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Cationic Vanadium(IV) Methyl Complexes $[Cp_2VMe(CH_3CN)][B(C_6H_5)_4]$ and $[Cp_2VMe(THF)][MeB(C_6F_5)_3]$

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The cationic vanadocene alkyl complex $[Cp_2VMe(CH_3CN)]^+$ with $[BPh_4]^-$ counteranion was structurally established. The reaction of Cp_2VMe_2 in THF in the presence of $B(C_6F_5)_3$ is also described: EPR evidence of the intermediate formation of the $[Cp_2VMe(THF)]^+$ species, which gives, via a disproportionation redox reaction, the V^{III} species $[Cp_2V(THF)][Me\ B(C_6F_5)_3]$, is demonstrated.

The chemistry of cationic complexes of group 4 is very well documented, and literature is abundant concerning the structural characterization of nearly all these complexes.[1] On the other hand, the chemistry and the X-ray structure of cationic complexes of vanadium is less developed[2] despite their potential application in Ziegler−Natta catalysis. Efforts have been made by our group to obtain types of cationic vanadium complexes from the protonolysis of vanadium alkylamido or vanadium alkyl complexes with $[NHMe_2Ph][BR_4]$ (R = C_6H_5 or C_6F_5).[3,4] Recently we carried out the reaction between Cp_2VMe_2 (**1**), and $[NHMe_2Ph][B(C_6H_5)_4]$ in acetonitrile, and $[Cp_2VMe(CH_3CN)][B(C_6H_5)_4]$ was isolated and spectroscopically and analytically characterized.[4] Its analogy with the well-known Ti and Zr analogue complexes[5−8] as well as its inertness toward ethylene polymerization in contrast to group 4 led us to ascertain the X-ray structure of this adduct vanadium complex to ensure that the formulated complex is −or is not−similar to the other structures already resolved and established in the Ti and Zr cationic chemistry. On the other hand the reactivity of **1** with the tris(perfluorophenyl)borane $B(C_6F_5)_3$ is hereby presented.

In the course of our studies of the reactivity of $[Cp_2VMe]^+$, we have recently crystallized $[Cp_2VMe(CH_3CN)][B(C_6H_5)_4]$ (**2**), which was confirmed by an X-ray crystal structure determination (Figure 1). The structure of **2** does not present new features in its tetrahedral structural geometry. Bond angles around the vanadium atom give a pseudo-tetrahedral geometry where both planes [Cp1, V, Cp2] and [N−V−C(3)] are nearly perpendicular (89.82°). Cyclopentadienyl rings are in a staggered position. V−C (2.221 Å) and V−N (2.096 Å) distances are consistent with other complexes containing V−C and $V(NCCH_3)$ units.[9−13]

Some chemistry of **1** with the tetraphenyl borate ammonium salt $[NHMe_2Ph][B(C_6H_5)_4]$ in THF was previously published.[4] Redox and disproportion reactions were demonstrated, according to Scheme 2. Similar pathways could be observed in the reaction of **1** with tris(pentafuorophenyl)borane, $B(C_6F_5)$, in toluene or THF, and the reactions can be monitored by EPR and NMR spectroscopies.

In toluene, the reaction of **1** with $B(C_6F_5)_3$ gives an immediate insoluble blue-violet oil with a nearly colorless supernatant solution. This is a rapid reaction that precluded observation of intermediates. Nevertheless, formation of C_2H_6 is observed by ^1H NMR when the reaction is performed in deuterated toluene or benzene. An NMR tube containing a weighted amount of **1** (0.05 mmol) and $B(C_6F_5)_3$ (0.05 mmol) is filled with deuterated solvent at −80 °C and sealed. After the temperature is allowed to reach room temperature, the tube is monitored by ^1H NMR. The presence of a peak at δ(C_6D_5-

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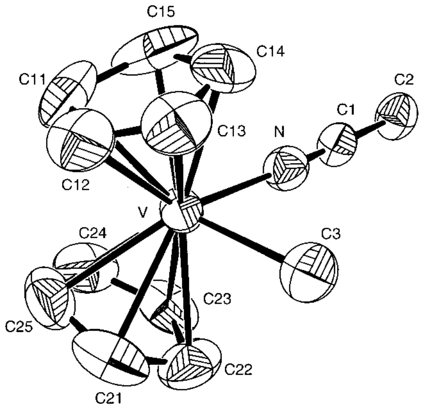
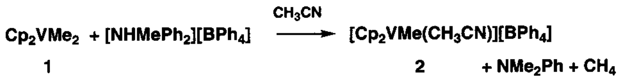
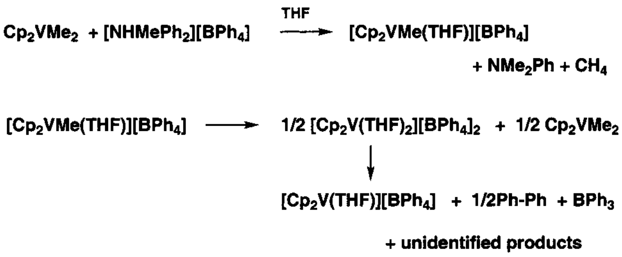


Figure 1. Molecular structure of the cation in **2** showing the labeling scheme; hydrogen atoms are omitted for clarity. The structure of the $[BPh_4]^-$ ion is normal. Selected bond lengths [Å] and angles [deg]: V−C(3) 2.221(5), V−N(1) 2.096(4), C(1)−N(1) 1.151(1), V−Cp1 1.950, V−Cp2 1.961, N(1)−V−C(3) 82.67(19), Cp1−V−CP2 136.69, Cp1−V−C(3) 103.53, Cp1−V−N(1) 107.30, Cp2−V−C(3) 104.74, Cp2−V−N(1) 108.46 (Cp1 and Cp2 are the centroids of C(11)−C(15) and C(21)−C(25) rings, respectively).

Scheme 1



Scheme 2



CD_3) 0.81 (δ(C_6D_6) 0.79) is in agreement with the values obtained for free C_2H_6 in these solvents. We suggest that the formation of ethane is probably due to a redox reaction between $[CH_3B(C_6F_5)_3]^-$ and the vanadium V^{IV} species, with concomitant formation of the borane $B(C_6F_5)_3$.

This oil is soluble in THF and gives, after addition of pentane, a solid characterized as $[Cp_2V(THF)][MeB(C_6F_5)_3]$ (**3**). The magnetic moment of **3** is consistent with a d^2 electronic configuration ($\mu_{eff} = 2.80\ \mu_B$). The ^1H NMR spectra of **3** in deuterated acetonitrile or acetone show free THF resonances, which indicate that ligand exchange occurs between THF and CD_3CN or $(CD_3)_2CO$ to give, presumably, $[Cp_2V(L)][MeB(C_6F_5)_3]$ (L = CD_3CN, $(CD_3)_2CO$) (L = $CD_3CN/(CD_3)_2CO$: δ (Cp) = 139.5/141.5 ppm; by comparison δ (Cp) = 138.7/140.5 ppm for $[Cp_2V(THF)BPh_4]$ in deuterated acetonitrile and acetone, respectively).[4,14] In THF, **1** and $B(C_6F_5)_3$ give a well-resolved EPR signal of a quadruplet of octets due to the interaction of the unpaired electron with ^{51}V ($I = 7/2$) and the three protons of a methyl group ($g = 1.991$; $A(^{51}V) = 73.2$ G; $A(^1H) = 5.1$ G), and the formation of $[Cp_2VMe(THF)][MeB(C_6F_5)_3]$ is suggested (Figure 2, Scheme 3, eq 1) (it is worth noting that very slightly soluble **2** in THF develops a less defined EPR spectrum[4] where the hyperfine coupling to the methyl group could not be observed). The formation of this species is nearly 90% in the experiments which we carried out, based on **1** (100%), by comparison with their EPR spectra, respectively. This complex in THF solution is unstable and leads to disproportionation and redox reactions, according to Scheme 3. Complete disappearance of $[Cp_2VMe(THF)]^+$ occurs in approximately 2−3 days, whereas the transient Cp_2VMe_2 EPR signal[15] ($A(^{51}V) = 63.4$ G) is observed before the formation of an EPR silent solution. A blue-purple solid was isolated from this solution and characterized by NMR (see the Experimental Section) as V^{III} complex **3**. To take into account the disappearance of the EPR signal of **1**, we suggest that the free borane formed from the redox reaction (Scheme 3, eq 3) reacted again with **1** formed from the disproportionation reaction (Scheme 3, eq 2). Only a major ^{11}B resonance ($\delta = 14.7$ ppm) was observed and was identified as $[MeB(C_6F_5)_3]^-$. The derivative organic byproduct from this cascade of disproportionation−redox reactions, i.e. the presence of ethane, confirms in part this pathway (the quantification of the mass balance of the reaction was not undertaken, due to the various oxidizing reactions of the counteranion with V^{IV}: the decapentafluorobiphenyl $(C_6F_5)_2$ was also identified in the reaction by GC/MS and its presence is probably due to another mode of redox reaction of the anion). On the other hand, with $B(C_6F_5)_3$ in the presence of acetonitrile, the formation of the adduct complex $CH_3CN{\cdot}B(C_6F_5)_3$[16] prevents further reaction with **1**.

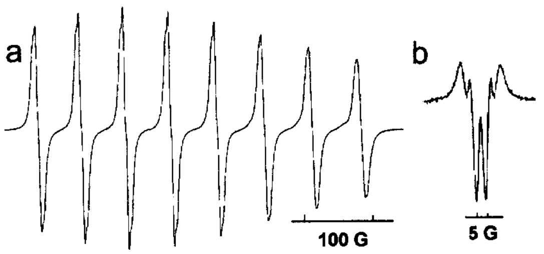
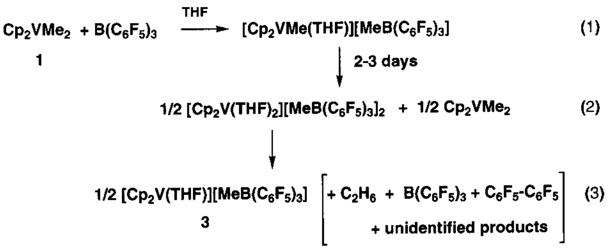


Figure 2. EPR (X-band) of a stoichiometric amount of **1** and $B(C_6F_5)_3$ in THF: (a) first derivative spectrum; (b) a part of the second derivative spectrum showing the superhyperfine coupling of the unpaired electron of the vanadium atom with a methyl group.

Scheme 3



In conclusion, when the reaction is performed in acetonitrile with the $[B(C_6H_5)_4]^-$ counteranion, the simplest member of the cationic vanadium series was structurally characterized. The reaction of Cp_2VMe_2 with the tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, in

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toluene or THF gives oily products. In THF, on the basis of EPR data, we were able to observe the formation of the intermediate $[Cp_2VMe]^+$ species. In this approach, the redox reaction of the V^{IV} species with the anionic part $[CH_3B(C_6F_5)_3]^-$ was slower than in the reaction of **1** with $[NHMe_2Ph][B(C_6H_5)_4]$ in THF, which gives immediate precipitation of $[Cp_2V(THF)][BPh_4]$ (Scheme 2). Disproportionation and redox reactions (to give Cp_2VMe_2 and V^{III} species) according to our previous results do occur and follow a similar sequence of events.

Experimental Section

General Procedures. All syntheses and subsequent manipulations were carried out under argon by conventional Schlenk tube techniques or using a drybox (Vacuum Atmosphere Dry-Lab) filled with argon. Liquids were transferred via syringe or cannula. All solvents were dried by conventional methods, distilled under argon, and degassed before use. Cp_2VMe_2[17] and $B(C_6F_5)_3$[18] were prepared according to previously reported procedures. We have reported the preparation of $[Cp_2VMe(CH_3CN)][B(C_6H_5)_4]$ in a previous paper.[4] Elemental analyses were performed at the laboratory (C, H) with a CCD-OMA4 detector and a Notch filter. Magnetic susceptibility measurements were carried out by Faraday's method. EPR spectra were obtained using a BRUKER ESP 300E spectrometer. NMR spectra were recorded at room temperature on Fourier transform NMR, Bruker AC200 (at 200.133 MHz for ^1H, 188.298 MHz for ^{19}F), and AMX400 (128.378 MHz for ^{11}B) spectrometers.

$[Cp_2V(THF)][MeB(C_6F_5)_3]$ (3). A toluene solution of $B(C_6F_5)_3$ (164 mg, 0.32 mmol) was added to **1** (63 mg, 0.3 mmol) dissolved in 5 mL of toluene at room temperature, under stirring. Viscous insoluble blue-violet oil was formed, which was allowed to settle nearly 1 day without stirring until the supernatant liquid became nearly colorless. Repeated decantations of the above liquid followed by toluene washings gave an oily product, which was solubilized in a small amount of THF (2−3 mL). Addition of pentane (15 mL) led to a precipitate, which was filtered, washed with pentane and toluene, and dried under vacuum; yield 70%. ^1H NMR (δ in ppm), in CD_3CN: 139.5 (br, $\Delta\nu_{1/2} = 1300$ Hz, 10H, Cp); 3.60, 1.78 (free THF in acetonitrile); 0.37 (br, 3H, $CH_3B(C_6F_5)_3$); in THF-d_8: 147.0 (br, $\Delta\nu_{1/2} = 1300$ Hz, 10H, Cp); 3.44, 1.65 (br, 4H,4H; a single set of broadened THF resonances is observed and shows that exchange of free and coordinated THF on the paramagnetic center is rapid); 0.66 (br, 3H, $CH_3B(C_6F_5)_3$). ^{19}F NMR in THF-d_8: −49.77 (*o*-F); −84.12 (*p*-F); − 85.12 (*m*-F). ^{11}B NMR in THF-d_8 (128.3776 MHz): −14.7. Anal. Calcd for $C_{32}H_{18}BF_{15}OV$: C, 50.23; H, 2.37. Found: C, 50.15; H, 2.26.

Reaction of Cp_2VMe_2 with $B(C_6F_5)_3$ in THF. A freshly prepared solution of $B(C_6F_5)_3$ (102 mg, 0.2 mmol) in THF (5 mL) was added to **1** (42 mg, 0.2 mmol) in 5 mL of THF at room temperature (an exact amount or a very slight excess of **1** was necessary to entirely consume the borane to avoid the polymerization of THF in the presence of $B(C_6F_5)_3$). The blue solution formed was monitored by EPR for 2−3 days until the complete disappearance of any EPR signal. The solution was reduced in vacuo to 1/3 of its volume and pentane added to give a blue-purple precipitate of **3**, characterized by ^1H NMR. Another unidentified minor species (roughly 10%) was also observed in the ^1H NMR and ^{11}B spectra ($\delta_{Cp} = 126$ ppm and −13.4 ppm, respectively).

EPR Experiments. A solution of **1** in THF was prepared, and an aliquot of the solution was introduced into a standardized capillary tube for EPR measurements. This EPR spectrum served as a standard for the reaction. The solid borane was then added to the solution, and aliquots were removed periodically, introduced into the capillary tube, and analyzed by EPR. The acquisition parameters were kept constant for both the unknown and the standard sample measurements.

Table 1. Crystallographic Data for 2

chemical formula	$C_{37}H_{36}BNV$
molecular wt	556.42
temperature	160(2) K
space group	monoclinic, $P2_1/n$
cell constants	$a = 9.5093(16)$ Å $b = 13.5601(15)$ Å $c = 22.947(4)$ Å $\beta = 95.78(2)°$
volume	2944.0(8) $Å^3$
Z, calcd density	4, 1.255 mg/m^3
abs coeff	0.363 mm^{-1}
$F(000)$	1172
no. of reflns collected/unique	19189/4220 [R(int) = 0.0912]
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4220/0/363
abs corr	semiempirical[24]
$T_{min} - T_{max}$	0.289−0.733
goodness-of-fit on F^2	1.115
final R indices [$I > 2\sigma(I)$]	R1 = 0.0646, wR2 = 0.1522
R indices (all data)	R1 = 0.0895, wR2 = 0.1676
largest diff peak and hole	(0.460 and −0.472) e $Å^{-3}$

X-ray Analysis of 2. A 10 mL CH_3CN solution of **1** (42 mg, 0.199 mmol) and $[NHMe_2Ph][BPh_4]$ (88 mg, 0.200 mmol) were mixed at room temperature. After 5 mn stirring, a large amount of purple solid **2** was filtered rapidly and the filtrate left for one week at 0 °C, to give suitable crystals of **2**.

Data were collected at low temperature, $T = 160$ K, on a IPDS STOE diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryosystems Cryostream cooler device. The final unit cell parameters were obtained by means of a least-squares refinement performed on a set of 5000 well-measured reflections; crystal decay was monitored during the data collection, and no significant fluctuations of intensities were observed. The structure was solved by direct methods using SIR92[19] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[20] included in the software package WinGX version 1.63.[21] The atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[22] All hydrogens atoms were located on a difference Fourier map and refined by using a riding model; consequently all coordinates of these H atoms have been introduced as fixed coordinates in the refinement with an isotropic thermal parameter fixed at 20% higher than those of the carbons atoms to which they are connected. All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Drawing of the molecule is performed with the program ORTEP32[23] with 50% probability displacement ellipsoids for non-hydrogen atoms. Crystallographic data of **2** are summarized in Table 1.

Supporting Information Available: Structural diagram with full atom labeling and tables of bond distances, angles, anisotropic parameters, and atomic coordinates for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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