Research Article

Solid State Structure of Bis[(bromo)(dicyclopentadienyl)vanadium(μ_2 -fluoro)][(bromo)(cyclopentadienyl)vanadium][tetrafluoroborate]

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The new complex $[V(C_5H_5)_2Br]_2(\mu_2-F)_2[V(C_5H_5)Br]^+[BF_4]^-$ has been isolated from the reaction of vanadocene monobromide with the ferrocenium cation. The complex is a mixed valence compound composed of two V(IV) and one V(III) centers. The V(III) center has one cyclopentadienyl ligand in its coordination sphere, as well as a bromide and two fluoride ligands. Each fluoride ligand is also attached to one of the V(IV) centers, which additionally is coordinated by a bromide and two cyclopentadienyl ligands. The complex crystallizes in the monoclinic space group $P2_1/m$, with $a = 7.66490(10)$ Å, $b = 15.2457(2)$ Å, $c = 13.3185(2)$ Å, and $\beta = 101.2721(8)^\circ$ at 150(1) K.

1. Introduction

While numerous $M(C_5H_5)_2X_2$ (X = halogen) complexes are known, species with two different halide ligands are significantly less common. For vanadium, the dichloride [1], dibromide [2], and diiodide [3] are all known and the dibromide [4], the dichloride, and some alkyl-substituted analogues [5–8] have been crystallographically characterized. No structures have been reported for any mixed species, nor for fluoride complexes, with the exception of species having two AsF_5 or SbF_5 fragments linked to the fluorides [9, 10]. Herein a reaction product isolated from an attempt to generate a mixed $V(C_5H_5)_2BrF$ complex is reported.

2. Materials and Methods

2.1. Synthesis. All operations were conducted under a nitrogen atmosphere using dried and deoxygenated solvents. 0.202 g of $V(C_5H_5)_2Br$ [11] was dissolved in 20 mL of methylene chloride in a 100 mL Schlenk flask. 0.211 g of $[Fe(C_5H_5)_2]^+[BF_4]^-$ [12] was then added, leading to a brownish-yellow solution. After the solution was allowed to stir for several hours, the solvent was removed in vacuo, and the

residue was washed with hexane to remove ferrocene, leaving a greenish colored solid. This was not very soluble in toluene and was redissolved in a small amount of methylene chloride. The solution exhibited a dark green color by reflection but pale brownish by transmission. After about a week at -60° in a freezer, a small amount of air- and moisture-sensitive crystals had formed.

2.2. X-Ray Crystallography. Single crystals were selected under Paratone oil and transferred to an Enraf-Nonius Kappa CCD diffractometer for low temperature unit cell determination and data collection. A cold nitrogen stream was used to maintain a nearly constant temperature and to protect the compound from air. The structure was solved by SIR 97 [13] and improved from difference Fourier maps and least-squares refinements using SHELXL97 [14], using published scattering factors [15]. Only one cyclopentadienyl ligand was found not to be disordered (C1–5 on V1), with the other two adopting two orientations each. For V1, its second C_5H_5 ligand images appear nearly equally well defined, as judged by their thermal parameters. In contrast, one of the two images for the single C_5H_5 ligand, with imposed m symmetry, on V2, is significantly better defined than the other

TABLE 1: Crystal and experimental data.

Empirical formula	$C_{26}H_{27}Br_3Cl_2F_6V_3$
Formula weight	927.74
Temperature (K)	150(1)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	
<i>a</i>	7.66490(10)
<i>b</i>	15.2457(2)
<i>c</i>	13.3185(2)
β (°)	101.2721(8)
Volume (Å ³)	1526.33(4)
<i>Z</i>	2
D_{calcd} (g cm ⁻³)	2.019
$\mu(\text{MoK}\alpha)$ (mm ⁻¹)	5.056
<i>F</i> (000)	900
θ range (°)	2.67–27.46
	$-9 \leq h \leq 9$
Limiting indices	$-19 \leq k \leq 19$
	$-17 \leq \ell \leq 17$
Reflections collected/unique	6956/3614
Completeness (%)	99.9
Goodness of fit on F^2	1.072
<i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0313, wR_2 = 0.0649$
<i>R</i> indices (all data)	$R_1 = 0.0409, wR_2 = 0.0688$
<i>R</i> (int)	0.0177
$(\Delta\rho)_{\text{max,min}}$	2.374, -2.321

and will be used exclusively for subsequent discussions of bonding parameters. All nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were modeled isotropically and were all allowed to ride on their attached carbon atoms. Pertinent crystallographic information is contained in Table 1, while selected bonding parameters are given in Table 2. The largest peak and hole observed in the final difference Fourier map are each within 0.75 Å of Br2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC, number 1430708. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ FAX [+44(1223)336-033] or e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/>.

3. Results and Discussion

The structure of the cationic portion of the isolated product is shown in Figure 1, while selected bonding parameters are given in Table 2. This portion may be formulated as $[V(C_5H_5)_2Br]_2(\mu_2-F)_2[V(C_5H_5)Br]^+ (I^+)$, having five C_5H_5 ligands, three terminal bromide ligands and two doubly bridging fluoride ligands. The first two vanadium centers

TABLE 2: Selected bond lengths (Å) and angles (°) for $[V(C_5H_5)_2Br]_2(\mu_2-F)_2[V(C_5H_5)Br]^+[BF_4]^-$.

Bond distances			
V1–Br1	2.5600(5)	V2–Br2	2.4293(8)
V1–F1	2.008(2)	V2–F1	1.680(2)
V1–C1	2.326(3)	V1–C6	2.31(2)
V1–C2	2.322(3)	V1–C7	2.29(2)
V1–C3	2.278(3)	V1–C8	2.28(2)
V1–C4	2.278(3)	V1–C9	2.30(2)
V1–C5	2.293(3)	V1–C10	2.29(2)
V2–C11	2.277(5)	V1–C6'	2.31(3)
V2–C12	2.350(5)	V1–C7'	2.34(3)
V2–C13	2.354(6)	V1–C8'	2.28(3)
V2–C11'	2.41(2)	V1–C9'	2.27(3)
V2–C12'	2.16(2)	V1–C10'	2.31(3)
V2–C13'	2.33(2)		
Bond angles			
Br1–V1–F1	87.74(6)	Br2–V2–F1	99.48(7)
V1–F1–V2	172.78(12)	F1–V2–F1'	107.28(13)

are equivalent due to a crystallographic mirror plane. As a result, the three vanadium centers have a total charge of +11, and the only reasonable formulation would have the two end vanadium centers (V1, V1') being tetravalent and the central one (V2) trivalent. This is consistent with the fact that the tetravalent V1 centers are bound by one more anionic ligand as compared to V2. Given the fact that V2 has lost a C_5H_5 ligand, the formation of the product appears to have required a one electron oxidation for each of the three vanadium centers, presumably forming $V(C_5H_5)_2Br^+$ ions. One of these could then abstract a fluoride ion from BF_4^- to give $V(C_5H_5)_2FBr$, which subsequently lost one of its C_5H_5 ligands, yielding $V(C_5H_5)FBr$. Its subsequent linking up with two other oxidized vanadium units, one in the form of $V(C_5H_5)_2Br^+$ and the other as $V(C_5H_5)_2FBr$, would lead to the observed product, in which the two V(IV) centers might presumably be stabilized through their sharing their fluoride ions with the central V(III) center.

Support for the proposed metal oxidation states may be obtained from a comparison with $V(C_5H_5)_2Br_2$ [4], whose V–Br bonds are ca. 0.28 Å longer than its V–C bonds (2.58 versus 2.30 Å). This is quite consistent with our observed V1–Br1 and average V1–C distances (2.5600(5) and 2.30 Å). The V2–C distances average 2.337(15) Å, only slightly longer than the V1–C distances. While a greater difference might have been expected based on data for $V(C_5H_5)_2Cl_2$ [5–8] and $V(C_5H_5)_2Cl$ [16], the reduced steric crowding in the present case for V2 should lead to some shortening. The V2–Br2 bond is somewhat shorter than the V1–Br1 bond, 2.4293(8) versus 2.5600(5) Å. In contrast, the V2–F1 bonds are much shorter than the V1–F1 bond, 1.680(2) versus 2.008(2) Å, opposite to expectations based upon relative metal ion acidities. Given that the V2 center can be formulated as having a 14-electron configuration, arising from the central $[V(C_5H_5)Br]^+$ unit

FIGURE 1: Structure of the cationic portion of $[V(C_5H_5)_2Br]_2(\mu_2-F)_2[V(C_5H_5)Br]^+[BF_4]^-$.

being further coordinated by a fluorine atom lone pair from each of the two $V(C_5H_5)_2FBr$ units, it would be quite feasible for these two fluorine atoms to serve as π donors also, thereby generating an 18-electron configuration for V2 and accounting for the V2–F bonds being shorter than the V1–F bonds. In this approach, the fluorides would each be serving as four electron donors to V2. One could alternatively invoke a resonance form in which fluoride lone pairs from the central $[V(C_5H_5)_2F_2Br]^-$ unit coordinate to the two terminal $[V(C_5H_5)_2Br]^+$ units. This would not change the electron counts at the vanadium centers but would lead to the fluoride coordination at V2 to be considered to be three electron interactions.

The local environments about V1 and V2 may be favorably compared with related species. For V1, some comparisons have already been made for its V–Br1 and V–C bonds. In addition, the F1–V1–Br1 angle of $87.74(6)^\circ$ can be compared to those for $V(C_5H_5)_2Br_2$ and $V(C_5H_5)_2Cl_2$, $86.60(4)^\circ$ and $87.20(3)^\circ$, respectively. The V1–F1 distance of $2.008(2)$ Å is slightly shorter than the V–F distances in $V(C_5H_5)_2[(\mu_2-F)AsF_5]_2$ and $V(C_5H_5)_2[(\mu_2-F)SbF_5]_2$ ($2.03(1)$ and $2.04(1)$ Å,

resp.) [9, 10], which likely reflects the high Lewis acidities of AsF_5 and SbF_5 .

For the piano stool coordination environment of V2, one observes F1–V2–F1' and F1–V2–Br2 angles of $107.28(13)^\circ$ and $99.48(7)^\circ$ and angles between the cyclopentadienyl ligand centroid and F1 and Br2 of 122.5° and 98.8° . For $[V(C_5H_5)Cl_3]^-$ [17] and $[V(C_5H_4Me)Cl_3]^-$ [18], the Cl–V–Cl angles ranged from $95.25(4)^\circ$ to $103.19(4)^\circ$ and from $95.0(1)^\circ$ to $100.0(1)^\circ$, while the centroid–V–Cl angles ranged from $117.4(2)^\circ$ to $120.1(2)^\circ$ and from 118.8° to $120.7(4)^\circ$, respectively. For the V(IV) complexes $V(C_5H_4Me)Cl_3$ [19] and $V(C_5Me_4Et)Cl_3$ [20], the Cl–V–Cl angles ranged from $98.7(1)^\circ$ to $103.3(1)^\circ$ and from $99.69(4)^\circ$ to $102.02(3)^\circ$, while the centroid–V–Cl angles ranged from $116.4(5)^\circ$ to $117.8(5)^\circ$ and from $115.13(9)^\circ$ to $117.65(5)^\circ$, respectively. For $V(C_5H_5)I_3$ [21], the I–V–I angles ranged from $99.5(1)^\circ$ to $101.6(1)^\circ$, while the centroid–V–I angles ranged from $115.6(1)^\circ$ to $119.5(2)^\circ$. These values show little difference as compared to the V(IV) chloride complexes. The V2 environment in **1**⁺ differs from the above primarily in its large F1–V2–F1' angle of $107.28(13)^\circ$ and small centroid–V–Br2 angle of 98.8° . These would likely

seem to be a result of the fact that F1 is also coordinated to V1 and perhaps furthermore to its apparent π donor interaction with V2.

4. Conclusions

The accessibility of both $V(C_5H_5)_2X$ and $V(C_5H_5)_2X'$ ($X, X' = \text{halides}$) complexes makes it possible to isolate $V(C_5H_5)_2XX'$ complexes. This work demonstrates how a combination of fluoride and bromide ligands may be added to the vanadocene fragment, yielding a complex that is of further interest due to its mixed valence character. Additional routes, such as those developed for pentadienyl complexes [22], may also be suitable for such preparations, as has also been demonstrated by the use of interhalogen molecules [3].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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