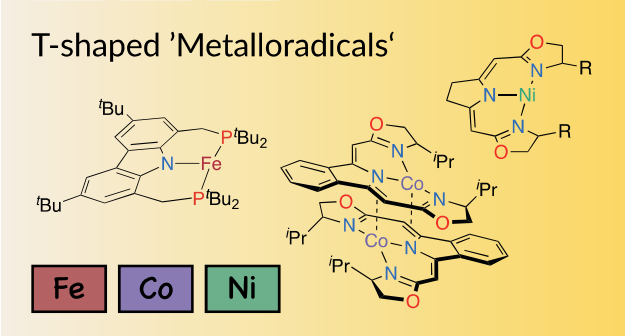
Open Shell Transition Metal Complexes as “Metalloradicals”: Key Intermediates in Homogeneous Catalysis.

Lutz H. Gade
Anorganisch-Chemisches Institut Universität Heidelberg,
Im Neuenheimer Feld 270, 69117 Heidelberg, Germany
Email: lutz.gade@uni-heidelberg.de

Abstract: Low-valent, low coordinate transition metal complexes represent a class of extraordinarily reactive compounds that can act as reagents and catalysts for challenging bond-activation reactions. The pursuit of these "electron-deficient" metal complexes demands ancillary ligands capable of providing not only energetic stabilization but also sufficient steric bulk.



In light of the intractable reaction pathways typically observed with unsaturated 3*d* transition metal complexes, the pincer coordination mode enables the isolation of low-valent compounds with more controlled and unique reactivity. We have investigated a series of T-shaped complexes which may be regarded as ‘metalloradicals’ due to their exposed unpaired electrons.[1] They provide specific modes of substrate activation which are distinct from the patterns observed for diamagnetic analogues.

The focus of the lecture will be the elucidation of structures and reactive patterns observed for such highly unsaturated complexes as well as catalytic reaction mechanisms. The identification and characterization of the paramagnetic species involved by NMR spectroscopy plays a central role.[2]

We shall also discuss the way in which the combination a full kinetic analysis of a reaction network combined with theoretical modelling provides deep insight into the available competitive reaction pathways, thus exposing the conceptual limits of the unique "catalytic cycle" for a given system.[3]

References

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