



Laboratory for Coordination Chemistry

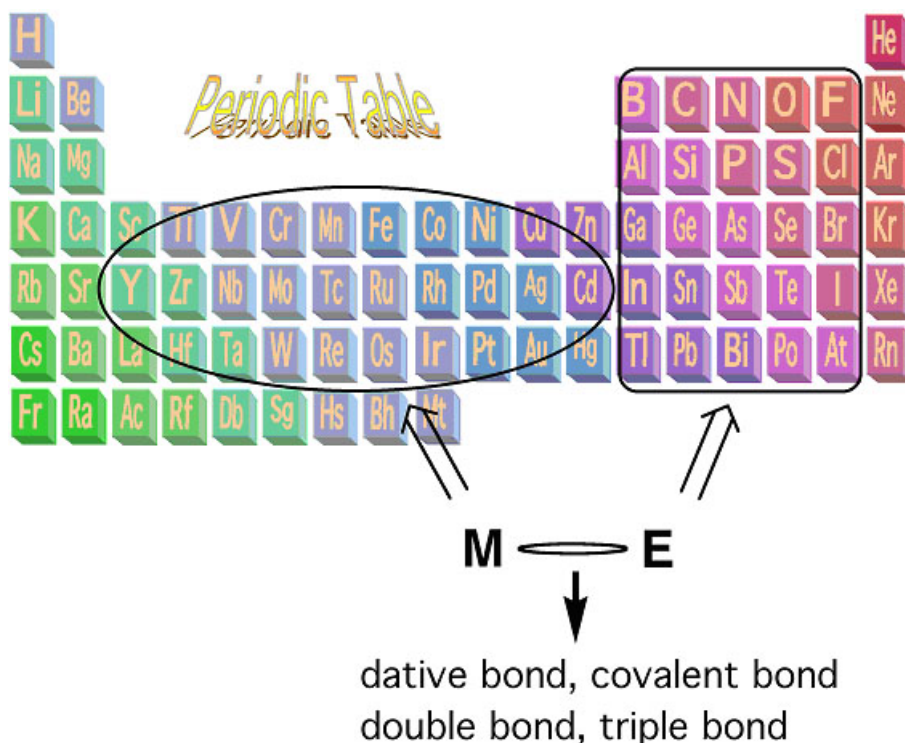
Hiroshi Nakazawa (Professor)

<http://www.sci.osaka-cu.ac.jp/chem/cc/index.html>

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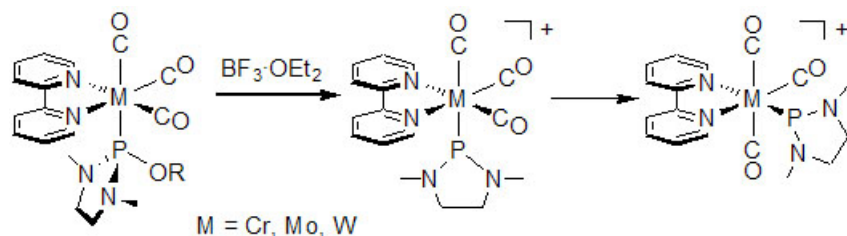
1. Current Research and Principal Research Interests

The group's interests are creation of new types of complexes involving dative, covalent, double, and triple bonds between a transition metal and a main group element in groups 13 to 17, and also development of new function of these complexes. An application of the new types of complexes in catalytic systems is also the group's interest.



(1) Transition Metal Complexes Containing a Phosphenium Ligand

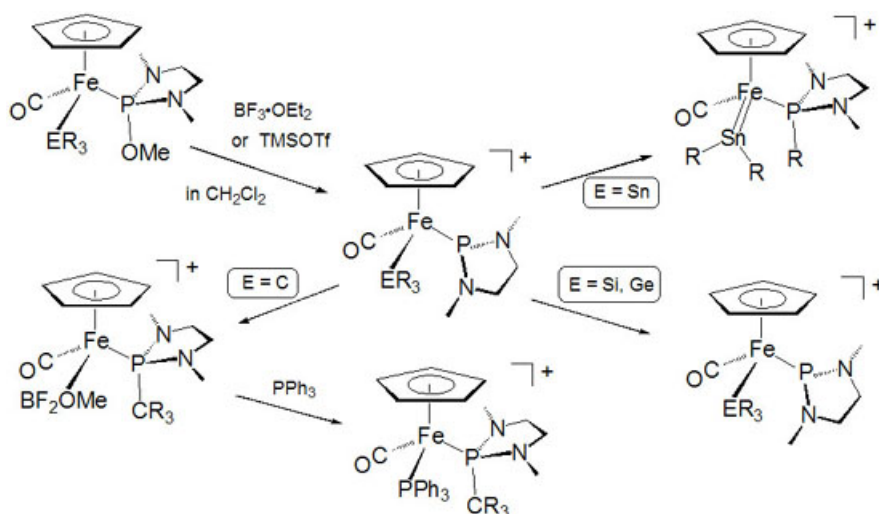
A new method for preparation of cationic phosphenium complexes of transition metals has been developed where an OR group on a coordinating phosphite is abstracted as an anion by a Lewis acid such as $BF_3 \cdot Et_2O$.



Reactions of iron complexes containing a group 14 element ligand (ER_3 ; $E = C, Si, Ge, Sn$) and diaminosubstituted phosphite, $Cp-(CO)(ER_3)Fe\{PN(Me)CH_2CH_2NMe-(OMe)\}$ with a Lewis acid revealed that the reaction product depends on E. In any case, an OMe anion abstraction by a

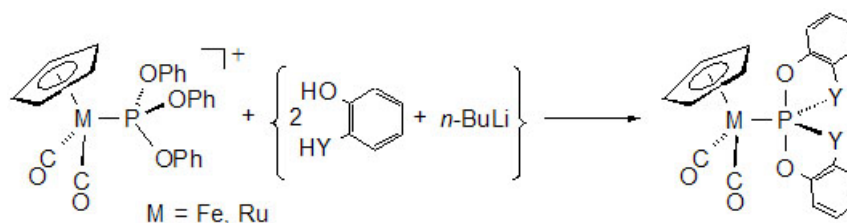
Lewis acid uniformly takes place at the first stage of the reaction to give a cationic phosphonium iron complex containing an ER_3 ligand. The subsequent reaction is strongly dependent on E.

When E is C, migratory insertion of the phosphonium ligand into the Fe-C bond or more simply an alkyl migration from Fe to phosphonium P occurs. When E is Si or Ge, the cationic phosphonium complex is stable and Fe-Si and Fe-Ge bonds remain intact. In contrast, when E is Sn, not SnR_3 but one alkyl group on the Sn migrates to the phosphonium P to give a stannylene complex.

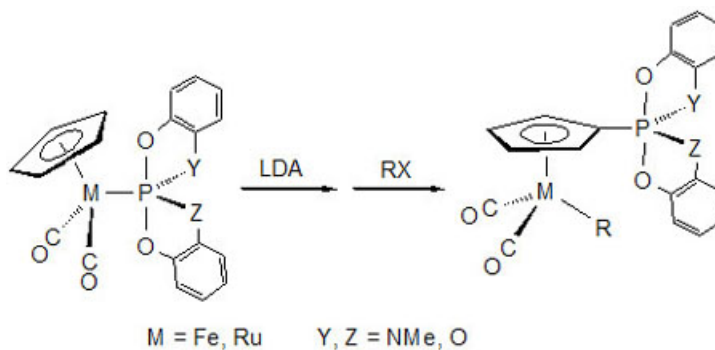


(2) Metallaphosphorane Chemistry

An unprecedented method for the preparation of metallaphosphorane was created involving nucleophilic attacks of an organic nucleophile at a trivalent phosphorus coordinated to an iron and substitution on the phosphorus. The character of the bond between a transition metal and a hypervalent phosphorus was revealed.



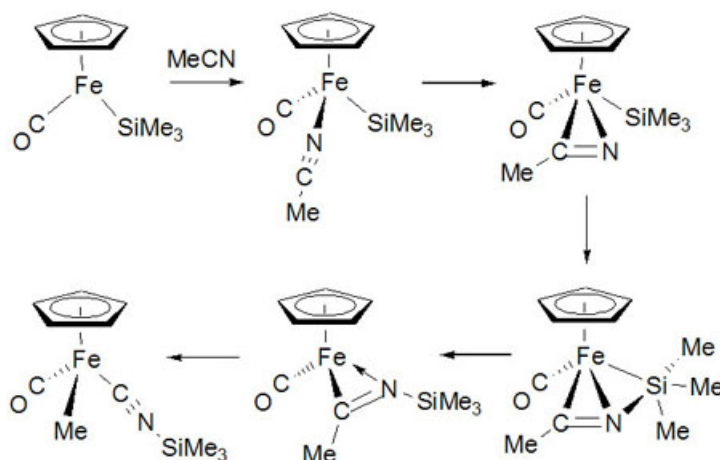
The reaction of metallaphosphorane with a Lewis base showed the first example of a hypervalent fragment migration, that is, phosphorane migration from a transition metal to a cyclopentadienyl ring.



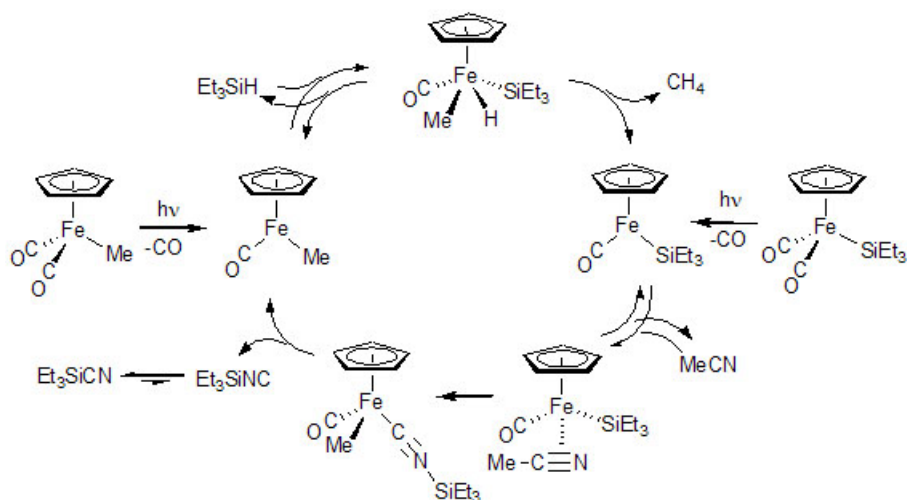
(3) C-C Bond Cleavage Reaction of Organonitriles Promoted by a Transition Metal Complex

A C-C bond in organonitrile, being relatively strong (133 kcal mol⁻¹ for MeCN), was found to be cleaved by a transition metal silyl complex. The photoreaction of a silyl complex $Cp(CO)_2Fe(SiMe_3)$ in the presence of acetonitrile produces Me_3SiNC and Me_3SiCN , showing that the C-C bond in MeCN is cleaved. The corresponding alkyl, germyl, and stannyl iron complexes do not cleave the C-C bond. Therefore, the silyl ligand on the iron is indispensable for the C-C bond cleavage. Theoretical studies proposed the mechanism: MeCN coordinates to

the 16e species $[\text{Cp}(\text{CO})\text{Fe}(\text{SiMe}_3)]$ in η^1 -fashion, and it isomerizes to η^2 -coordination mode. Then, the SiMe_3 group migrates from Fe to N of MeCN to give a silyl imono complex, followed by the slippage of the $\text{Me-C}\equiv\text{N}$ portion in the coordination sphere to finally give the methyl silylisocyanide complex.



The iron complexes, $[\text{Cp}(\text{CO})_2\text{Fe}(\text{SiMe}_3)]$ and also $[\text{Cp}(\text{CO})_2\text{FeMe}]$, serve as a catalyst for C-CN bond cleavage in the reaction of HSiEt_3 with MeCN. The catalytic system can be applied for aryl nitrile C-C bond cleavage. The catalytic cycle has been proposed.



2. Selected Publications

1. "Iron-catalyzed Silylcyanation of Aldehydes and Ketones with Silyl Cyanide Prepared from Silane and Acetonitrile", M. Itazaki and H. Nakazawa, *Chem. Lett.*, **37**, 1054-1055 (2005).
2. "Catalytic C-C Bond Cleavage and C-Si Bond Formation in Reaction of RCN with Et_3SiH Promoted by an Iron Complex", H. Nakazawa, K. Kamata, and M. Itazaki, *Chem. Commun.*, 4004-4006 (2005).
3. "Transition Metal Complexes Bearing a Phosphenium Ligand", H. Nakazawa, *Advances in Organometallic Chemistry*, **50**, 107-143 (2004).
4. "C-C Bond Cleavage of Acetonitrile by a Carbonyl Iron Complex with a Silyl Ligand", H. Nakazawa, T. Kawasaki, K. Miyoshi, C. H. Suresh, and N. Koga, *Organometallics*, **23**, 117-126 (2004).
5. "Synthesis and Characterization of Some Zirconium and Hafnium Complexes with a Phosphide-Pendant Cyclopentadienyl Ligand", T. Ishiyama, T. Mizuta, K. Miyoshi, and H. Nakazawa, *Organometallics*, **22**, 1096-1105 (2003).

6. "Synthesis of Group 4 Transition-metal Complexes Bearing a Secondary Phosphine Pendant Cyclopentadienyl Ligand", T. Ishiyama, H. Nakazawa, and K. Miyoshi, *J. Organomet. Chem.*, **648**, 231-236 (2002).
7. "Metallaphosphorane Chemistry: Preparations, Structures, and Reactivities", H. Nakazawa, K. Kubo, and K. Miyoshi, *Bull. Chem. Soc. Jpn.*, **74**, 2255-2267 (2001).
8. "The Chemistry of Transition-Metal Complexes Containing a Phosphenium Ligand", H. Nakazawa, *J. Organomet. Chem.*, **611**, 349-363 (2000).
9. "Phosphorane Migration from Ruthenium to the Cyclopentadienyl Ring", H. Nakazawa, K. Kawamura, K. Kubo, and K. Miyoshi, *Organometallics*, **18**, 4518-4523 (1999).
10. "Migration Reaction of a Hypervalent Fragment: Base-Induced Migration of a Phosphorane Fragment from Iron to the Cyclopentadienyl Ring in $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$ (Y, Z = NMe, NH, O)", K. Kubo, H. Nakazawa, K. Kawamura, T. Mizuta, and K. Miyoshi, *J. Am. Chem. Soc.*, **120**, 6715-6721 (1998).