150

THE CHEMISTRY OF HIGHLY OXIDIZED METALLOCENE HEXAFLUOROPNICOGENATE COMPLEXES

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Quite recently we reported the synthesis of covalent and cationic metallocene hexafluoropnicogenate complexes of the type $Cp_2M(EF_6)_2$ (M = Ti, V; E = As, Sb) and $Cp_2M'Cl_2(EF_6)_n$ (M' = V, Nb; n = 1. M' = Mo, W; n = 2). The per(hexafluoropnicogenate) species can be obtained quantitatively from the dichlorides according to eqs. (1) and (2):

$$Cp_2M^{Cl}_2 + 3n/2 EF_5 \xrightarrow{SO_2} Cp_2M^{Cl}_2^{n+}(EF_6)_n + n/2 EF_3$$
 (1)

$$Cp_2M'Cl_2^{n+}(EF_6)_n + 2 AgEF_6 \longrightarrow Cp_2M'(EF_6)_2^{n+}(EF_6)_n$$
 (2)
- 2 AgCl+

The reaction of the covalent $Cp_2Ti(AsF_6)_2$ with strong Lewis bases leads to cationic derivatives according to eqs. (3) and (4):

$$Cp_{2}Ti(AsF_{6})_{2} + 2 CH_{3}CN \longrightarrow Cp_{2}Ti(CH_{3}CN)_{2}^{2+}(AsF_{6})_{2}$$
(3)

$$cp_2 Ti(ch_3 cn)_2^{2+}(AsF_6)_2 + Ch_3 cn \implies cp_2 Ti(ch_3 cn)_3^{2+}(AsF_6)_2$$
 (4)

The solution equilibria are discussed on the basis of ${}^{1}\text{H}$ and ${}^{19}\text{F}$ n.m.r. data. Although the chemistry of neutral metallocene dichlorides is well documented it is interesting to investigate the reactivity of the corresponding highly oxidized cations. For example, Cp_2MoCl_2 reacts with two equivalents of sodium mercaptide yielding $\text{Cp}_2\text{Mo(SR)}_2$. Surprisingly (or not?) $\text{Cp}_2\text{MoCl}_2^{2+}$ oxidizes the sulphur yielding the disulfide.