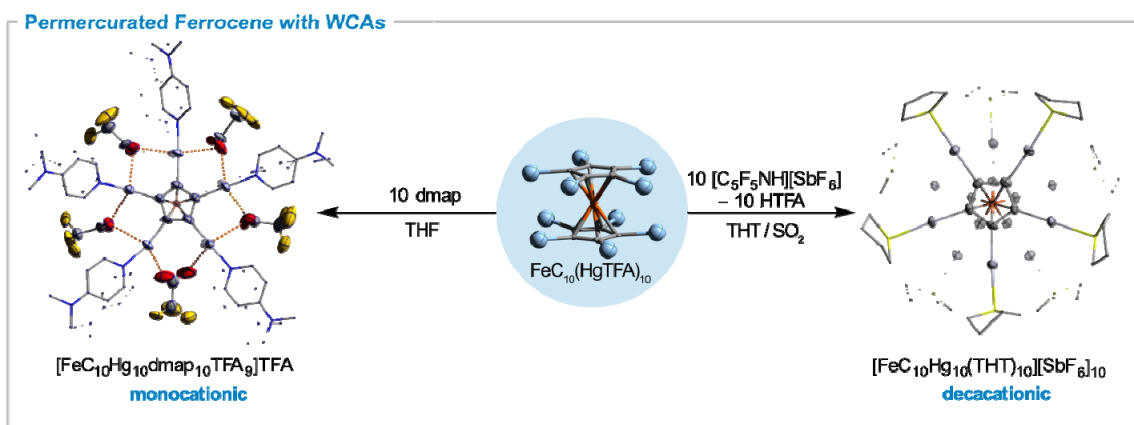


SYNTHESIS OF A FERROCENE DECA- AND UNDECACATION

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Mercury(II) compounds HgX_2 ($X = \text{carboxylate}$) react with aromatic molecules by an electrophilic substitution mechanism to replace the aromatic protons by HgX substituents under liberation of HX [1]. This reactivity can be used for achieving multiple metalations in one-pot reactions. Recently, we reported a procedure for a clean tenfold mercuriation of ferrocene with mercury(II) butyrate in high yields [2]. Although the compound $[\text{FeC}_{10}(\text{HgO}_2\text{CC}_3\text{H}_7)_{10}]$ offers relatively weak Hg-C bonds allowing transmetalation and electrophilic substitution reactions, we demonstrated recently that they are chemically inert towards air and strong Brønsted acids (e.g. $\text{CF}_3\text{CO}_2\text{H}$ $\text{p}K_{\text{a}} = -2.7$) [2,3]. In this work we investigated the reactivity towards Brønsted superacids. We were able to introduce labile ligands, e.g. by protonation of $[\text{FeC}_{10}(\text{HgO}_2\text{CCF}_3)_{10}]$ with $(\text{C}_5\text{F}_5\text{NH})(\text{SbF}_6)$ ($\text{p}K_{\text{a}} = -11$) [4]. In the resulting compound, $[\text{FeC}_{10}\text{Hg}_{10}(\text{NC}_5\text{F}_5)_n][\text{SbF}_6]_{10}$, the pentafluoropyridine ligands are readily displaced by a series of other neutral ligands ($\text{C}_5\text{F}_3\text{H}_2\text{N}$, MeCN , THT , $\text{Fe}(\text{CO})_5$). The compounds were characterized by vibrational and NMR spectroscopy in case of soluble compounds as well as single-crystal XRD. Moreover, cyclic voltammetry measurements reveal that the compounds $[\text{FeC}_{10}(\text{Hg}(\text{MeCN}))_{10}]^{10+}$ and $[\text{FeC}_{10}(\text{Hg}(\text{THT}))_{10}]^{10+}$ can be further oxidized. By reaction of $[\text{FeC}_{10}(\text{Hg}(\text{MeCN}))_{10}]^{10+}$ with MoF_6 the cation $[\text{FeC}_{10}(\text{Hg}(\text{MeCN}))_{10}]^{11+}$ could be isolated and characterized via single-crystal XRD.



Scheme 1. Reaction of $[\text{FeC}_{10}(\text{HgTFA})_{10}]$ with dmap (left) and with $(\text{C}_5\text{F}_5\text{NH})(\text{SbF}_6)$ in a THT/SO_2 mixture (right) and molecular structures in solid state of $[\text{FeC}_{10}(\text{Hg dmap})_{10}\text{TFA}_9]^+$ and $[\text{FeC}_{10}(\text{HgTHT})_{10}]^{10+}$. Disorder and hydrogen atoms as well as selected anions are omitted for clarity. Color code: light grey – mercury, light yellow – sulfur, yellow – fluorine, red – oxygen, blue – nitrogen, grey – carbon.

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