

Catalytic Applications of Mn(I) and Fe(II) Complexes involving E-H (E = H, C, Si, B) Bond Activation Reactions

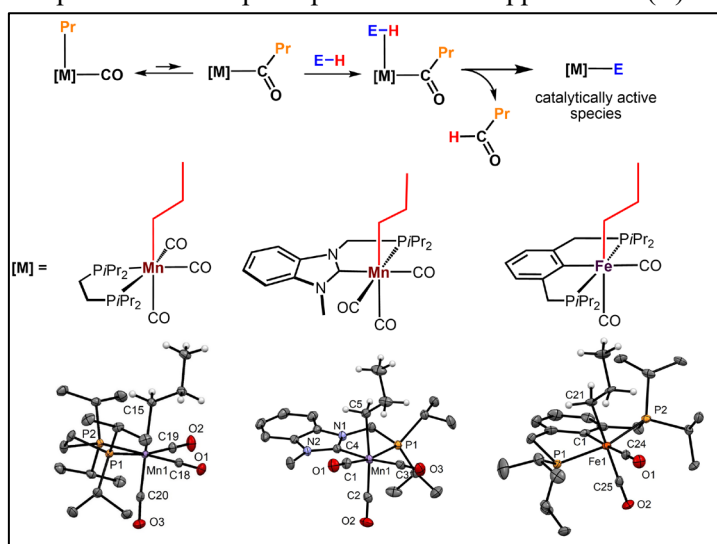
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The utilization of base-metal catalysts represents an emerging field in homogeneous catalysis. Among others, manganese-based complexes were proven to be highly competitive catalysts for several (de)hydrogenation reactions.

This lecture outlines the potential of Mn(I)- and Fe(II)-carbonyl complexes for the activation of non-polar and moderately polar E-H (E = H, C, Si, B) bonds and disclose our successful approach for the utilization of complexes in the field of homogeneous catalysis.¹⁻⁵ We took advantage of the fact that Mn(I)-alkyl carbonyl complexes undergo migratory insertion of the nucleophilic alkyl ligand into the polarized CO moiety, yielding a coordinatively unsaturated acyl complex. The same principle is now also applied to Fe(II) complexes.



This involves the rational design of manganese and iron alkyl complexes and derivatives thereof such as borohydride complexes. Our investigations unveiled novel insights in reaction pathways of the silylation and hydroboration of alkenes and alkynes, the *trans*-1,2-diboration of terminal alkynes, hydrogenations of alkenes, alkynes, ketone and the selective isomerization of alkenes.

References

1. "Hydroboration of Terminal Alkynes Catalyzed by a Mn(I) Alkyl PCP Pincer Complex following Two Diverging Pathways", Zobernig, D. P.; Stöger, B.; Veiros, L. F.; Kirchner, K. *ACS Catal.* **2024**, *14*, 12385-12391.
2. "Alkene Isomerization Catalyzed by a Mn(I) Bisphosphine Borohydride Complex", Blaha, I.; Weber, S.; Dülger, R.; Veiros, L. F.; Kirchner, K. *ACS Catal.* **2024**, *14*, 13174-13180.
3. "Manganese Alkyl Carbonyl Complexes: From Ionic Stoichiometric Textbook Reactions to Catalytic Applications", Weber, S.; Kirchner, K. *Acc. Chem. Res.* **2022**, *55*, 2740-2751
4. "Efficient hydroboration of alkenes and *trans*-diboration of alkynes catalyzed by Mn(I) alkyl complexes", Weber, S.; Zobernig, D. P.; Stöger, B.; Veiros, L. F.; Kirchner, K. *Angew. Chem., Int. Ed.* **2021**, *60*, 24488-24492.
5. "Manganese-Catalyzed Dehydrogenative Silylation of Alkenes Following two Parallel Inner-Sphere Pathways", Weber, S.; Glavic, M.; Stöger, B.; Pittenauer, E.; Podewitz, M.; Veiros, L. F.; Kirchner, K. *J. Am. Chem. Soc.* **2021**, *143*, 17825-17832.