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# Redox Properties of Cationic Vanadium(IV): $[Cp_2VCH_3(CH_3CN)][BPh_4]$

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The cationic vanadium complexes $[Cp_2VCH_3(CH_3CN)]^+$ and $[Cp_2V(THF)]^+$ with $[BPh_4]^-$ as counterion are obtained from $Cp_2VMe_2$ and $[NHMe_2Ph]BPh_4$ in $CH_3CN$ or THF, respectively; in $CH_2Cl_2$, chloride abstraction from the solvent occurs via a redox decomposition, evidenced by the X-ray crystal structure of $[N(CH_2Cl)Me_2Ph]BPh_4$ and the formation of $Cp_2VCl$. In presence of the phosphine $PMe_2Ph$, $[Cp_2VCH_3(CH_3CN)]^+$ affords the intermediate species $[Cp_2VCH_3(PMe_2Ph)]^+$ (characterized by the EPR spectrum with resolved methyl hyperfine interaction) followed by a disproportionation and a redox reaction with $[BPh_4]^-$, giving $Cp_2VMe_2$ and $[Cp_2V(PMe_2Ph)]^+$. Preliminary studies show that $[Cp_2VCH_3]^+$ is unreactive toward ethylene polymerization.

The chemistry of cationic transition metals of group 4 has challenged both experimentalists and theoricians due to its importance with regard to Ziegler–Natta or Kaminsky catalysts.[1] The extreme reactivity of the 14-electron species $[Cp_2MR]^+$ (M = Ti, Zr) allowed only occasional isolation of such compounds, stabilized by trapping with a donor. The synthesis of these stable 16-electron species is now well documented.[2] In contrast to the well-developed field of cationic dicyclopentadienyl–Ti and –Zr complexes,[3] the chemistry of cationic vanadium complexes has attracted much less attention.[4] In order to extend the cationic chemistry already described for Ti and Zr to V, we studied the protonolysis of $Cp_2VMe_2$ (**1**) with $[NHMe_2Ph]BPh_4$.

## Results and Discussion

The general procedure used in the synthesis of the 16-electron compounds $[Cp_2MR(L)]^+$ and base-free 14-electron compounds $[Cp_2MR]^+$ (M = Ti, Zr) was used for the synthesis of analogues of vanadium.[5,6] Reaction of $Cp_2VMe_2$ (**1**) with $[NHMe_2Ph]BPh_4$ in $CH_3CN$ at room temperature afforded a nearly quantitative precipitate of pale violet $[Cp_2VCH_3(CH_3CN)]BPh_4$ (**2**). The presence of the methyl group in **2** was confirmed by evolution of $CH_4$ (characterized by IR and mass spectra) on adding HCl to a suspension of **2** in THF. The adduct is paramagnetic, with one unpaired electron and a formal oxidation state of IV for the vanadium ($\mu = 1.88\ \mu_B$). The IR spectrum showed bands due to $CH_3CN$ at 2308 and 2279 $cm^{-1}$ (free $CH_3CN$ bands at 2287 and 2251 $cm^{-1}$).

When the reaction was carried out in THF at room temperature or at −80 °C, 1 equiv of methane was evolved and a blue-violet precipitate of $[Cp_2V(THF)]BPh_4$ (**3**) was obtained, identified by elemental analysis, magnetism ($\mu = 2.75\ \mu_B$, indicating two unpaired electrons), and $^1H$ NMR spectroscopy. The filtrate contains unreacted **1** and biphenyl (by EPR[7] and $^1H$ NMR and GC/MS, respectively). No $CH_4$ was observed on acidic hydrolysis of **3**, verifying the absence of the methyl group. The yield of the reaction was roughly 50% based on vanadium. We propose a disproportionation and a redox reaction[8] between $V^{IV}$ and $[BPPh_4]^-$. It is reasonable to assume that the intermediate $[Cp_2VMe(THF)]BPh_4$ disproportionates to $[Cp_2V(THF)_2](BPh_4)_2$ and $Cp_2VMe_2$, the $[Cp_2V(THF)_2]^{2+}$ oxidizing the counteranion $[BPh_4]^-$ to $BPh_3$ and PhPh. Compound **3** was also obtained from **1** and 2 equiv of the ammonium salt. In this case, 2 equiv of $CH_4$ and nearly 100% of **3**

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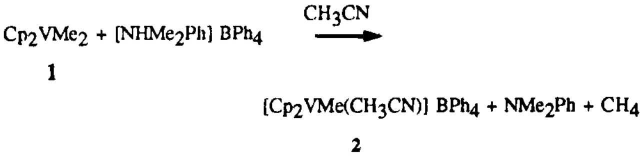
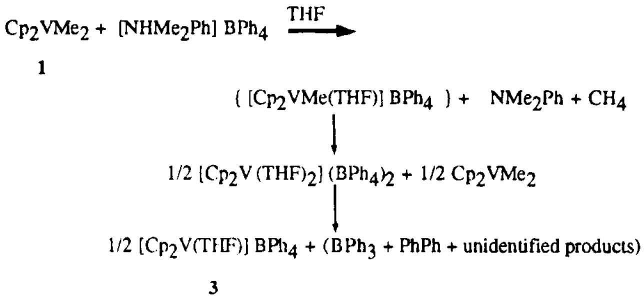
### Scheme 1



### Scheme 2



are obtained. Attempts to improve the mass balance of the reaction described in Scheme 2 by quantification of liberated PhPh was impossible (attributable to the formation of other unidentified boron species[8b,10] which leads us to underestimate PhPh), even through a quantitative yield of **3** is observed.

The instability of the THF intermediate adduct [$Cp_2VMe(THF)$]$BPh_4$ was demonstrated on treating complex **2**. A characteristic EPR spectrum for vanadium(IV) was obtained in THF, where **2** is slightly soluble, consistent with the suggested species [$Cp_2VMe(THF)$]$BPh_4$ ($I = {}^7/_2$, $g = 1.995$, $A(^{51}V) = 69.7$ G; no hyperfine coupling to the methyl group). Development of the EPR spectrum into the characteristic EPR spectrum of $Cp_2V(CH_3)_2$ occurs over 2 days, with formation of [$Cp_2V(THF)$]$BPh_4$, which was transformed after workup in acetone and identified by $^1$H NMR spectroscopy as [$Cp_2V(OCMe_2)$]$BPh_4$.[4] A similar disproportionation redox reaction occurs when **2** is treated with $PR_3$ ($PMePh_2$ or $PMe_2Ph$). Addition of $PR_3$ to a $CH_3CN$ suspension or a THF solution of **2** slowly displaced the $CH_3CN$ and generated a spectrum attributable to [$Cp_2VCH_3(PR_3)$]$BPh_4$. The unpaired electron interacts with the $^{51}V$ ($I = {}^7/_2$) nucleus and one $^{31}P$ ($I = {}^1/_2$) nucleus of the phosphine, giving a doublet of octets ([$Cp_2VCH_3(PMePh_2)$]$BPh_4$: $g = 2.007$, $a(^{31}P) = 23.3$ G, $A(^{51}V) = 66.7$ G). In the case of $PMe_2Ph$ in $CH_3CN$ (Figure 1), the methyl group on the vanadium gave a hyperfine coupling to the three protons of the methyl, observed as a quartet ([$Cp_2VCH_3(PMe_2Ph)$]$BPh_4$: $g = 1.999$, $a(^{31}P) = 30.8$ G, $a(^1H) = 6.25$ G, $A(^{51}V) = 61.2$ G). The change from [$Cp_2VCH_3(PMe_2Ph)$]$BPh_4$ to $Cp_2V(CH_3)_2$ occurs over 3–4 days with concomitant formation of [$Cp_2V(PMe_2Ph)$]$BPh_4$, identified after workup by $^1$H and $^{31}$P NMR spectroscopy and by comparison with an authentic sample prepared *in situ* from **3** and $PMe_2Ph$ in $CD_3CN$ (the relative intensities of liberated THF and $PMe_2Ph$ signals show the formation of the mono(phosphine) adduct; $^1$H NMR (ppm) 140 (Cp), 3.68, 1.83 (free THF), 1.75 ($J_{PH} = 13$ Hz, $V(PMe_2Ph)$), 1.42 (free $PMe_2Ph$); $^{31}$P NMR (ppm) 37.9). All these reactions leading to **1** and [$Cp_2V(L)$]$BPh_4$ (L = THF, $PR_3$) suggest that the intermediate complexes ([$Cp_2VCH_3(L)$]$BPh_4$) are probably kinetic products rather than thermodynamic ones, as for **2**. Exchanges of the THF in **3** with acetone and acetonitrile were followed by $^1$H NMR spectroscopy and give the corresponding adducts [$Cp_2V(L)$]$BPh_4$ (L = $OCMe_2$, $CH_3CN$) and free THF. The similar species [$Cp_2V(L)$]$BPh_4$[4] were previously isolated, but the THF adduct was not obtained from $Cp_2VCl$ by the chemical procedure used.

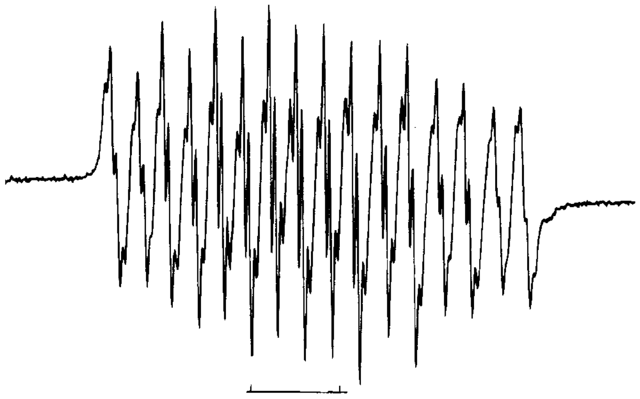


**Figure 1.** EPR spectrum in $CH_3CN$ at room temperature of **2** in the presence of an excess of $PMe_2Ph$.

It was recently shown that base-free 14-electron alkyl cations of titanium and zirconium in weakly coordinating solvents such as dichloromethane are active in the homogeneous polymerization of olefins.[5,6] Although the ammonium salt is known to be modestly stable in solution,[10] treatment of **1** and solid [$NHMe_2Ph$]$BPh_4$ in $CH_2Cl_2$ at −80 °C or at room temperature leads to a blue-green solution and a vanadium-free microcrystalline product in approximately 5–10% yield, depending on the experiment. An X-ray diffraction analysis showed this to be [$N(CH_2Cl)Me_2Ph$]$BPh_4$, instead of the expected $V^{IV}$ complex. The salt has a classical ammonium structure in which the $CH_2Cl$ fragment is the most significant (see the supporting information). Chloride abstraction from $CH_2Cl_2$ occurs frequently with 14- or 16-electron cationic zirconium or titanium complexes;[9] however, we have been able to trap the carbocation $[CH_2Cl]^+$ formed from the supposed transient adduct $[Cp_2VCH_3(CH_2Cl_2)]^+$. We believe that the reaction of the ammonium salt with **1** competes with its decomposition in $CH_2Cl_2$.[10] A similar reaction involving nucleophilic attack of $NR_3$ at a $Zr-ClCH_2Cl$ adduct, leading to a chloromethylammonium salt and a chlorozirconium complex, was recently reported by Jordan et al.[11] In our experiments, the formation of the neutral $Cp_2VCl$ was observed by $^1$H NMR spectroscopy and by comparison with an authentic sample. After the reaction, the solution was EPR silent and no $CH_4$ evolution was observed when HCl was added to the reaction mixture. The mechanism of the reaction, a disproportionation and a redox reaction between $V^{IV}$, $[BPh_4]^-$, and $CH_2Cl_2$, giving respectively $V^{III}$, $BPh_3$ (and other unidentified boron species), and $[N(CH_2Cl)Me_2Ph]^+$, was not studied in detail.

Since $Cp_2VCl_2$ in the presence of alkylaluminum halide as cocatalyst yields catalytic systems able to polymerize ethylene,[12] we have performed different

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ethylene polymerization tests with **1** containing the counteranions $[NHMe_2Ph]B(C_6F_5)_4$ and $B(C_6F_5)_3$ in various solvents (THF, toluene, $CH_3CN$, $CH_2Cl_2$, and $ClCH_2CH_2Cl$), at different temperatures (−30, 20, 40 °C) and pressures (2, 20, and 40 bar of $C_2H_2$), without success. Although the participation of cationic $d^0$ Ti and Zr complexes in Ziegler−Natta catalysis is well established, inclusion of cationic vanadium $[Cp_2VMe]^+$ within this framework has failed and will require additional effort. Our results seem to confirm that the presence of the intact $Cp_2V$ unit in the catalyst inhibits polymerization, as was previously observed.[12]

## Experimental Section

All manipulations were carried out under argon by conventional Schlenk tube techniques or using a drybox (Vacuum Atmosphere Dri-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: THF is distilled from sodium/benzophenone, toluene from sodium/potassium alloy, and $CH_2Cl_2$ from calcium dihydride. $Cp_2VMe_2$,[13] $[NHMe_2Ph]BPh_4$,[14] $[NHMe_2Ph]B(C_6F_5)_4$,[15] and $B(C_6F_5)_3$[16] were prepared and isolated via procedures described elsewhere. $^1H$ and $^{31}P$ NMR spectra were recorded on a Bruker WM 250 spectrometer (values of $^1H$ and $^{31}P$ chemical shifts are positive downfield from $SiMe_4$ or 85% $H_3PO_4$ in $D_2O$, respectively). Magnetic susceptibility measurements were carried out by Faraday's method. EPR spectra were recorded on a Bruker ER 200 T spectrometer. Elemental analyses were performed by the Service Central de Microanalyse du CNRS.

**$[Cp_2VMe(CH_3CN)]BPh_4$ (2).** A 10 mL $CH_3CN$ solution of $[NHMe_2Ph]BPh_4$ (800 mg, 1.81 mmol) was added to $Cp_2VMe_2$ (380 mg, 1.80 mmol) dissolved in 10 mL of $CH_3CN$ at 20 °C. Gas evolution was monitored by means of a Toepler pump, the gas being identified as $CH_4$ by IR and MS (approximately 1 equiv), and a purple solid formed. After 12 h of stirring, the purple mixture was filtered, leading to a brown filtrate and a violet solid which was washed with $CH_3CN$ and dried under vacuum; yield 80%. Anal. Calcd for $C_{37}H_{36}BNV$: C, 79.86; H, 6.52; N, 2.52; V, 9.15. Found: C, 79.42; H, 6.22; N, 2.46; V, 9.17.

Attempts to crystallize the compound by different experiments at lower temperature (−20 °C) with slow addition of the ammonium salt led to a similar precipitate of **2**.

**$[Cp_2V(VHF)]BPh_4$ (3).** A freshly prepared solution of $[NHMe_2Ph]BPh_4$ (585 mg, 1.33 mmol) in THF (10 mL) was added to $Cp_2VMe_2$ (280 mg, 1.33 mmol) in 10 mL of THF at 20 °C. Gas evolution was monitored by means of a Toepler pump (approximately 1 equiv of $CH_4$ identified by IR and MS), and a purple solid was formed. After 12 h, the mixture was filtered, giving a brown filtrate and purple solid **3**, which was washed with THF and dried under vacuum; yield 50%. The filtrate was identified by EPR spectroscopy as **1**. Acid hydrolysis of the solution gave the expected evolution of $CH_4$, whereas a suspension of **3** did not. GC/MS analysis of the filtrate confirmed the presence of biphenyl in the solution. Attempts to crystallize **3** in experiments at −80 °C with slow addition of solid ammonium salt (1 or 2 equiv per V atom) led to the same purple powder **3**. $^1H$ NMR (250 MHz, $\delta$ in ppm): in $[^2H_6]$acetone, $\delta$ 140.5 (broad signal, $\Delta\nu_{1/2}$ = 1170 Hz, Cp), 7.45, 7.06, 6.9 (s, t, t, $BPh_4$), 3.74, 1.90 (free THF in acetone); in $[^2H_3]$acetonitrile, $\delta$ 138.7 ((broad signal, $\Delta\nu_{1/2}$ = 1160 Hz, Cp), 7.27, 7.0, 6.85 (s, t, t, $BPh_4$), 3.64, 1.80 (free THF in acetonitrile). Anal. Calcd for $C_{38}H_{38}BOV$: C, 79.72; H, 6.64, V, 8.91. Found: C, 79.68; H, 6.59; V, 8.60.

**Reaction of $[Cp_2VCH_3(CH_3CN)]BPh_4$ (2), $[Cp_2V(THF)]BPh_4$ (3), and $PMe_2Ph$.** In a typical reaction, an NMR tube was charged with **3** (55 mg, 0.1 mmol), $[^2H_6]$acetone (0.5 mL), and a slight excess of $PMe_2Ph$ (200 mg, 1.48 mmol). The reaction was monitored by $^1H$ and $^{31}P\{^1H\}$ spectroscopy. Formation of $[Cp_2V(PMe_2Ph)]BPh_4$ was observed immediately. $^1H$ NMR (250 MHz, $\delta$ in ppm): in $[^2H_6]$acetone, $\delta$ 140 (broad signal, $\Delta\nu_{1/2}$ = 1170 Hz, Cp), 6.8−8.2 (m, Ph, $BPh_4$), 3.74, 1.90 (free THF in acetone), 1.74 (d, $J_{PH}$ = 13 Hz, $PMe_2Ph$), 1.42 (free $PMe_2Ph$); in $[^2H_3]$acetonitrile, $\delta$ 140 (broad signal, $\Delta\nu_{1/2}$ = 1170 Hz, Cp), 6.8−8.2 (m, Ph, $BPh_4$), 3.68, 1.83 (free THF in acetonitrile), 1.67 (d, $J_{PH}$ = 13 Hz, $PMe_2Ph$), 1.33 (broad signal, free $PMe_2Ph$). $^{31}P$ NMR (81 MHz): $\delta$ 37.9 (free $PMe_2Ph$, −40.2).

**Reaction of $Cp_2VMe_2$ and $[NHMe_2Ph]BPh_4$ in $CH_2Cl_2$.** Solid $[NHMe_2Ph]BPh_4$ (345 mg, 0.781 mmol) was added to $Cp_2VMe_2$ (172 mg, 0.781 mmol) in 10 mL of $CH_2Cl_2$ at −80 °C. The reaction mixture was warmed slowly to room temperature. After 12 h, the mixture was filtered, leading to a blue-green solution and a crystalline solid, which was washed with $CH_2Cl_2$ and dried under vacuum. The solid was identified as $[N(CH_2Cl)Me_2Ph]BPh_4$ by an X-ray structure determination (the description of the data collection and structural analysis as well as the structural results are in the supporting information). A part of the filtrate was evaporated to dryness and dissolved in $CD_2Cl_2$. The $^1H$ NMR spectrum showed a broad peak at 130 ppm, identified by comparison with an authentic sample as $Cp_2VCl$. $^{11}B$ NMR spectroscopy showed peaks at −5 and 70 ppm due to $[BPh_4]^-$ and $BPh_3$, respectively, and a third unidentified peak at 46 ppm. GC/MS analysis of the remaining filtrate confirmed the presence of biphenyl in the solution as well as benzene due to the decomposition of the ammonium salt.[10]

**General Procedure for Polymerization Reactions.** A 75 mL autoclave with a magnetic stirrer was connected via a pressure regulator to a 125 mL tank of ethylene. The tests were made according to the procedure described previously.[2b] In a typical run, aliquots of toluene solutions of **1** (80 mg, 0.378 mmol) and $[NHMe_2Ph]B(C_6F_5)_4$ (150 mg, 0.187 mmol) were injected into the autoclave, previously charged with toluene saturated with ethylene, at the required temperature. After 2 h the reaction was terminated by injecting 5 mL of methanol. In any case, no polymer was observed in the solution. Experimental conditions: (i) solvents toluene, THF, $CH_2Cl_2$, and $ClCH_2CH_2Cl$; (ii) temperatures −20, 20, and 40 °C; (iii) ethylene pressure 1, 2, and 20 bar.

**Supporting Information Available:** Tables giving details on the data collection and structure of $[N(CH_2Cl)Me_2Ph]BPh_4$, all atomic coordinates, thermal parameters, bond distances, bond angles, and least-squares-planes equations and deviations therefrom and an ORTEP plot of the structure (10 pages). Ordering information is given on any current masthead page.

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