

Lecture Announcement



Professor Karsten Meyer

Friedrich-Alexander-Universität
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**"Mid- to High-Valent Iron Nitrido and Oxido
Complexes in tris-Carbene Ligand Environments,
Including a Reactive Fe(VII) Nitride"**

Date & Time : September 22 (Mon), 17:00~18:30

Location : Meeting Room 2 (Room 345, 3rd floor, Main Building)

Contact : Mio Kondo(Department of Chemistry, School of Science, Ext.3659)

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“Mid- to High-Valent Iron Nitrido and Oxido Complexes in *tris*-Carbene Ligand Environments, Including a Reactive Fe(VII) Nitride”

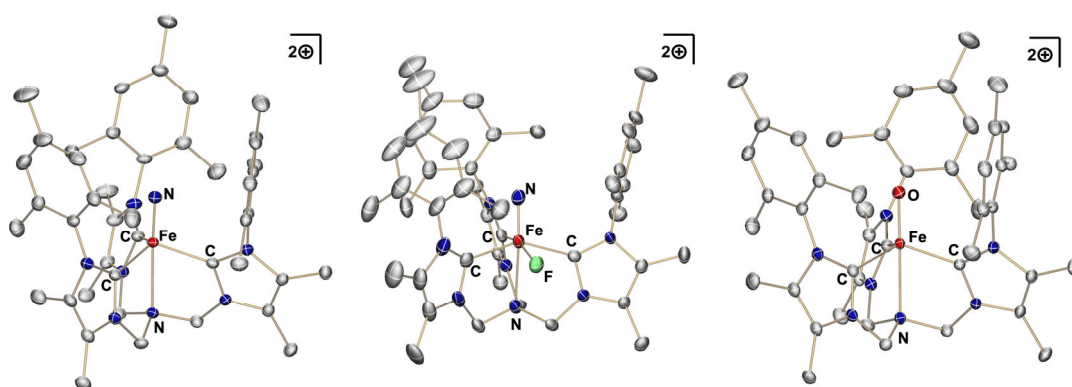
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<Abstract> Iron nitrido complexes $[(\text{TIMMN}^{\text{mes}})\text{Fe}(\text{N})]^{1+/2+}$ and $[(\text{TIMMN}^{\text{mes}})\text{Fe}(\text{N})(\text{X})]^{2+/3+}$ ($\text{X} = \text{F}, \text{Cl}$) in oxidation states Fe(IV), Fe(V), Fe(VI), and Fe(VII), as well as the tetravalent iron oxide $[(\text{TIMMN}^{\text{mes}})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$, were synthesized using the sterically encumbered, N-anchored *tris*-N-heterocyclic carbene ligand $\text{TIMMN}^{\text{mes}}$. The mid-valent Fe(IV) and high-valent Fe(V) and Fe(VI) nitrido complexes are isolable, air- and temperature-stable. In contrast, the super-oxidized Fe(VII) nitrido species is highly reactive and undergoes ligand rearrangement, akin to skeletal editing. The Fe(IV) oxo complex represents, to the best of our knowledge, the first isolable and fully characterized closed-shell Fe(IV)=O molecular complex. Comprehensive spectroscopic, magnetochemical, electrochemical, and crystallographic analyses, supported by computations, provide deep insight into the electronic structures across this unique series of iron nitrido and oxido complexes spanning oxidation states +4 to +7 within the same *tris*-carbene coordination environment. Progress toward the synthesis of an isolable Fe(VII) nitride and a complete series of Fe(III), Fe(IV), and Fe(V) oxides is presented. A direct comparison of the electronic structures of the two structurally identical tetravalent $[(\text{Me}_2\text{TIMMN}^{\text{mes}})\text{Fe}(\text{N})]^+$ and $[(\text{Me}_2\text{TIMMN}^{\text{mes}})\text{Fe}(\text{O})]^{2+}$ reveals the intricate differences of nitrido versus oxo electronic structures in a rigorously controlled ligand environment.



Molecular representations of the dicationic pentavalent $[\text{Me}_2\text{TIMMN}^{\text{Mes}}\text{Fe}^{\text{V}}\text{N}]^{2+}$ (left), hexavalent $[\text{Me}_2\text{TIMMN}^{\text{Mes}}\text{Fe}^{\text{VI}}(\text{N})(\text{F})]^{2+}$ (middle), and tetravalent $[\text{Me}_2\text{TIMMN}^{\text{Mes}}\text{Fe}^{\text{IV}}\text{O}]^{2+}$ (right).

References

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2. M. Keilwerth, W. Mao, M. Malischewski, S. A. V. Jannuzzi, K. Breitwieser, F. W. Heinemann, A. Scheurer, S. DeBeer, D. Munz, E. Bill, K. Meyer *Nat. Chem.* **2024**, *16*, 514–520.
3. W. Mao, Z. Zhang, F.W. Heinemann, K. Meyer *et al.*, *unpublished* **2025**.