

# An Iron Catalyst for O-Transfer Reactions: Coordination and Halogen-Bonding Assisted Iodosylbenzene Activation

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We have discovered an iron catalyst which efficiently catalyzes selective oxidations of electron-rich olefins and sulfides by the practical terminal oxidant, “hypervalent” iodosylbenzene (PhIO).<sup>[1]</sup> An intermediate in the reaction is a unique Fe<sup>III</sup>-OIPh complex. This species has been trapped and studied in the gas, solution and solid phases. Two molecules of the high spin diastereoisomer of the iron(III) precursor are proposed to work in unison to break the polymeric structure of insoluble [PhIO]<sub>n</sub>, concomitantly activating it. To our surprise these catalytic heterogeneous reactions are faster and more selective than homogeneous reactions using the soluble terminal oxidant methyl-morpholine-N-oxide.<sup>[2]</sup>

The X-ray crystal structure of the seven coordinated iron-OIPh complex shows remarkably short intermolecular I...O distances in a dimeric structure. The shortest is 0.94 Å less than the sum of the van der Waals radii of the respective atoms (3.50 Å) and is an unmistakable example of supramolecular halogen-bonding. This, together with coordination, results in reduction of the previously “hypervalent” PhIO. Mössbauer spectroscopy<sup>[2]</sup> indicates the presence of high spin iron(III) and L<sub>3</sub>-edge XANES indicate a +1.6 oxidation state for the I atom<sup>[3]</sup>.

[1] D. P. de Sousa, C. Wegeberg, M. V. Sørensen, S. Mørup, C. Frandsen, W. A. Donald and C. J. McKenzie, *Chemistry, Eur. J.* 2015, DOI: 10.1002/chem.201503112.

[2] A. Lennartson and C. J. McKenzie, *Angew. Chem., Int. Ed.*, 2012, 51, 6767-6770.

[3] C. Wegeberg, C. G. Frankær and C. J. McKenzie, unpublished results