5)_3B{\bullet}\underset{\underset{Cp_2}{V}}{N{=}C}(CH_2)_4\overset{\overset{Cp_2}{V}}{C{=}N}{\bullet}B(C_6F_5)_3$$

8

solvent, to give a microcrystalline blue-violet solid. Unfortunately, efforts to obtain suitable crystals for an X-ray diffraction analysis have failed to date (it is noteworthy that it is more advisable to characterize paramagnetic isolated vanadium IV complexes by an X-ray structure determination to assess without ambiguity its chemical environment around the paramagnetic vanadium center). The formation of the solid as $[(VCp_2)_2\{\eta^2{:}C,N\text{-}(C_6F_5)_3B{\cdot}N{=}C(C_6H_4)C{=}N{\cdot}B(C_6F_5)_3\}]$ (**6**) was based on the analytical and spectroscopic data (Scheme 2; see Experimental Section). Malononitrile $N{\equiv}CCH_2C{\equiv}N$ and adiponitrile $N{\equiv}C(CH_2)_4C{\equiv}N$ were also investigated toward [VCp_2] in the presence of borane $B(C_6F_5)_3$ to give a platform for the attachment of two VCp_2 units separated by one or four methylene spacers, leading to the formation of a d^1–d^1 system. However with malonitrile in the presence of 2 equiv of borane, whatever the stoichiometry of **1** (1 or 2 equiv), only the monometallic $[VCp_2\{\eta^2{:}C,N\text{-}(C_6F_5)_3B{\cdot}N{=}CCH_2\text{-}C{\equiv}N{\cdot}B(C_6F_5)_3\}]$ complex (**7**) was isolated (Scheme 3). In the case of adiponitrile, a homobimetallic complex, $[(VCp_2)_2\{\eta^2{:}C,N\text{-}(C_6F_5)_3B{\cdot}N{=}C(CH_2)_4C{=}N{\cdot}B(C_6F_5)_3\}]$ (**8**), was isolated (Scheme 4). Both **7** and **8** were isolated in crystallized forms with toluene and studied by X-ray crystallography (Figure 3 and Figure 4). A summary of the crystallographic data is listed in Table 2 and is closely similar to those of compounds **2**, **3**, **4**, and **5**. Complex **8** has a dihedral angle between the VCN units (V(1)C(1)N(1) and V(2)C6)N(2)) of nearly 76°, and only carbon atoms C(1) to C(5) lie in the same plane. The relevant distances and angles of the X-ray structure elucidation of the malonitrile with one $B(C_6F_5)_3$ as Lewis acid adduct $[N{\equiv}CCH_2C{\equiv}N{\cdot}B(C_6F_5)_3]$ (**9**) are also reported in Table 2. The adduct with two borane groups

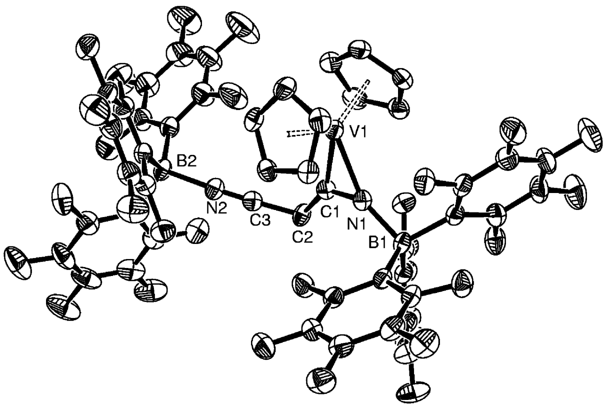


Figure 3. Molecular structure of **7** with partial atom labeling. Hydrogen atoms are omitted for clarity.

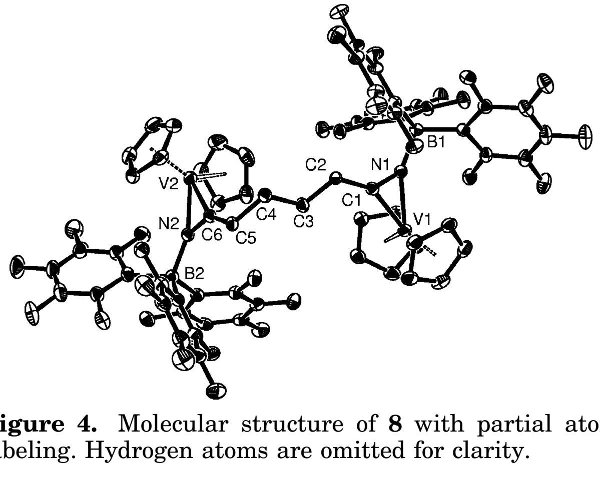


Figure 4. Molecular structure of **8** with partial atom labeling. Hydrogen atoms are omitted for clarity.

on malonitrile $[(C_6F_5)_3B{\cdot}N{\equiv}CCH_2C{\equiv}N{\cdot}B(C_6F_5)_3]$ (**10**) was also isolated (see Experimental Section).

IR spectroscopy shows $\nu_{C=N}$ frequencies at 1735 cm^{-1} for **6**, two bands $\nu_{C\equiv N}$ and $\nu_{C=N}$ at 2356 and 1740 cm^{-1}, respectively, for **7**, and two bands $\nu_{C=N}$ at 1744 and 1734 cm^{-1} for **8**. X-band EPR spectra of **6**, **7**, and **8** were carried out in THF. The formation of a doublet of octets was observed and confirmed by Q-band EPR experiments. Coupling of the unpaired electron of the vanadium atom with the ^{51}V ($I = 7/2$) nucleus and the *ortho*-fluorine atoms of the borane $B(C_6F_5)_3$ via a C−F···V interaction give rise to these spectra (**6**, $g = 1.997$, $a(^{51}V)$ 43.6 G, $a(^{19}F)$ 17.7 G; **7**, $g = 1.996$, $a(^{51}V)$ 43.4 G, $a(^{19}F)$ 17.4 G; **8**, $g = 1.996$, $a(^{51}V)$ 43.6 G, $a(^{19}F)$ 17.7 G). Mononuclear complex **7** is paramagnetic to one electron as V^{IV} species ($\mu_{eff} = 1.72\ \mu B$). Complexes **6** and **8** have been studied by variable-temperature magnetic susceptibility measurements resulting from homobimetallic d^1-d^1 situations. The effective magnetic moment μ_{eff} per vanadium is nearly the same from 300 to 2 K (1.63−1.66 μ_B for **6** and 1.60−1.55 μ_B for **8**) and denotes two noninteracting d^1 vanadium atoms in both complexes. Unfortunately, these paramagnetic d^1-d^1 systems do not present any antiferromagnetism interaction due to the presence of a long sp^3 alkyl chain when adiponitrile is used (in **8**) and to a suggested disfavored orientation of the VCp_2CN units within the $NC-(C_6H_4)-CN$ ligand (in **6**). This latter situation was already observed in the case of $[(VCp_2)_2(1\text{-}2\eta{:}3\text{-}4\eta\text{-}Me_3SiC{=}C{-}C{=}CSiMe_3)]$ and $[(VCp_2)_2(1\text{-}2\eta{:}7\text{-}8\eta\text{-}PhC{=}C{-}(C{\equiv}C)_2C{=}CPh)]$, where the dihedral angle between both Cp_2VC_2 units is nearly 110−120° and prevents a favorable "in-plane π type" geometry in the molecule.[7]

Conclusion

It has been demonstrated that a Lewis-acid-activated nitrile reacts with $[VCp_2]$ to give a large variety of vanada(IV)azirine complexes; BPh_3 as a soft Lewis acid is a rare example of an interaction with a nitrile. This reaction was extended to dinitrile compounds activated with the borane $B(C_6F_5)_3$ to access a new synthetic route for d^1-d^1 homobimetallic vanadium complexes. Regarding the lack of ferromagnetic interaction observed on d^1-d^1 homobimetallic complexes **6** and **8**, efforts on the structure of the organic bridge between the unpaired electron on each vanadium center would be the next step.

Experimental Section

All experiments were performed under an inert atmosphere of argon using standard Schlenk and glovebox techniques. All solvents were dried by conventional methods, distilled under argon, and degassed before use. $[VCp_2]$ was prepared according to the method given in ref 8 and $B(C_6F_5)_3$ according to that in ref 9. ^1H NMR data were recorded using an AC-200 spectrometer and referenced internally to residual protio solvent (^1H) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{19}F NMR (188.298 MHz) spectra were recorded on a Bruker AC-200 spectrometer (reference CF_3CO_2H). ^{11}B NMR (128.378 MHz) spectra were recorded on a Bruker AC-400 spectrometer (reference $BF_3{\cdot}Et_2O$). Elemental analyses were performed in the laboratory (C,H,N). Magnetic susceptibilities were determined by Faraday's method and a Squid susceptometer within the temperature range 2−300 K. EPR spectra were obtained by using a Bruker ESP300E spectrometer.

$[VCp_2\{\eta^2\text{-}(F_3CC_6H_4)C{=}N{\cdot}B(C_6H_5)_3\}]$ (2). In a typical experiment, $F_3CC_6H_4C{\equiv}N$ (42 mg, 0.24 mmol) in 10 mL of pentane was added to a solution of borane $B(C_6H_5)_3$ (65 mg, 0.27 mmol) in pentane (5 mL) and the freshly resulting solution added to Cp_2V (45 mg, 0.25 mmol) in pentane (5 mL). The solution was left for 2−3 days at room temperature to give purple crystals of **2**. Yield of **2**: 105 mg (72%). Anal. Calcd for **2**, $C_{36}H_{29}BF_3NV$ (594.3): C 72.75, H 4.92, N 2.36. Found: C 72.63,H 5.05, N 2.42.

$[VCp_2\{\eta^2\text{-}(F_3CC{=}N{\cdot}BCl_3\}]{\cdot}$toluene (3). By using a procedure identical to that described above for **2** and using toluene as solvent, compound **3** was synthesized starting from $[Cp_2V]$ (18 mg, 0.1 mmol), $F_3CC_6H_4CN$ (19 mg, 0.11 mmol), and BCl_3 (0.3 mL, 1 M in hexane). A slight excess (0.015 mmol) of the nitrile or borane gives also microcrystalline products directly from the solution. Yield of **3**: 44 mg (79%). Anal. Calcd for **3**·toluene, $C_{25}H_{22}BCl_3F_3NV$ (561.55): C 53.47, H 3.95, N 2.49. Found: C 53.56, H 3.97, N 2.77.

$[(Cp_2V)_2\{\eta^2\text{-}(C_6F_5)_3B{\cdot}N{=}C(C_6H_4)C{=}N{\cdot}B(C_6F_5)_3\}]$ (6). By using a procedure identical to that described above for **2** and using toluene as solvent, compound **6** was synthesized starting from $[Cp_2V]$ (36 mg, 0.2 mmol) and $NC(C_6H_4)CN$ (13 mg, 0.1 mmol). The presence of toluene in **6** as solvate molecule was observed by ^1H NMR. Yield of **6**: 85 mg (53%). Anal. Calcd for **6**·1toluene, $C_{71}H_{32}B_2F_{30}N_2V_2$ (1606.48): C 53.08, H 2.01, N 1.74. Found: C 53.45, H 2.09, N 1.70.

$[(VCp_2)_2\{\eta^2\text{-}(C_6F_5)_3B{\cdot}N{=}CCH_2C{\equiv}N{\cdot}B(C_6F_5)_3\}]{\cdot}$1.5toluene (7). By using a procedure identical to that described above for **2** and using toluene as solvent, compound **7** was synthesized starting from $[Cp_2V]$ (18 mg, 0.1 mmol), $NCCH_2CN$ (6 mg, 0.1 mol), and $B(C_6F_5)_3$ (105 mg, 0.2 mmol). Yield of **7**: 110 mg (78%). Anal. Calcd for **7**·1.5toluene, $C_{59.5}H_{24}B_2F_{30}N_2V$ (1409.11): C 50.71, H 1.72, N 1.99. Found: C 50.42, H 1.52, N 2.02.

$[(VCp_2)_2\{\eta^2\text{-}(C_6F_5)_3B{\cdot}N{=}C(CH_2)_4C{=}N{\cdot}B(C_6F_5)_3\}]{\cdot}$toluene (8). By using a procedure identical to that described above for **2** and using toluene as solvent, compound **8** was synthesized starting from $[Cp_2V]$ (18 mg, 0.1 mmol), $NC(CH_2)_4CN$ (10 mg, 0.1 mmol), and $B(C_6F_5)_3$ (105 mg, 0.2 mmol). Yield of **8**: 100 mg (63%). Anal. Calcd for **8**·toluene, $C_{69}H_{36}B_2F_{30}N_2V_2$ (1586.49): C 52.24, H 2.29, N 1.77. Found: C 52.65, H 2.17, N 1.65.

$[F_3CC_6H_4C{\equiv}N{\cdot}B(C_6F_5)_3]$ (4). $F_3CC_6H_4C{\equiv}N$ (34 mg, 0.2 mmol) in 5 mL of toluene was added to a solution of borane $B(C_6F_5)_3$ (102 mg, 0.2 mmol) in pentane (5 mL), and the solution was left for 2−3 days at room temperature to give crystals of **4**. Yield of **4**: 60 mg (44%). Anal. Calcd for **4**: $C_{26}H_4BF_{18}N$ (683.10): C 45.71, H 0.59, N 2.05. Found: C 45.62,H 5.05, N 2.12. IR: ν(C≡N) (KBr) 2321 cm^{-1}. ^1H NMR (C_6D_6): 6.73, 6.61 (AB system, dd, C_6H_4). ^{11}B NMR (C_6D_6): −9.3. ^{19}F NMR (376.41 MHz, 298 K, C_6D_6): 12.0 (s, CF_3), −58.6 (dd, 6 *o*-F, C_6F_5), −78.53 (t, 3 *p*-F, C_6F_5), −86.6 (m, 6 *m*-F, C_6F_5).

$[N{\equiv}CCH_2C{\equiv}N{\cdot}B(C_6F_5)_3]$ (9). To $NCCH_2CN$ (13 mg, 0.2 mmol) dissolved in 2 mL of CH_2Cl_2 was added $B(C_6F_5)_3$ (102 mg, 0.2 mmol) in 1 mL of CH_2Cl_2. After 1 h stirring, 3 mL of pentane was added and the solution left at −30 °C, giving **9** as a colorless and white crystalline product. Yield of **9**: 70 mg (62%). Anal. Calcd for **9**, $C_{21}H_2BF_{15}N_2$ (578.01): C 43.63, N 4.85. Found: C 43.49, N 4.81. IR: ν(C≡N) 2377, 2285 cm^{-1}. ^1H NMR (C_6D_6): 1.19 (CH_2). ^{11}B NMR (C_6D_6): −3.2. ^{19}F NMR (376.41 MHz, 298 K, C_6D_6): −58.3 (d, 6 o-F, C_6F_5), −77.5 (t, 3 p-F, C_6F_5), −86.1 (m, 6 m-F, C_6F_5).

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[7] (a) Choukroun, R.; Donnadieu, B.; Malfant, I.; Haubrich, S.; Frantz, R.; Guerin, C.; Henner, B. *Chem. Commun.* **1997**, 2315−2316. (b) Choukroun, R.; Donnadieu, B.; Lorber, C.; Pellny, P.-M.; Baumann, W.; Rosenthal, U. *Chem. Eur. J.* **2000**, *6*, 4505−4509.

[8] Eisch, J. J.; King, R. B. *Organometallic Synthesis of Transition Metal Compounds*; Academic Press: New York, 1965; pp 64−66.

[9] (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218−225.

Table 3. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for 2, 3, 4, 7, 8, and 9

	2	**3**·toluene	**4**	**7**·1.5toluene	**8**·toluene	**9**
formula	$C_{36}H_{29}BF_3NV$	$C_{25}H_{22}BCl_3F_3NV$	$C_{26}H_4BF_{18}N$	$C_{59.5}H_{24}B_2F_{30}NV$	$C_{69}H_{36}B_2F_{30}N_2V_2$	$C_{21}H_2BF_{15}N_2$
fw	594.35	561.55	683.11	1409.11	1586.50	578.06
a (Å)	9.059(5)	9.168(5)	8.897(5)	11.6741(12)	10.170(5)	19.502(4)
b(Å)	9.743(5)	11.104(5)	12.017(5)	13.0802(13)	17.885(5)	10.866(2)
c (Å)	17.635(5)	24.741(5)	13.367(5)	19.202(2)	34.917	19.177(4)
α (deg)	83.292(5)		65.416(5)	71.067(11)		
β (deg)	79.672(5)	95.704(5)	7551.510(5)	86.025(13)	97.893(5)	92.11(3)
γ (deg)	70.255(5)		83.317(5)	71.755(11)		
V (Å^3)	1438.6(12)	2506.2(18)	1232.3(10)	2777.7(5)	6291(4)	4061.2(14)
Z, d_{calc} (g/cm^3)	2, 1.372	4, 1.488	2, 1.841	2, 1.630	4, 1.675	8, 1.891
space group	$P\bar{1}$	$P21/n$	$P\bar{1}$	$P\bar{1}$	$P21/c$	$C2/c$
linear abs coeff (mm^{-1})	0.391	0.753	0.204	0.391	0.433	0.209
T (K)	180	180	180	180	180	180
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
F(000)	614	1140	668	1346	3160	2256
2 θ range (deg)	2.23−24.25	2.01−26.10	1.86−21.96	1.65−23.05	2.02−24.20	2.09−24.71
no. of indep reflns	6460	19 299	7826	10 254	39 785	13 826
no. of params	379	362	415	885	1011	352
R1, wR2 (all data)	0.0713, 0.1442	0.0853, 0.1543	0.2319, 0.3041	0.1334, 0.1210	0.1140, 0.1554	0.0833, 0.0850
R1, wR2 (>2σ)	0.0498, 0.1325	0.0556, 0.1382	0.0830, 0.1978	0.0460, 0.0919	0.0533, 0.1180	0.0370, 0.0722

[$(C_6F_5)_3B{\cdot}N{\equiv}CCH_2C{\equiv}N{\cdot}B(C_6F_5)_3$] (10). To $NCCH_2CN$ (7 mg, 0.1 mmol) dissolved in 2 mL of CH_2Cl_2 was added $B(C_6F_5)_3$ (102 mg, 0.2 mmol). After 1 h stirring, 3 mL of pentane was added and the solution left at −30 °C, giving **10** as a colorless and white crystalline product. Yield of **10**: 40 mg (36%). Anal. calcd for **10**, $C_{39}H_2B_2F_{30}N_2$ (683.10): C 42.97, N 2.57. Found: C 42.63, N 2.42. IR: ν(C≡N) (KBr) 2370 cm^{-1}. ^{1}H NMR (C_6D_6): 1.17 (CH_2). ^{11}B NMR (C_6D_6): 3.7. ^{19}F NMR (376.41 MHz, 298 K, C_6D_6): −57.5 (d, 6 o-F, C_6F_5), −75.1 (t, 3 p-F, C_6F_5), −85.7 (m, 6 m-F, C_6F_5).

Crystallographic Data for 2, 3, 4, 7, 8, and 9. The selected crystals, sensitive to air and moisture, were suspended in oil on a glass slide. Under a microscope, a single block was isolated. Data were collected on a Stoe imaging plate diffraction system (IPDS) using Mo Kα radiation (λ = 0.71073 Å). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. No significant fluctuation of the intensity was observed over the course of the data collection. All structures were solved by means of direct methods using SIR92[10] and refined by least-squares procedures on F^2 with the aid of SHELXL97[11] included in WinGX (version 1.63).[12] All hydrogen atoms were located on a difference Fourier map and refined with a riding model, and all remaining non-hydrogen atoms was anisotropically refined. In the last cycles of refinement a weighting scheme was used for each structure where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. The high R factor obtained for **4** is due to the poor quality of the crystal. The crystallographic data for all compounds are summarized in Table 3.

Supporting Information Available: Crystallographic data for compounds **2**, **3**, **4**, **7**, **8**, and **9** including ORTEP diagrams, tables of crystal data and data, collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Boitsov, S.; Songstad, J.; Törnroos, K. W. *Acta Crystallogr.* **2002**, *C58*, 66−68.

[11] Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[12] Sheldrick, G. M. *SHELX97* [includes *SHELXS97*, *SHELXL97*, *CIFTAB*], Programs for Crystal Structure Analysis (Release 97-2); Institüt für Anorganische Chemie: Göttingen, Germany, 1998.

[13] Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.