Reactivity of Vanadocene with a Nitrile −C≡N Bond Activated by a Tris(fluorophenyl)borane as Lewis Acid: Formation of Borane Adducts of Vanada(IV)azirine Complexes—EPR Evidence for an Intramolecular C−F···V Interaction

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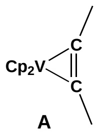
Abstract: Reaction of vanadocene [V(Cp)$_2$] with "activated" nitrile R^{1}CN · L (L: Lewis acid), obtained by the reaction of borane adducts (L = BR$_3$; R = C$_6$F$_5$, 2,6-F$_2$C$_6$H$_3$, 3,4,5-F$_3$C$_6$H$_2$) with nitriles (CH$_3$CN, F$_3$CC$_6$H$_4$CN), yields the borane adduct of vanada(IV)azirine complexes [V(Cp)$_2$(η^2-R^{1}C=N · L)]. EPR studies of a fluid solution were conducted on these complexes. A doublet of octets due to the coupling of one unpaired electron of the vanadium with the ^{51}V (I = 7/2) nucleus and to an additional hyperfine coupling to the *ortho*-F atom borne by the phenyl ring of the borane was elucidated by means of the different Lewis acids used in this work. This EPR behaviour gives evidence for the presence of a C−F···V interaction in a fluid solution with L = B(C$_6$F$_5$)$_3$ and B(2,6-F$_2$C$_6$H$_3$)$_3$. In contrast, the expected eight line EPR pattern is observed with L = B(3,4,5-F$_3$C$_6$H$_2$)$_3$, in which no *ortho*-F atoms are present in the phenyl ring. A model can be drawn to take into account this flexibility and V···F distances between V and *ortho*-F atoms are in the expected range for such an interaction.

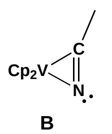
Keywords: boranes · EPR spectroscopy · nitriles · structure elucidation · vanadium

Introduction

It is well known that vanadocene reacts with activated alkynes to give vanadacycloprene complexes of type **A**.[1] We have recently found that the vanadocene complex [V(Cp)$_2$] reacts



A



B

with polyyne ligands to give various vanada(IV)cyclopropene complexes with novel structures.[2] In this context, the addition of a nitrile bond −C≡N on [V(Cp)$_2$] to give VCN ring **B** as vanadaazirine complex is still unknown. Literature reveals that the reaction between vanadocene and nitrilium salt [RC≡NMe][BF$_4$] (R = Me, Ph) produces iminoacyl vanadocene and the ionic complex [V(Cp)$_2${η^2-(Ph)C=NCH$_3$}][BF$_4$] was characterized by an X-ray structure.[3] On the other hand, adducts of nitrile RC≡N with Lewis acid have been reported for a long time and widely studied.[4] From the large increase in ν(C≡N) stretching frequency induced by complexing with a strong Lewis acid, it was found that the polarity of the nitrile group is increased in the complex.[5] More recently, Erker's group have studied the reactivity of a series of nitrile and isonitrile ligands towards the Lewis acid B(C$_6$F$_5$)$_3$.[6] This work, based on different X-ray analysis of the adduct complexes and complemented by a density functional study, shows that the coordination of a Lewis acid to a nitrile leads to a strengthening of the −C≡N bond caused by a significant increase of its electron density.[4f][6] Considering that the Lewis acid could modify the reactivity of the −C≡N bond, the adduct RCN · Lewis acid can be now considered as a ligand containing an "activated" −C≡N bond. With this in mind, we have explored the reactivity of the nitrile Lewis acid adducts with [V(Cp)$_2$].

Results and Discussion

Synthesis and structural studies of [V(Cp)$_2${η^2-(CH$_3$)C=N · B(C$_6$F$_5$)$_3$}] (1) and [V(Cp)$_2${η^2-(F$_3$CC$_6$H$_4$)C=N · B(C$_6$F$_5$)$_3$}] (2): Addition of Lewis acid B(C$_6$F$_5$)$_3$ to nitrile (CH$_3$C≡N, F$_3$CC$_6$H$_4$C≡N) in toluene forms, in situ, the expected adduct

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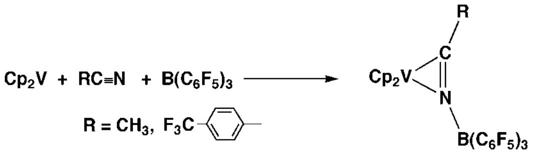
$RC{\equiv}N \cdot L$; addition of $[V(Cp)_2]$ dissolved in toluene to the this adduct gives, after two days, the crystalline borane adduct of the vanadaazirine complexes $[V(Cp)_2\{\eta^2\text{-}(CH_3)C{=}N \cdot B(C_6F_5)_3\}]$ (**1**) and $[V(Cp)_2\{\eta^2\text{-}(F_3CC_6H_4)C{=}N \cdot B(C_6F_5)_3\}]$ (**2**) (Scheme 1). These complexes are paramagnetic due to one unpaired electron ($\mu_{eff} = 1.85$ and $1.72\,\mu_B$ for **1** and **2**, respectively) in agreement with the spin value for a formally vanadium(IV) (d^1) system. To support our findings on paramagnetic V^{IV} species, complexes **1** and **2** were characterized by X-ray crystallography (Figures 1 and 2, respectively). The main feature of both structures gives evidence of the nitrile bond attached to the vanadium atom through two σ-type V–C and V–N bonds of 2.03 Å (av) and 2.10 Å (av) for **1** and **2**, respectively. This produces a metallacyclo-imine structure with an acute C-V-N angle of 34.7°(av). The nitrile coordination is reflected by an average 0.11 Å increase of the C≡N bond length (for $CH_3C{\equiv}N \cdot L$ and $p\text{-}O_2N\text{-}C_6H_4C{\equiv}N \cdot L$ ($L = B(C_6F_5)_3$), $d(C{\equiv}N) = 1.124(3)$ Å and 1.135(3) Å, respectively[6]) and by the geometrical alterations which accompany the nitrile upon coordination (the C-N-B and the R-C-N bond angles ($R = CH_3$, $F_3CC_6H_4$) are reduced from 180° in the free nitrile · borane adduct to 140° (av) in the vanadocene adduct).



Scheme 1. Synthesis of borane adduct of vanada(IV)azirine complexes.

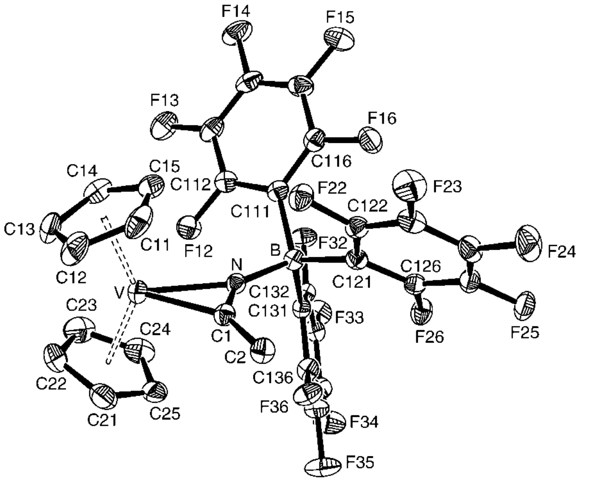


Figure 1. Molecular structure of **1** showing the labelling scheme; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V–C1 2.032(2), V–N 2.0922(17), N–C1 1.236(3), N–B 1.586(3), Cp1–V 1.951, Cp2–V 1.961, C1-V-N 34.83(7), C2-C1-N 137.9(2), C1-N-B 138.52(18), Cp1-V1-Cp2 138.33.

EPR spectroscopy and model considerations: X-band EPR studies of **1** and **2** were carried out in THF. For **1** and **2**, the formation of a doublet of octets was observed. Variable temperature experiments from −60 to +90 °C do not show any change except that both spectra are well resolved at higher temperatures at which these lines sharpen. As an example of a typical spectrum, the EPR of **2** registered at room temperature and 90 °C is shown in Figure 3. The Q-band of the EPR THF solution of **1** and **2** confirms the registered X-band spectra. Coupling of the unpaired electron of the vanadium atom with the ^{51}V ($I = 7/2$) nucleus should have given rise to the expected eight-line pattern. An additional hyperfine coupling of the unpaired electron of the vanadium atom with an unknown spin nucleus belonging to the molecule is responsible for this puzzling feature. The ligand framework contains other active spin nuclei: ^1H, ^{19}F ($I = 1/2$), ^{14}N ($I = 1$) and ^{11}B ($I = 3/2$) nuclei [natural abundance 99.98 %, 100 %, 99.64 % and 81.17 % respectively; the interaction with the ^{13}C ($I = 1/2$) nucleus of natural abundance 1.10 % was ignored]. To demonstrate and confirm that one of them is the effective nucleus responsible for the additional coupling, we decide to investigate step by step (i.e., active spin nucleus by active spin nucleus) each part of the ligand. In our strategy, we modified a part of the environment of the complex **1** by using labelled acetonitrile CD_3CN and $CH_3C^{15}N$. In both cases, the EPR spectra give a doublet of octets identical to the EPR spectrum of **1** and with the same EPR characteristics as **1**. Both experiments eliminate any coupling of the unpaired electron of the vanadium with the different active spin nuclei of acetonitrile. If we exclude an interaction with the boron atom ($I = 3/2$) that could give a more complicated EPR spectrum, we suggest that an interaction of a fluorine atom of the borane $B(C_6F_5)_3$ with the

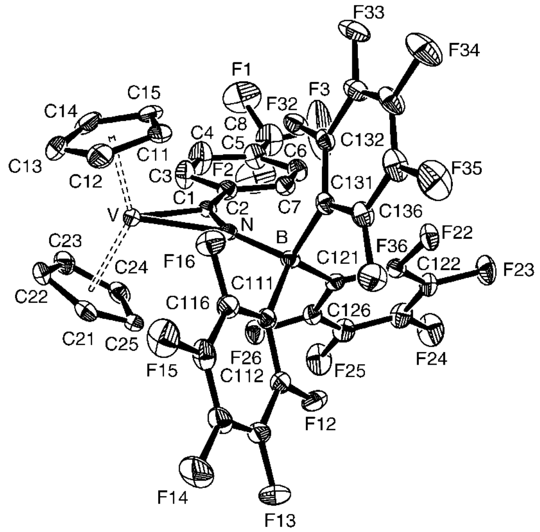


Figure 2. Molecular structure of **2** showing the labelling scheme; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V–C1 2.0357(19), V–N 2.1217(15), N–C1 1.239(3), N–B 1.588(3), Cp1–V 1.948, Cp2–V 1.949, C1-V-N 34.59 (7), C2-C1-N 140.00(18), C1-N-B 144.08(17), Cp1-V-Cp2 138.21.

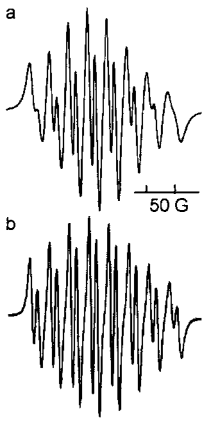


Figure 3. X-band EPR spectra of **2** in THF: a) room temperature; b) 90 °C.

vanadium is responsible for the coupling constant observed (vide infra) (**1**: $g = 1.996$, $A(^{51}V) = 43.3$ G; $a(^{19}F) = 17.4$ G; **2**: $g = 1.997$, $A(^{51}V) = 42.3$ G; $a(^{19}F) = 14.9$ G).

A careful investigation of the X-ray structure of **1** and **2** does not indicate such an interaction in the solid state. However, in a fluid solution, a dynamic process along the rotation of B–C and N–B bonds allows the fluorine atom to approach the vanadium centre. A model can be drawn to take into account this flexibility and the best situation for a C–F···V interaction is a plane containing the V-C(1)-N-B-$C_{ipso}(C_6F_5)$ atoms in which one *ortho* fluorine atom of the fluorophenyl ligand could approach the vanadium centre through the formation of a six-membered ring picture (Figure 4). With this model and taking into account the rotation of the fluorophenyl group along the B–C_{ipso} axis, six V···F distances in the range of 2.10–2.40 Å are obtained for **1** and **2**. For each of the three fluorophenyl groups, different short distances V···F were observed: 2.098, 2.130 and 2.168 Å for **1**, 1.834, 2.112 and 2.129 Å for **2**. The V···F separations observed here are in the same range as those obtained in the literature for fluorine atoms which bridge neighbouring vanadium atoms 2.044–2.173 Å.[7–8]

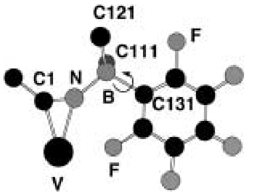


Figure 4. Schematic view of a six-membered ring V-N-B-C-C-F.

Synthesis, X-ray characterization and EPR of [V(Cp)$_2${η^2-(F$_3$CC$_6$H$_4$)C=N·B(2,6-F$_2$C$_6$H$_3$)$_3$}] (3) and [V(Cp)$_2${η^2-(F$_3$CC$_6$H$_4$)C=N·B(3,4,5-F$_3$C$_6$H$_2$)$_3$}] (4): In this context, we address the question of whether another borane, bearing hydrogen atoms in place of fluorine atoms, could confirm our hypothesis, that is, the presence or not of a doublet of octets in the EPR spectrum. In the course of this study, we have prepared and isolated two new complexes: [V(Cp)$_2${η^2-(F$_3$CC$_6$H$_4$)C=N·B(2,6-F$_2$C$_6$H$_3$)$_3$}] (**3**) which contains only two fluorine atoms in the 2- and 6-positions of the borane phenyl group and [V(Cp)$_2${η^2-(F$_3$CC$_6$H$_4$)C=N·B(3,4,5-F$_3$C$_6$H$_2$)$_3$}] (**4**) which contains fluorine atoms in the 3-, 4- and 5-positions of the borane phenyl group, leaving two hydrogen atoms in the 2- and 6-positions. Both complexes were characterized by an X-ray structure determination (Figures 5 and 6). The bond lengths and angles of **3** and **4** are very similar to those found for **1** and **2**, except the N–B distances which are longer, due to the lesser acidity of the borane.[9] As expected, the EPR spectrum of a solution of **3** gives the doublet of octets with the same EPR characteristics as **1** and **2** (**3**: $g = 1.997$; $A(^{51}V) = 42.3$ G; $a(^{19}F) = 15.4$ G). The EPR spectrum of **4** gives a well-resolved octet (Figure 7; $g = 1.998$; $A(^{51}V) = 40.8$ G). This fact can now be explained by the absence of a fluorine atom in the *ortho*-position of the borane B(3,4,5-F$_3$C$_6$H$_2$)$_3$.[10] In contrast, the presence of two fluorine atoms in *ortho* position of the phenyl rings in **3**, as well as in in **1** and **2**, contributes to the C–F···V interaction[11] and subsequent hyperfine coupling a(^{19}F) is observed. Moreover, the presence of a doublet signal indicates the retention of only one V···F coordinative bond in solution. The results support the view that the *ortho* fluorine atom of phenyl borane interacts with the vanadium.[13]

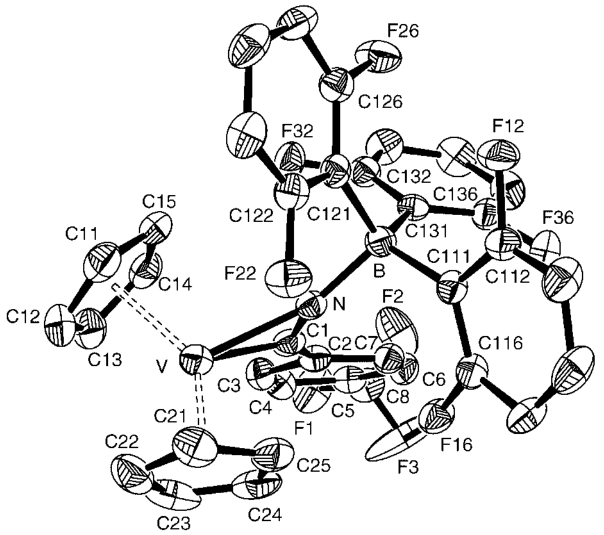


Figure 5. Molecular structure of **3** showing the labelling scheme; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V–C1 2.049(3), V–N 2.131(2), N–C1 1.231(3), N–B 1.610(4), Cp1–V 1.955, Cp2–V 1.961, C1-V-N 34.17(9), C2-C1-N 138.9(3), C1-N-B 140.4(2), Cp(1)-V1-Cp(2) 137.87.

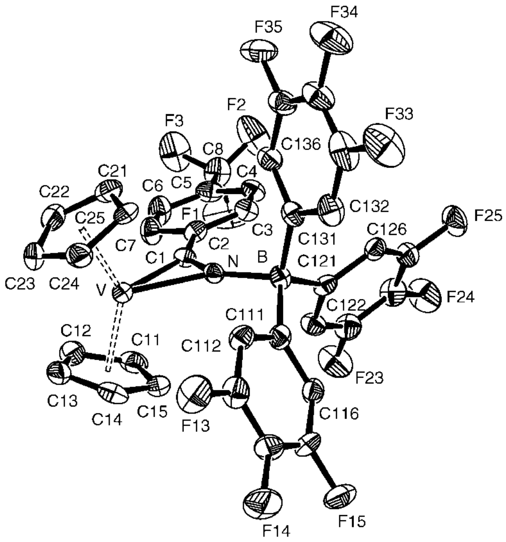


Figure 6. Molecular structure of **4** showing the labelling scheme; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: V–C1 2.036(5), V–N 2.096(4), N–C1 1.232(5), N–B 1.614 (6), Cp1–V 1.937, Cp2–V 1.953, C1-V-N 34.66(15), C2-C1-N 138.4(4), C1-N-B 145.0(4), Cp(1)-V1-Cp(2) 138.85.

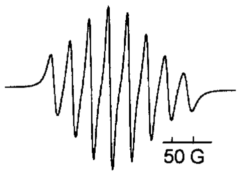


Figure 7. X-band EPR spectrum of **4** in THF.

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Conclusion

In summary, this study shows that a Lewis-acid-activated nitrile can assist the reactivity of organometallic complexes towards $-C\equiv N$ bond. $[V(Cp)_2]$ is the first example of this reactivity and borane adducts of vanada(IV)azirine complexes were fully identified. The Lewis-acid-activated nitrile is used in our laboratories as a reagent for facile η^2:C,N interactions with other unsaturated organometallic complexes.[14] On the other hand, with respect to located *ortho*-fluorine atoms in tris(fluorophenyl)borane, the EPR spectra provide evidence for a C–F ··· V intramolecular interaction in fluid solution, in contrast to the nonobservable C–F ··· V interaction in the rigid X-ray structure determinations.

Experimental Section

All experiments were performed under an inert atmosphere of argon by using standard Schlenk and glove-box techniques. All solvents were dried by conventional methods, distilled under argon and degassed before use. $[V(Cp)_2]$ was prepared according to the method given in reference [15] and $B(C_6F_5)_3$, $B(2,6\text{-}F_2C_6H_3)_3$, $B(3,4,5\text{-}F_3C_6H_2)_3$ according to that in reference [16]. Elemental analyses were performed in the laboratory (C,H,N). Magnetic susceptibilities were determined by Faraday's method. EPR spectra were obtained by using a BRUKER ESP300E spectrometer.

$[V(Cp)_2\{\eta^2\text{-}(F_3CC_6H_4)C{=}N\cdot B(C_6F_5)_3\}]$ (2): In a typical experiment, $F_3CC_6H_4C\equiv N$ (18 mg, 0.1 mmol) in toluene (2 mL) was added to a solution of borane $B(C_6F_5)_3$ (52 mg, 0.1 mmol) in toluene (5 mL); the freshly resulting solution added to $[V(Cp)_2]$ (18 mg, 0.1 mmol) in toluene (5 mL). The solution was left for 2–3 days at room temperature to give dark red crystals of **2**. Yield 62 mg (71 %); elemental analysis calcd (%) for $C_{36}H_{14}BF_{18}NV$ (864.2): C 50.03, H 1.63, N 1.62; found: C 50.23, H 1.48, N 1.62.

$[V(Cp)_2(\eta^2\text{-}(H_3CC{=}N\cdot B(C_6F_5)_3\}]$ (1), $[V(Cp)_2\{\eta^2\text{-}(F_3CC_6H_4)C{=}N\cdot B(2,6\text{-}F_2C_6H_3)_3\}]$ (3) and $[V(Cp)_2\{\eta^2\text{-}(F_3CC_6H_4)C{=}N\cdot B(3,4,5\text{-}F_3C_6H_2)_3\}]$ (4): By using a procedure identical to that described above compounds **1**, **3** and **4** were synthesized starting from $[V(Cp)_2]$ (18 mg, 0.01 mmol), RCN (CH_3CN: 5.1 µL, 0.01 mmol, $(F_3CC_6H_4)CN$: 18 mg, 0,01 mmol) and the appropriate borane $[B(C_6F_5)_3$ (52 mg, 0.01 mmol), $B(2,6\text{-}F_2C_6H_3)_3$ (35 mg, 0.01 mmol), $B(3,4,5\text{-}F_3C_6H_2)_3$ (40 mg, 0,01 mmol)]. A slight excess (0.015 mmol) of the nitrile or borane also gave microcrystalline products directly from the solution. The yields of these complexes were not optimized (**1**: 44 mg, yield 60 %; **3**: 38 mg, yield 54 %; **4**: 32 mg yield 42 %). Elemental analysis calcd (%) for **1**, $C_{30}H_{13}BF_{15}NV$ (734.16): C 49.08, H 1.78, N 1.91; found: C 49.29, H 2.00, N 1.95; elemental analysis calcd (%) for **3**, $C_{36}H_{23}BF_9NV$ (702.30): C 61.57, H 3.30, N 1.99; found: C 61.69, H 3.28, N 2.00 ; elemental analysis calcd (%) for **4**, $C_{36}H_{20}BF_{12}NV$ (756.28): C 57.17, H 2.67, N 1.85; found: C 57.55, H 2.77, N 1.91.

Crystallographic data for 1–4: For structures **1–4**, data collection were collected on a Stoe imaging-plate diffraction system (IPDS) with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Any fluctuations of the intensity were observed over the course of the data collection. All structures were solved by direct methods and refined by least-squares procedures on F_o^2. All hydrogen atoms were located on a difference Fourier map and refined with a riding model; all the remaining of non-hydrogen atoms was anisotropically refined. In the last cycles of refinement a weighting scheme was used for each structure in which weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ in which $P = (F_o^2 + 2F_c^2)/3$.

Compound 1: $C_{30}H_{13}BF_{15}NV$, $M_r = 734.16$, dark red crystals, $T = 160$ K, monoclinic, space group $P2_1/n$, $a = 10.2003(8)$, $b = 24.4078(19)$, $c = 10.7573(8)$ Å, $\beta = 95.759(9)^\circ$, $V = 2664.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.830$ mg m^{-3}, $\mu = 0.503$ mm^{-1}, $F(000) = 1452$, $R = 0.0611$, $R_w = 0.0752$ for all 5222 reflections and 434 parameters.

Compound 2: $C_{36}H_{14}BF_{18}NV$, $M_r = 864.23$, $T = 180$ K, dark red crystals, orthorhombic, $P2_12_12_1$, $a = 18.8588(14)$, $b = 9.0255(6)$, $c = 19.1627(12)$ Å, $V = 3261.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.760$ mg m^{-3}, $\mu = 0.439$ mm^{-1}, $F(000) = 1708$, $R = 0.0378$, $R_w = 0.0642$ for all 6374 reflections and 514 parameters.

Compound 3: $C_{36}H_{23}BF_9NV$, $M_r = 702.30$, $T = 170$ K, dark red crystals, orthorhombic, $Pbca$, $a = 17.200(5)$, $b = 18.511(5)$, $c = 18.657(5)$ Å, $V = 5940(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.571$ mg m^{-3}, $\mu = 0.420$ mm^{-1}, $F(000) = 2840$, $R = 0.0714$, $R_w = 0.0820$ for all 4710 reflections and 462 parameters.

Compound 4: $C_{36}H_{20}BF_{12}NV$, $M_r = 756.28$, $T = 160$ K, dark red crystals, orthorhombic, $P2_12_12_1$, $a = 9.152(5)$, $b = 18.318(5)$, $c = 18.913(5)$ Å, $V = 3171(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.584$ mg m^{-3}, $\mu = 0.413$ mm $^{-1}$, $F(000) = 1516$, $R = 0.07640$, $R_w = 0.1066$ for all 5148 reflections and 460 parameters.

CCDC-175646 to 175649 contain the supplementary crystallographic data for this paper (compounds **1–4**, respectively). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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