Reactivity of $B(C_6F_5)_3$ with Oxovanadium(V) Complexes VOL_3 ($L = OCH_2CF_3$, NEt_2): Formation of the Organometallic Vanadium(V) Complex $[VO(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)(C_6F_5)]_2$ and the Lewis Acid Adduct $[(Et_2N)_3VO{\cdot}B(C_6F_5)_3]$

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Treatment of the oxovanadium(V) complex $[VO(OCH_2CF_3)_3]_2$ (**3**) with the Lewis acid $B(C_6F_5)_3$ leads to aryl/alkoxy group exchange and formation of the unexpected organometallic oxovanadium(V) $[VO(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)(C_6F_5)]_2$ (**1**), while reaction of $B(C_6F_5)_3$ and $[VO(NEt_2)_3]$ produces the Lewis acid adduct $[(Et_2N)_3VO{\cdot}B(C_6F_5)_3]$ (**2**). The crystal structures of **1**, **2** and **3** were determined. ^{51}V NMR chemical shifts for complexes **1**–**3** and $[VO(NEt_2)_3]$ are discussed. A concentration-dependant monomer-dimer equilibrium for **3** is observed in solution.

Introduction

The reactivity and bonding of tris(pentafluorophenyl)-borane $B(C_6F_5)_3$ to transition metal complexes continues to be a field of intense interest in both fundamental and applied chemistry.[1] The Lewis acid properties of $B(C_6F_5)_3$ influence the reactivity greatly, and C−F···metal interactions or perfluoroaryl/alkyl exchange reactions have been observed.[2] More recently, the reactivity of tris(pentafluorophenyl)borane towards different oxo metal complexes M=O has been investigated and oxo-group adducts isolated, particularly $[(acac)_2VO{\cdot}B(C_6F_5)_3]$.[3] Additionally, a Lewis acid adduct derived from the coordination of an alkylaluminium complex to the terminal oxygen of the oxovanadium(V) complex $[VO(CH_2SiMe_3)_{3-x}(OSiPh_3)_x$ (x = 0−3)] was observed by multinuclear NMR spectroscopy (^{17}O, ^{51}V).[4]

We are interested in vanadium chemistry[5] and, among our recent work, we have identified a C−F···V interaction in vanada(IV)azirine complexes isolated from a new type of reaction between $[VCp_2]$ and the activated nitrile $RC{\equiv}N{\cdot}B(C_6F_5)_3$.[6] We have recently extended our study to the oxovanadium(V) complexes $[VO(NEt_2)_3]$[7] and $[VO(OCH_2CF_3)_3]$,[8] and have found that the reactivity of these complexes is influenced by the substituents L (L = NEt_2, OCH_2CF_3) attached to the vanadium center. In agreement with the ^1H NMR scale that we deduced from the chemical shift measurements of the mixed series $[VOL_2(O\textit{i}Pr)]$ or $[VOL(O\textit{i}Pr)_2]$, the relative Lewis acidity of $[VO(OCH_2CF_3)_3]$ toward $[VO(NEt_2)_3]$ can be inferred.[7−9]

Results and Discussion

Synthesis and Molecular Structures of $[VO(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)(C_6F_5)]_2$ (1) and $[VO(OCH_2CF_3)_3]_2$ (3)

The reaction of $[VO(OCH_2CF_3)_3]_2$ (**3**) in pentane with $B(C_6F_5)_3$ gives the dimeric organometallic complex $[VO(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)(C_6F_5)]_2$ (**1**), as shown in Equation (1). Complex **1** is the second example[10a] of an organometallic oxovanadium(V) to be fully characterized by an X-ray structure determination (Figure 1).

$$[VO(OCH_2CF_3)_3]_2 + 2B(C_6F_5)_3 \longrightarrow [VO(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)(C_6F_5)]_2 \quad \text{(+ unidentified products)} \qquad (1)$$

The formation of this organometallic oxovanadium(V) complex is due to an exchange reaction between the $B(C_6F_5)_3$ and the fluoroalkoxy ligand OCH_2CF_3. Such an exchange is not unique and is already known in zirconium chemistry.[2a−2c] The distance of the vanadium atom to the basal plane O(2), C(11), O(3), O′(2) in **1** is 0.5476(19) Å. The molecular structure establishes that **1** is a complex with a five-coordinate distorted square pyramidal geometry with the three oxygen atoms and the C_{ipso} atom of the perfluorophenyl group occupying the basal site (79.6% on the Berry pseudorotation path between D_{3h} and C_{4v} [11]) for the vanadium center. The V−C distance [2.066(4) Å] is in the expected range for such a bond.[10] In order to compare the

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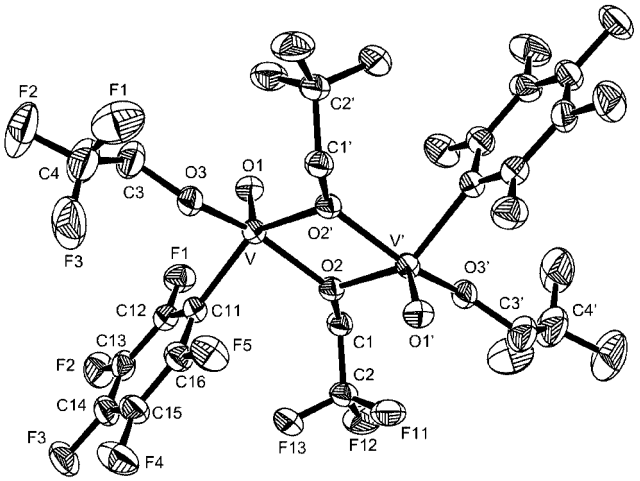

Figure 1. Molecular structure of **1** with selected bond lengths (Å) and angles (°), showing the labeling scheme; hydrogen atoms are omitted for clarity: V−C(11) 2.069(5), V−O(1) 1.569(4), V−O(2) 1.998(3), V−O(2)′ 1.995(3), V−O(3) 1.748(3); O(2)−V−O(2)′ 72.03(15), O(1)−V−O(3) 105.99(18), O(1)−V−C(11) 100.7(2), O(3)−V−C(11) 90.50(18), O(2)−V−C(11) 87.77(17), O(2)′−V−C(11) 141.13(18), V-[O(2)−V′ 107.97(15), V−O(2)−C(1) 126.4(3), V−O(3)−C(3) 134.8(3)

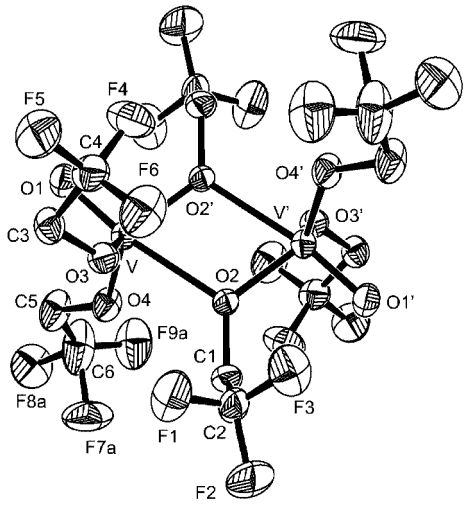

Figure 2. Molecular structure of **3** with selected bond lengths (Å) and angles (°), showing the labeling scheme; hydrogen atoms are omitted for clarity: V−O(1) 1.579(2), V−O(2) 2.297(2), V−O(3) 1.757(2), V−O(4) 1.771(2), V−O′(2) 1.843(2); V−O(2)−V′ 108.85(9), O(2)−V−O(2)′ 71.15(9), O(1)−V−O(2) 170.63(11), O(1)−V−O(2)′ 99.49(11), O(1)−V−O(3) 101.69(12), O(1)−V−O(4) 102.97(12), V−O(2)−C(1) 124.15(19), V′−O(2)−C(1) 126.3(2), V−O(3)−C(3) 131.0(2), V−O(4)−C(5) 129.9(3)

vanadium-oxygen bond lengths with the parent compound, a single-crystal X-ray diffraction study was performed on **3** (Figure 2). The vanadium centre is trigonal bipyramidal, as seen by the larger O(1)−V−O(2) angle of 170.6°, the sum of the O−V−O angles containing O(3), O(4) and O′(2) around the vanadium atom being 348.6° (18.7% on the Berry pseudorotation path[11]).

Both complexes **1** and **3** are centrosymmetric dimers in the solid state. A disymmetrical bridge V−O(R)−V is observed for **3**, and the average V−O bond length is similar to that in **1** (**1**: 1.997 Å (av); **3**: 1.843(2) Å, 2.296(3) Å]. The other V−OR (terminal) and V=O distances around the vanadium atom in **1** and **3** are essentially the same (**1**: 1.748(3) Å, 1.568(3) Å; **3**: 1.757(3) Å and 1.771(3) Å, 1.579(3) Å, respectively).

Although the V−O−C angle of the terminal OR group for **1** (134.8°) is similar to other V−O−C angles observed in different vanadium alkoxides ([$VO(OtBu)_3$]: 139.0° (av),[12] [$V(OiPr)_4]_2$: 126.27°, 134.67°, 140.27°,[13] [$VO(OSiPh_3)_3$]: V−O−Si (av) 155° [14]) the V−O−C angles of **3** are more acute (130.5° (av)), suggesting a poorer p_π-d_π overlap between the oxygen atoms and the vanadium center of **3**. It is worth noting that in a previous work published by one of us, a synthetic route for the preparation of the phenylvanadium(v) complexes [$PhVO(OiPr)_2$] and [PhVOCl(O*i*Pr)] was reported using LiPh or $HgPh_2$ as phenylating agents, although these vanadium complexes are unstable and decompose with time.[15] Attempts to prepare the phenyl analogue [$PhVO(OCH_2CF_3)_2$] by these routes were unsuccessful, in contrast to the easy formation of **1** using $B(C_6F_5)_3$ as an alkylating agent.

Synthesis and Molecular Structure of $[(Et_2N)_3VO{\cdot}B(C_6F_5)_3]$ (2)

Treatment of the more basic complex $[VO(NEt_2)_3]$ with $B(C_6F_5)_3$ gave the oxovanadium Lewis acid adduct compound $[(Et_2N)_3VO{\cdot}B(C_6F_5)_3]$ (**2**) as dark red crystals [Equation (2)].

$$[VO(NEt_2)_3] + B(C_6F_5)_3 \longrightarrow [(Et_2N)_3VO{\cdot}B(C_6F_5)_3] \quad (2)$$

The crystal structure of complex **2** (Figure 3) reveals the coordination of the Lewis acid $B(C_6F_5)_3$ to the V=O moiety. Both vanadium and boron atoms have a pseudo-tetrahedral structure (O−V−N and N−V−N average angles 113.3° and 105.4° respectively; O−B−C and C−B−C average angles 106.6° and 112.3°, respectively). The longer V=O distance of 1.6983(16) Å and the shorter B−O bond length [1.498(3) Å] indicate the reduction in bond order of the V=O moiety and the formation of a boron−oxygen single bond with a nearly linear V−O−B angle of 174.87 (15)°. It is worth noting that: i) the V−O bond length indicates the formation of a single V−O bond {cf. V−O (for terminal OR group) and V=O distances in $[VO(OR)_3]$: 1.753 Å (av), 1.790 Å and 1.595(2) Å and 1.591 Å (av) for R = *t*Bu and Me, respectively};[11] ii) the B−O bond length is shorter than that observed in $F_3B{\cdot}OPPh_3$ [1.516(3) Å][16] (for comparison, in $[(acac)_2VO{\cdot}B(C_6F_5)_3]$,[3a] V=O 1.648(1) Å, B−O 1.527(2) Å, V−O−B 168.9(1)°].

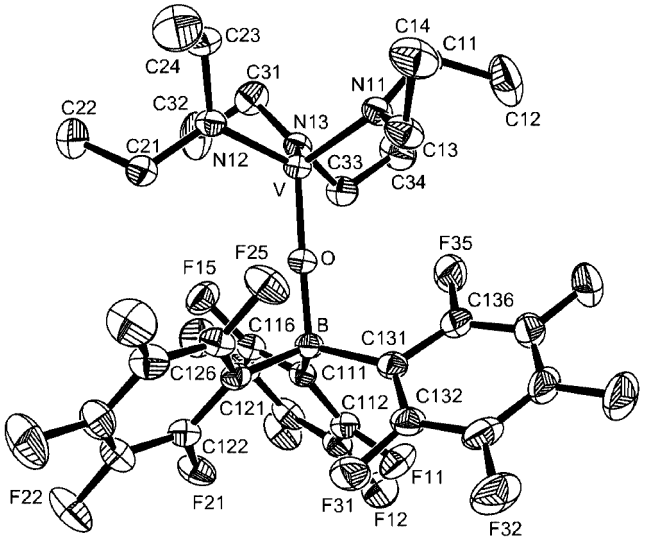

Figure 3. Molecular structure of **2** with selected bond lengths (Å) and angles (°), showing the labeling scheme; hydrogen atoms are omitted for clarity: V−O 1.6983(16), V−N(11) 1.8255(19), V−N(12) 1.8285(19), V−N(13) 1.8211(19), O−B 1.498(3); V−O−B 174.87(15), O−V-(N11) 104.03(9), O−V−N(12) 106.39(9), O−V−N(13) 112.97(8), O−B−C(111) 107.41(19), O−B−C(121) 105.49(18), O−B−C(131) 106.60(18).

^{1}H and ^{51}V NMR Spectroscopy

The ^{1}H NMR spectrum of **1** at room temperature shows a unique quadruplet resonance for the OCH_2CF_3 group (δ = 4.50 ppm), which reflects a rapid exchange of both terminal and bridging OR groups in solution. This persists at low temperature (in [D_8]toluene at −90 °C), indicating that the exchange is extremely rapid.[9] In contrast the ^{1}H NMR spectrum of **3** is concentration dependant, a well-known aspect of the monomer-dimer/polymer behavior in early transition metal alkoxides.[9,17] At low concentration, **3** is monomeric (δ = 4.56 ppm) whereas it dimerizes at higher concentration (δ = 4.95 ppm) showing an equilibrium between both forms in solution (see Exp. Sect.). The upfield shift of the methylene protons observed for **1** (δ = 4.50 ppm) relative to **3** (δ = 4.95 ppm) reflects the difference between an OR group which allows some π-donation and a purely electron-withdrawing σ-group (C_6F_5). The relative overall electron-withdrawing capability of both ligands (OCH_2CF_3 > C_6F_5) was deduced from these chemical shifts. Addition of one equivalent of $B(C_6F_5)_3$ to **1**, and monitoring of the reaction by ^{1}H and ^{19}F NMR spectroscopy for two days, confirmed that vanadium complex remains unchanged.

The ^{51}V NMR spectra for the series **1**, **2**, **3** and [$VO(NEt_2)_3$] were recorded in C_6D_6 solution at two different concentrations (see Exp. Sect.) to ensure that association phenomena do not interfere with the observed chemical shifts. We also verified that the synthesis of **2** gives only one compound in solution. For complex **1**, the preparative solution shows the peak assigned to the formation of **1** (isolated in high yield) and three other minor ^{51}V signals that could not be assigned. The two different ^{51}V NMR signals observed for **3** at low and high concentration (δ = −625 ppm and −570 ppm, respectively) confirm the above ^{1}H NMR results, i.e. a concentration-dependant monomer-dimer equilibrium. The values observed at δ = −481 ppm for the dimer **1** and δ = −570 ppm for dimer **3** show a deshielding effect for **1** due to the replacement of a fluoroalkoxy group with an alkyl perfluorophenyl group as a purely σ-bonding ligand. From the relative overall electron-withdrawing capability of both ligands already pointed out above, the ^{51}V chemical shifts of **1** and **3** follow an "inverse" halogen dependence, i.e. a shielding of the metal in the d^0 configuration upon increasing the electronegativity of the ligands attached to the coordination center.[18−21]

The ^{51}V chemical shifts for [$VO(NEt_2)_3$] and the borane adduct **2** (δ = −205 ppm and +57 ppm, respectively) are puzzling. If we consider that the sp^2 hybridization observed for the planar nitrogen atom of the NEt_2 ligands in **2** is unchanged in [$VO(NEt_2)_3$] before borane coordination (based on recent X-ray diffraction studies of different dialkylamido vanadium(IV) and vanadium(V) complexes recently carried out by our group[22] and others[23]) the observed deshielding shift could be attributed mainly to a decrease in electron density at the vanadium atom when the Lewis acid $B(C_6F_5)_3$ is attached to the oxygen atom. A similar consequence of poorer π-donation from O to V is also observed in the Lewis acid adducts [$VO(CH_2SiMe_3)_{3-x}(OSiPh_3)_x$ (x = 0−3)] with $Al(CH_2SiMe_3)_3$.[4b]

Conclusion

We have demonstrated that the reactivity of the Lewis acid $B(C_6F_5)_3$ with [VOL_3] is modulated by the electronic properties of the ligands L. The reaction with V=O is facilitated by the nucleophilic oxo group when L is an electron-donating dialkylamido group whereas formation of the organometallic complex **1** containing a V−C_6F_5 bond is promoted by an exchange reaction with $B(C_6F_5)_3$ when L is OCH_2CF_3 (an electron-withdrawing group). Potentially, this provides a suitable synthetic route for the development of new organometallic fluoroalkoxy complexes.

Experimental Section

General Remarks: All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Starting materials were purchased from Aldrich Inc. or Fluka Inc. and used without further purification. 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. NMR spectroscopic data were recorded using Bruker AMX-400, DPX-300 and AC-200 spectrometers, and referenced internally to residual protonated-solvent (^{1}H) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F NMR (188.298 MHz) spectra were recorded on a Bruker AC-200 spectrometer (reference CF_3CO_2H). The AA′MM′X system in the ^{19}F NMR spectrum of compound **2** was simulated using the MestRe-C sofware package. ^{51}V NMR

(105.17 MHz) spectra were recorded on a Bruker AMX-400 spectrometer (reference $VOCl_3$ in C_6D_6: 9:1). Infrared spectra were prepared as KBr pellets under argon in a glove box and were recorded on a Perkin−Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France).

$[VO(NEt_2)_3]$ and **3** were prepared as described previously[7,8] and $B(C_6F_5)_3$ according to the literature.[24] Crystals of **3** were obtained by sublimation under vacuo (10^{-2} Torr) at 40 °C. The ^{51}V NMR spectrum of $[VO(NEt_2)_3]$ (EPR silent) was recorded in C_6D_6 at different ratios (9:1; 1:9) and found at δ = −205 ppm (we note that the value published by Rehder et al. for $[VO(NEt_2)_3]$ at δ = −389 ppm,[20] as a neat liquid, differs notably from our result). **$[VO(OCH_2CF_3)_3]$:** 2 experiments: a) 100 mg and b) 2 mg in 0.6 mL C_6D_6: a) ^1H NMR (C_6D_6): δ = 4.95 (q, $^3J_{H\text{-}F}$ = 8.3 Hz, CH_2) ppm. ^{19}F NMR (C_6D_6): δ = −0.8 (t, $^3J_{F\text{-}H}$ = 8.3 Hz, CF_3) ppm. ^{13}C NMR (C_6D_6): δ = 124.0 ($^1J_{C,F}$ = 279.3 Hz, CF_3), 80.6 ($^2J_{C,F}$ = 36.1 Hz, CH_2) ppm. ^{51}V NMR (C_6D_6): δ = −570. b) ^1H NMR (C_6D_6): δ = 4.55 (q, $^3J_{H\text{-}F}$ = 8.3 Hz, CH_2) ppm. ^{19}F NMR (C_6D_6): δ = −0.2 (t, $^3J_{F\text{-}H}$ = 8.3 Hz, CF_3) ppm. ^{51}V NMR (C_6D_6): δ = −625. $VO(NEt_2)_3$ ppm. ^1H NMR (C_6D_6): δ = 3.74 (q, ^3J = 6.9 Hz, CH_2), 1.25 (t, ^3J = 6.9 Hz, CH_3) ppm. ^{13}C NMR (C_6D_6): δ = 52.7 (CH_2), 16.5 (CH_3) ppm. ^{51}V NMR (C_6D_6): δ = −205 ppm.

$[VO(C_6F_5)(\mu\text{-}OCH_2CF_3)(OCH_2CF_3)]_2$ (1): A solution of $B(C_6F_5)_3$ (281 mg, 0.55 mmol) in pentane (4 mL) was added dropwise to a solution of $[VO(OCH_2CF_3)_3]$ (200 mg, 0.55 mmol) in pentane (3 mL) at room temperature. The reaction mixture was stirred for 2 h at room temperature and then cooled in the freezer overnight. Red crystals were filtered off, washed with pentane and dried under vacuum (152 mg, 64%). ^1H NMR (2 experiments at 5 mg and 60 mg in 0.6 mL C_6D_6 give same δ values): δ = 4.50 (q, $^3J_{H,F}$ = 8.0 Hz, CH_2CF_3). ^{13}C NMR (C_6D_6): δ = 149.2, 146.3, 145.2, 142.2, 138.8, 134.8 (C_6F_5) 123.5 (q, $^1J_{C,F}$ = 279.2 Hz, OCH_2CF_3), 79.4 (q, $^2J_{C,F}$ = 36.2 Hz, OCH_2CF_3) ppm. ^{19}F NMR (C_6D_6): δ = −0.2 (t, $^3J_{F,H}$ = 8.0 Hz, OCH_2CF_3), −40.7 (d, ^3J = 85.6 Hz, *o*-F, C_6F_5), −70.3 (t, ^3J = 11.3 Hz, *p*-F, C_6F_5), −84.2 (br. s, *m*-F, C_6F_5) ppm. ^{51}V NMR (C_6D_6) (2 experiments as for ^1H NMR): δ = −481 ppm. IR (KBr): $\tilde{\nu}$ = 2359 (m), 1636 (w), 1540 (s), 1510 (s), 1466 (m), 1359 (w), 1268 (s, br), 1182 (s, br), 1074 (s, br), 1035 (m, br), 962 (s), 839 (m), 746 (m), 669 (m), 581 (w), 497 (w). $C_{20}H_8F_{22}O_6V_2$: calcd. C 27.80, H 0.93; found C 27.80, H 0.85.The ^1H, ^{11}B and ^{51}V NMR spectra of the filtrate, after workup, show peaks for three minor unidentified species (^1H NMR: δ = 4.09, 3.86, 3.74 ppm. ^{11}B NMR: δ = 42, 27, 25 ppm. ^{51}V: δ = −531, −840, −885 ppm). Some of these high-field resonances could correspond to species where fluorines are attached directly to the vanadium atom.[20]

$[V(NEt_2)_3O{\cdot}B(C_6F_5)_3]$ (2): A solution of $B(C_6F_5)_3$ (362 mg, 0.70 mmol) in pentane (4 mL) was added dropwise to a solution of $[VO(NEt_2)_3]$ (200 mg, 0.70 mmol) in pentane (3 mL) at room temperature. After 4 days at room temperature, dark red crystals were filtered off, washed with pentane and dried under vacuum (122 mg, 22%). In another experiment, a solution of $B(C_6F_5)_3$ (15 mg, 0.03 mmol) in C_6D_6 (0.3 mL) was added to a solution of $[VO(NEt_2)_3]$ (8 mg, 0.03 mmol) in C_6D_6 (0.3 mL). The ^1H and ^{51}V NMR of the solution were identical to those of isolated **2** in the same solvent. ^1H NMR (C_6D_6): δ = 3.59 (q, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 0.62 (t, ^3J = 7.0 Hz, 9 H, CH_2CH_3) ppm. ^{13}C NMR (C_6D_6): δ = 151.2, 147.5, 140.1, 138.5, 136.1 [$B(C_6F_5)_3$], 54.7 (CH_2CH_3), 14.6 (CH_2CH_3) ppm. ^{19}F NMR (C_6D_6): δ = −56.7 (AA′MM′X system, $^3J_{AM} = {}^3J_{A'M'}$ = −24.5, $^5J_{A'M} = {}^5J_{AM'}$ = 9.0 Hz, 2F, *o*-F, $B(C_6F_5)_3$], −82.9 (AA′MM′X system, $^3J_{M'X} = {}^3J_{MX}$ = −20.8 Hz, *p*-F, $B(C_6F_5)_3$], −88.7 (AA′MM′X system, $^3J_{AM} = {}^3J_{A'M'}$ = −24.5, $^5J_{A'M} = {}^5J_{AM'}$ = 9.0, $^4J_{MM'} = \pm$ 3.1 Hz, 2 F, *m*-F, $B(C_6F_5)_3$] ppm. ^{11}B NMR (C_6D_6): δ = 1.2. ^{51}V NMR (C_6D_6): δ = 57 ppm. IR (KBr): $\tilde{\nu}$ = 2983 (m), 2944 (m), 2360 (m), 2341 (m), 1643 (m), 1515 (s), 1458 (s, br), 1374 (m), 1358 (m), 1279 (m), 1182 (w), 1144 (m), 1096 (s, br), 972 (s, br), 909 (w), 848 (w), 793 (m), 771 (m), 738 (w), 676 (m), 626 (m), 613 (w), 574 (w), 478

Table 1. Crystallographic data, data collection and refinement parameters for compounds **1**, **2** and **3**

Compound	**1**	**2**	**3**
Chemical formula	$C_{10}H_4F_{11}O_3V$	$C_{30}H_{30}BF_{15}N_3OV$	$C_6H_6F_9O_4V$
Molecular weight	432.07	795.32	364.05
T (K)	180	180	180
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	12.462(5)	10.226(1)	8.4858(8)
b (Å)	12.311(5)	19.575(2)	10.0566(7)
c (Å)	9.250(5)	17.178(2)	14.498(2)
β (deg)	95.175(5)	104.85(1)	92.59(1)
V (Å)	1413.3(11)	3323.6(5)	1235.9(2)
μ (mm^{-1})	0.844	0.413	0.928
Z, $D_{calcd.}$ (g/cm^3),	4, 2.031	4, 1.589	4, 1.956
Measured reflections	8096	26141	6940
Unique reflections	1986	6213	1752
R_{int}	0.0520	0.0575	0.0489
no. of variables	254	466	208
$t_{min.} - t_{max.}$	0.2970−0.7380	0.6080−0.8830	0.3930−0.7920
GOF on F^2	1.069	0.930	1.038
*R*1 [$I > 2\sigma(I)$]	0.0476	0.0386	0.0384
*wR*2 [$I > 2\sigma(I)$]	0.1299	0.0777	0.1085
*R*1 (all data)	0.0580	0.0711	0.0428
*wR*2 (all data)	0.1370	0.0875	0.1126
$\rho_{min.}$ and $\rho_{max.}$, e·Å^{-3}	0.942 and −0.478	0.255 and −0.290	0.399 and −0.354

(w). $C_{30}H_{30}BF_{15}N_3OV$: calcd. C 45.28, H 3.77, N 5.28; found C 45.33, H 3.66, N 5.07).

X-ray Analysis of 1, 2 and 3: Data were collected at low temperature (T = 180 K) for the three compounds, on a IPDS STOE diffractometer equipped with an Oxford Cryosystems Cryostream Cooler Device and using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Final unit-cell parameters were obtained by means of a least-squares refinement of a set of well-defined reflections; crystal decay was monitored during data collection and no significant fluctuations of intensities were observed. The structures were solved by direct methods using SIR92,[25] refined by least-squares procedures on F^2 with the aid of SHELXL-97[26] included in the program package WinGX version 1.63.[27] The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[28] All hydrogens atoms were located on difference Fourier maps and refined using a riding model with an isotropic thermal parameter fixed at 20% higher than those of the carbons atoms to which they are connected. For **3** a disorder was located on the fluorine group: the fluorine atoms were found to be statistically disordered over two distinct orientations with an occupancy ratio of 55/45. Some restraints on interatomic C−F distances and F−C−F angles were imposed in order to reach a reasonable geometry and regularize the motion of the F atoms. For the three compounds all non-hydrogens atoms were refined anisotropically and, in the last cycles of refinement, a weighting scheme was used whose weights were calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. For all structures the criteria for a satisfactory complete analysis were a ratio of rms shift to standard deviations of less than 0.1 and no significant residual electronic densities in the final differences maps. Drawings of molecules were performed with the program ORTEP32[29] with 50% probability displacement ellipsoids for non-hydrogen atoms. The crystallographic data of **1**, **2** and **3** are summarized in Table 1. CCDC-190469 (**1**) -190470 (**2**) and -190471 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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