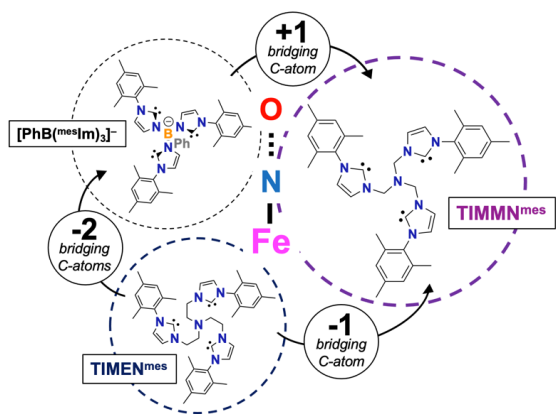


“Super-Oxidized” Iron Nitrido & “Super-Reduced” Iron Nitrosyl Complexes in *tris*-Carbene Coordination Spheres – and How Iron Really Feels About it

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Abstract: In this seminar, we will present our work on the synthesis and reactivity of metal nitrido and nitrosyl complexes. First, we report our studies on high-valent Fe(IV, V, VI and VII)^[1,2] nitrido complexes, synthesized *via* photolytic azide cleavage followed by oxidation with Ag^{II} and Xe^{II}-salts. In this series of complexes, the Fe≡N unit is stabilized by the sterically encumbered *N*-anchored *tris-N*-heterocyclic carbene chelates *tris*{2-(3-mesitylimidazol-2-ylidene)*alkyl*}amine (**alkyl**: methyl = TIMMN; ethyl = TIMEN). Based on the iron nitrido complex [(TIMEN^{Mes})Fe^{IV}(N)]⁺,^[1] we show how very subtle changes in ligand design (TIMEN *vs.* TIMMN) lead to tremendously different reactivity, and the stabilization and isolation of high-valent Fe(V)^[3] and super-oxidized Fe(VI)^[4] and Fe(VII)^[4] complexes.



Subsequently, we address the question to what extent the complexes' electronic and structural properties change when – formally – atomic oxygen is added to the nitrido ligand; thus, transforming a high-valent metal nitrido to a low-valent metal nitrosyl complex. Treatment of [(TIMEN^{Mes})Fe^{IV}(N)]⁺ with Me₃NO yields [(TIMEN^{Mes})Fe(NO)]⁺, thus providing access to a unique series of five iron nitrosyl complexes in a single ligand environment, [(TIMEN^{Mes})Fe(NO)]^m (m = 3+ to 1–), which – according to the Enemark & Feltham notation –

is formulated as {FeNO}⁶⁻¹⁰. The synthetic study was complemented with in-depth crystallographic, spectroscopic and computational analyses, giving detailed insights into the electronic structure of the currently most complete series of iron nitride and nitrosyl complexes.

Formally, the transformation of the all trigonal-symmetric Fe^{IV}≡N to {Fe–NO}⁶, or even {Fe–NO}⁹, is a two- or even five-electron reduction, respectively, which is expected to be associated with striking structural changes. However, the formally high-valent iron nitrides and low-valent iron nitrosyls are structurally remarkably similar; thus, questioning the concept of oxidation states in {Fe–N(O)}ⁿ complexes! We conclude that – at least in this series of complexes – nitrosyls are better described as oxo-imidos, more related to the classic imido and nitrido complexes.^[5,6]

Key References

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