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SYNTHESIS AND CHARACTERIZATION OF EARLY TRANSITION METAL COMPLEXES IN THEIR HIGHEST OXIDATION STATES

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Neutral metallocene dichlorides (Cp_2MCl_2) of the early transition metals (M = gp. 4-6 metal) have been known for a long time. However, only the gp. 4 derivatives (like Cp_2TiCl_2) possess the central metal atom in its highest oxidation state (+IV). Whereas $Cp_2NbCl_2^+$ was unknown in substance prior to our work, even aqua regia is able to oxidize the gp. 6 species only to oxidation state +V. On the basis of a simple thermodynamic cycle we estimated that $NO^+SbF_6^-$, SbF_5, AsF_5 and $I_3^+AsF_6^-$ should oxidize Cp_2NbCl_2. Subsequently we prepared in 100% yield and characterized the complex by chemical analyses and single crystal X-ray diffraction. Whereas Cp_2VCl_2 reacts with $AgAsF_6$ quantitatively (in analogy to Cp_2TiCl_2) in a substitution reaction yielding $Cp_2V(AsF_6)_2$ it can be oxidized by AsF_5 or F_2/BF_3 leading to the cationic species $Cp_2VCl_2^+$. The covalent F co-ordinated derivatives $Cp_2M(EF_6)_2$ with linear M····F····E interaction were characterized by vibrational spectroscopy and X-ray diffraction.

Finally we succeeded in preparing the gp. 6 dicationic complexes $Cp_2MoCl_2^{2+}$ and $Cp_2WCl_2^{2+}$ as their AsF_6^- or SbF_6^- salts, respectively. Both cations are structurally characterized by X-ray diffraction and are of interest as they complete the series of gp. 6 metallocene dichlorides of the type $Cp_2MCl_2^{n+}$ (n = 0, d^2; n = 1, d^1; n = 2, d^0). The novel cations are of interest in terms of structure and bonding and open up the chemistry of cationic highly oxidized species of the early transition metals.