Towards Terminal High-Valent Metal-Oxo Motifs on Multimetallic Scaffolds

The versatility by which iron-containing metalloenzymes are able to activate and oxygenate C–H bonds with molecular dioxygen, has sparked much interest into the underlying mechanism. It has been shown that high-valent iron metal centers bearing terminal oxo ligands are common intermediates and consequently, many monometallic iron model complexes exhibiting terminal oxo ligands have been investigated. Despite the intense research efforts, terminal oxo motifs on a multimetallic scaffold have not yet been reported. Recently we presented a new class of tetra-iron complexes that are site differentiated, with three iron centers that are six-coordinate and one unique four-coordinate iron center. The site-differentiated apical iron metal center is coordinatively unsaturated and allow for binding of additional ligands. Treating [LFe3(PhPz)3OFe][OTf]2 (PhPz = phenyl pyrazolate) with oxygen-atom transfer reagents (e.g. iodosobenzene or TBAIO4) results in regioselective hydroxylation by C–H activation of the arene ring. Interestingly, using the fluorinated analog [LFe3(F2PhPz)3OFe][OTf]2 (F2PhPz = 2,6-difluorophenyl pyrazolate) resulted in the conversion of the C–F bond to a C–OH bond. The regioselective intramolecular hydroxylation of the bridging pyrazolate in both [LFe3(PhPz)3OFe][OTf]2 and [LFe3(F2PhPz)3OFe][OTf]2 suggests the formation of a high-valent metal center bearing a terminal oxo ligand. These reactivity patterns and the likely involvement of an FeIV-oxo are rare on well-defined multi-metallic scaffolds involving iron metal
centers. Moreover, the possibility for intramolecular electron transfer to alter the reactivity of terminal iron-oxo species (FeIV–O vs. FeIII–O) in a multimetallic scaffolds will be discussed.