HOMOLEPTIC Pt(IV)$-CF_3$ AND $-OTeF_5$ COMPLEXES: SYNTHESIS, REACTIVITY, AND OSLO-BASED BONDING ANALYSIS

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Homoleptic transition metal complexes are prototypical species in the development of coordination and organometallic chemistry due to their simple nature. In the particular case of homoleptic d-block metal trifluoromethyl ($-CF_3$) and pentafluoroorthotellurate (teflate, $-OTeF_5$) complexes, only a few representatives are known for metals of Groups 10-12, with oxidation states ranging from +I to +III. Six-coordinate homoleptic $-CF_3$ and $-OTeF_5$ complexes are even more scarce and virtually unknown for late transition metals. For the $-CF_3$ ligand, only the synthesis of $W(CF_3)_6$ and $U(CF_3)_6$ in a C_2F_6 plasma has been reported,[1] whereas for the $-OTeF_5$ group, octahedral homoleptic complexes are largely confined to early d-block metals (Groups 4-6).[2]

Herein, we present the multi-step synthesis of $[Pt(CF_3)_6]^{2-}$, the first structurally characterized d-block metal complex bearing six trifluoromethyl ligands. The synthesis starts from the highly trifluoromethylated precursor $[Pt(CF_3)_5I]^{2-}$,[3] with the final step involving fluorination of a cyanido ligand with the ClF/KF system (Figure 1). Additionally, we demonstrate a one-step synthesis of $[Pt(OTeF_5)_6]^{2-}$ using the strong oxidizer $ClOTeF_5$, yielding the first late d-block metal pentafluoroorthotellurate complex with an oxidation state higher than +III.

Quantum-chemical analyses of a series of homoleptic metal teflate complexes employing the oxidation state localized orbital (OSLO)[4] approach reveal a linear correlation between the degree of localization (FOLI value) of the σ Pt–O bonding orbital and the O–Te bond length. This relationship provides quantitative insight into the balance between covalent and ionic contributions to the metal–ligand interaction and underscores the potential of the OSLO method as a general tool for assessing bond ionicity in coordination chemistry. Furthermore, the oxidation of the platinum(IV) center to attain Pt complexes in higher oxidation states is investigated.

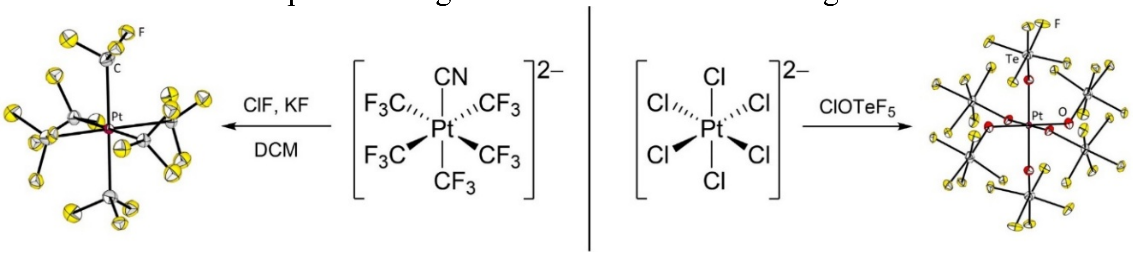

Figure 1 Syntheses and molecular structures in the solid state of the homoleptic platinum(IV) complexes $[Pt(CF_3)_6]^{2-}$ and $[Pt(OTeF_5)_6]^{2-}$.

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