PREPARATION AND CHARACTERIZATION OF VANADOCEN(IV) HEXAFLUOROARSENATE COMPLEXES AND THE HF CATALYZED OXIDATION TO VANADOCENIUM(V) SPECIES

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Whereas in the Reaction of Cp_2VCl_2 ($Cp = \eta^5\text{-}C_5H_5$) with pure AsF_5 (eq. 1a,b) chloride is oxidized to yield Cl_2, AsF_3 and $Cp_2VCl(AsF_6)$ traces of anhydrous HF facilitate the (thermodynamically favoured) oxidation of vanadium to give $[Cp_2VCl_2]^+[AsF_6]^-$ in 98% yield and AsF_3 (eq. 2). Similarly $Cp_2V(AsF_6)_2$ is oxidized by AsF_5 in the presence of of HF to yield $[Cp_2V(AsF_6)_2]^+[AsF_6]^-$ and AsF_3 but $Cp_2V(AsF_6)_2$ does not react with pure AsF_5 in SO_2 at room temperature.

$$2\ Cp_2VCl_2 + 3\ AsF_5 \longrightarrow 2\ Cp_2VCl(AsF_6) + AsF_3 + Cl_2 \qquad (1a)$$

$$Cp_2VCl_2 + 3\ AsF_5 \longrightarrow Cp_2V(AsF_6)_2 + Cl_2 + AsF_3 \qquad (1b)$$

$$2\ Cp_2VX_2 + 3\ AsF_5 \xrightarrow{HF} 2\ [Cp_2VX_2]^+[AsF_6]^- + AsF_3 \qquad (2)$$

$$X = Cl,\ AsF_6$$

The structure of $Cp_2V(SbF_6)_2$ and $[Cp_2VCl_2]^+[AsF_6]^-$ has been determined by a X-ray diffraction study. The paramagnetic species $Cp_2V(AsF_6)_2$, $Cp_2V(SbF_6)_2$ and $Cp_2VCl(AsF_6)$ were characterized by e.p.r. spectroscopy on polycrystalline samples and in THF, CH_2Cl_2 and SO_2 solution.

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