Chapter I. Introduction to Low-Coordinate Late Transition Metal Complexes
I.1. Low-coordinate metal chemistry

The strategy of using exposed metal centers to efficiently perform chemical transformations is shared by enzymes, metal surfaces and synthetic homogeneous catalysts. Many metal clusters in biology contain either low coordinate metal centers (the “low-coordinate” here means a coordination number of 4 or less) or labile ligands that open sites for reactions (Figure I.1).\textsuperscript{1,2} For example, an interesting case of four-coordination is found in the MoFe cofactor of nitrogenase, as deduced from crystallographic studies of that protein from two organisms, Azotobacter vinelandii and Clostridium pasteurianum (Figure I.1a).\textsuperscript{2b} In the MoFe cofactor, a Fe\textsubscript{7}Mo cluster constitutes the site for nitrogen binding and reduction, and the Fe atoms are believed to be coordinated by three sulfur atoms in a trigonal geometry, although short Fe···Fe distances in the cluster (2.4–2.6 Å) suggest the existence of possible metal–metal bonding, also supported by theoretical studies.\textsuperscript{3}
Figure 1.1. Selected examples of metalloenzymes containing low-coordinate metal center.$^{1,2}$

Chemists know about a myriad of homogeneous synthetic reactions having important applications that involve unsaturated metal centers.$^{4}$ In heterogeneous catalysis chemistry, the unique reactivity displayed by surfaces is often attributed
to highly active, low coordinate metals in the edges of the material. For example, nano gold particles dispersed on inorganic oxide supports have attracted much attention in the last years as catalysts for a wide number of reactions including the water gas shift reaction,\(^5\) CO and alcohol oxidation, propylene epoxidation,\(^6\) C-C bond formation,\(^7\) and selective hydrogenations.\(^8\) It seems to be generally accepted that the oxidation activity of gold nanoparticles is determined by the number of low coordinated gold atoms, which increases with decreasing particle size but is also dependent on particle shape.\(^9\)

Three-coordinate complexes of the transition metals are rare, because it is difficult with only three ligand donors to reach preferred configurations with 16 or 18 electrons in the metal bonding and nonbonding orbitals. By using extremely bulky ligands, chemists have been able to stabilize three-coordinate and even two-coordinate metal centers. Bradley's work initially showed that bulky monodentate dialkylamide or disilylamine ligands could be used to isolate three-coordinate complexes such as Cr(NR\(_2\))\(_3\) (R=(CH\(_3\))\(_3\)Si).\(^10\) The development of a variety of other sterically demanding monodentate ligands was later exploited as a powerful tool for isolating three-coordinate complexes of many transition metals, as well as the main group elements. These ligands include alkoxide, chalcogenolate (ER, E = S, Se), pnictide (ER\(_2\), E = N, P), alkyl, aryl and silyl ligands.\(^11,7\) For example, Power developed routes to unusual three-coordinate transition metal complexes containing metal-metal bonds by using bulky aryl
ligands (Figure I.2). Wolczanski and Cummins used other ligands of prodigious size to access low coordinate complexes of group 4-6 metals and demonstrated the ability to cleave C-H bonds of alkanes, the N-N bond of nitrous oxide, and even triple bonds of CO, NO, and N₂ (Scheme I.1). These reactions are each driven by the formation of strong metal-ligand bonds between the transition metal and the substrate. The metal-ligand bonds formed are so strong that the low-coordinate starting material cannot be reform ed in situ to complete a catalytic cycle.

**Figure I.2.** Selected examples of low-coordinate transition metal complex containing unusual metal-metal bond supported by bulky aryl ligands and amide ligands. (a) reference 7e; (b) reference 7f; (c), (d) reference 7g.
Scheme I.1. Selected examples of small molecule activation by low-coordinate metal complexes. (a) reference 9b; (b) reference 9e; (c) reference 9h.

I.2. Introduction to β-Diketiminate ligands

To overcome the above problems, several strategies might be considered: (1) Utilize the biologically relevant 3d transition metals Mn, Fe, Co, Ni, and Cu to form comparatively weaker metal-ligand bonds. (2) Design ligands which could coordinate strongly but not too tightly with metal to allow for flexible binding modes.

β-Diketimimates have an important role as such ligands, by virtue of their strong binding to metals, their tunable and extensive steric demands, and the diversity of their binding modes. Many diketiminate ligands can be synthesized by the condensation reaction between two equivalents of an aromatic amine and
2,4-pentanedione. However, for bulkier ligands like L\textsuperscript{tBu} (Figure I.3), this method will lead to an undesired mono-substituted ketoimine product, which cannot undergo the second condensation desired. As a result, a multi-step synthesis is used (Scheme I.2).


TMEDA = tetramethylethylenediamine;
imCl = 1-chloro-1-(2,6-diisopropylphenylimido)-2,2-dimethylpropane.

I.3. Low coordinate metal complexes of diketiminate ligands

A number of chemists have contributed to the coordination chemistry of diketiminate ligands. Through these studies, the diketiminate ligands showed their ability to stabilize complexes in unusually low metal oxidation states. Many such complexes are coordinatively unsaturated, which is one of the keys to their
ability to function as catalysts for processes like olefin polymerization, ring-opening polymerization of lactide or related monomers, and copolymerization of epoxides and carbon dioxide.\textsuperscript{17}

The Holland group has been focusing on low coordinate chemistry of late transition metal complexes of $\beta$-diketiminate ligands and have begun to elucidate the reactions in low-coordinate iron complexes, the spectroscopic and magnetic properties of these complexes, and the electronic structures underlying the molecules.\textsuperscript{13,15} The following is a short summary of these studies.

I.3.1. Synthesis of low-coordinate late transition metal complexes of $\beta$-diketiminate ligands

![Figure I.3. $\beta$-diketiminate ligand L\textsuperscript{1Bu} used in this work.](image)

Two $\beta$-diketiminate ligands (L\textsuperscript{MeH}, L\textsuperscript{tBuH}) were used mostly in our group’s work (Figure I.3).\textsuperscript{18} By deprotonation of the diketimines L\textsuperscript{MeH} and L\textsuperscript{tBuH} with nBuLi, the lithium salt of the monoanionic diketiminate ligands could be accessed. Similar potassium salts of these ligands could also be prepared by reacting diketimines with potassium hydride.\textsuperscript{19} These lithium and potassium salts could react with MCl\textsubscript{2}(thf)\textsubscript{n} (M = Fe, Co, Ni) to give three- or four-coordinate high-spin M(II) chloride complexes,\textsuperscript{13c} which are useful synthetic precursors to
low-coordinate complexes with a variety of ligands.\textsuperscript{13,15} In these complexes, the isopropyl groups on the phenyl ring extend above and below the \textit{N}_2M plane, protecting the metal center with two donors and only a small space is available for additional ligands. In this way, the \textit{β}-diketiminate gives an excellent balance between adequate and overbearing steric protection.\textsuperscript{13k}

\subsection*{I.3.2. Reactivity of low-coordinate iron complexes of diketiminate ligands}

A series of low-coordinate iron(II) complexes LFeX with X = H, BR\textsubscript{2}, alkyl, aryl, acetylide, vinyl, NHR, OR, F, SR, Cl, Br, and I have been synthesized and explored.\textsuperscript{13, 20} One particularly interesting result involves reducing iron(II) chloride complex under nitrogen atmosphere to obtain iron(I) dinitrogen complexes, which give anomalously strong Fe-N\textsubscript{2} bonding and weak N-N bonds.\textsuperscript{13b,13i} As far as we know, this was the first work to show the binding of N\textsubscript{2} to low-coordinate iron centers. Diketiminate-bound iron(I) also binds other nitrogenase substrates like alkynes, carbon monoxide, isocyanides, and diazenes.\textsuperscript{15f} The relative binding constants for different donors to iron(I) center were determined. Alkynes bind much more strongly than alkenes, providing a rationale for why Mo-nitrogenase reduces acetylene but not ethylene.\textsuperscript{15f}

Considering the new evidence for iron-hydride species in nitrogenase,\textsuperscript{21} it is important to understand the structures and reactivity of low-coordinate high-spin iron hydride species like the FeMoco. The Holland group reported the synthesis and reactivity of the first low-coordinate high-spin iron-hydride complexes.\textsuperscript{13d,15j}
These hydride complexes could reduce alkynes, alkenes, nitriles, azides, CO$_2$, and protons. Many of the products are reminiscent of the reductions catalyzed by nitrogenase. Because some of these reductions have never been observed with previous iron hydride complexes, the low coordination number probably heightens the reactivity of the iron hydride species.

**I.3.3. Potential application as catalyst**

Precious metals currently are the basis of catalysts that are well understood by chemists and widely used in industrial processes. But the metals—such as platinum, palladium, and rhodium—are rare and expensive, and they can be toxic and difficult to recycle. Considering how to foster a more sustainable future, chemists are seeking alternatives that are greener and less expensive than current catalysts but also as effective or better. Late transition metal such as Mn, Fe, Co, Ni, Zn and Cu are potential homogeneous catalysts that can contribute to a more sustainable chemical enterprise. The Holland group has been attempting to utilize their understanding of the low-coordination chemistry of late transition metal complexes of β-diketiminate ligands for catalytic applications. For example, Vela discovered that three-coordinate iron compounds could catalyze the transfer of F from fluoroaromatics to a silyl group (Scheme I.3).$^{13h}$ Cowley and Eckert discovered that the metastable iron(III) imido species $L^{\text{Bu}}$FeNAd could catalyze transfer of the nitrene fragment NAd from an organic azide to isocyanides or CO, forming unsymmetrical carbodiimides or isocyanates (Scheme I.4).$^{20k}$
Scheme I.3. Catalytical hydrodefluorination of fluorocarbons by iron fluoride complexes of β-diketiminate ligands.\textsuperscript{13h}

Scheme I.4. Catalytic nitrene transfer from an imidoiron(III) complex to form carbodiimides and isocyanates.\textsuperscript{15k}


The isolation of a large number of β-diketiminate iron complexes has led to some useful generalizations about their geometry and electronic structure. Because of diketiminate nitrogens form nearly a 90° angle at the iron, it has an effect of destroying the degeneracy of the lower two levels observed in a perfect trigonal planar D\textsubscript{3h} symmetry. The resulting distorted trigonal-planar geometry (C\textsubscript{2v} symmetry) has non-degenerate orbitals as shown in a Walsh diagram (Figure
I.4. The $z^2$ and $yz$ orbitals have roughly the same energy so that there is extensive spin-orbit coupling between them. This spin-orbit coupling increases the orbital angular momentum along the axis that rotates the $z^2$ into the $yz$ orbital ($C_2$ axis in this case). The increased orbital angular momentum has several effects: (1) directional paramagnetic response to the application of an external field. (2) huge zero-field splitting that makes the $m_S = \pm 2$ levels by far the lowest in energy (D values of ca. -50 cm$^{-1}$). (3) large and axial magnetic susceptibility, as evident from magnetic and NMR measurements.\textsuperscript{13k}

![Diagram showing changes in d orbital energies resulting from the ∼90° bite angle of the β-diketiminate ligand.\textsuperscript{13k}]

**Figure I.4.** Changes in d orbital energies that result from the ∼90° bite angle of the β-diketiminate ligand.\textsuperscript{13k}

### I.4. Conclusions and outline of thesis

The strategy of using exposed metal centers to efficiently perform chemical transformations is shared by enzymes, metal surfaces and synthetic
homogeneous catalysts. Three-coordinate complexes of the transition metals are rare, because it is difficult with only three ligand donors to reach preferred configurations with 16 or 18 electrons in the metal bonding and nonbonding orbitals. By using extremely bulky β-diketiminate ligands, chemists have been able to stabilize three-coordinate iron centers. However, there has been much less attention to the area of diketiminate cobalt chemistry, which promised to be equally exciting. This thesis mainly describes the synthesis and reactivity of low-coordinate cobalt dinitrogen, hydride, fluoride complexes supported by β-diketiminate ligand $L^{tBu}$. The final chapter discusses the synthesis of unusual iron(I) alkyl complexes of $L^{tBu}$ and their catalytic suitability for aryl-alkyl cross coupling reactions.

In Chapter II, three low-coordinate cobalt dinitrogen complexes were synthesized, structurally characterized and compared to their iron analogues. Despite the identical ligand environment, there are significant differences between the cores of the two $L^{tBu}MNNML^{tBu}$ ($M = Fe, Co$) compounds: the Co-N bonds are longer than the Fe-N bonds, and the N-N bond is significantly shorter in the Co complex than in the Fe complex. These data suggest that π-backbonding is not as important in the Co complex. Because of the exact correspondence of ligands, it is possible to unambiguously conclude that $L^{tBu}Co$ is poorer at weakening $N_2$ than $L^{tBu}Fe$ at this oxidation level. In contrast to the differences between formally cobalt(I) and iron(I) species above, the formally cobalt(0) compounds have
metrical parameters that are similar to their Fe analogues, with N-N distances of 1.21-1.22 Å. These are the longest N-N distances observed in any cobalt dinitrogen complex.

In Chapter III, two rare low-coordinate cobalt hydride complexes were synthesized from LCoCl and KHBEt3. These isolable cobalt hydride complexes are highly reactive with dinitrogen, to give cobalt dinitrogen complexes. Such a transformation might be an important method of binding N2 to a transition metal complex in a catalytic system because the coordination and activation of the substrate N2 have been demonstrated to occur in a facile manner. It is also notable that there is a connection to the biological fixation of dinitrogen. It is known that the nitrogenase enzyme produces at least 1 equiv of H2 gas in the conversion of N2 to NH3. Although it is still not clear whether this arises from a necessary step in this reaction or from a side-reaction, there is a similarity to the formation of cobalt hydride complexes because H2 is also eliminated in the latter reaction.

Chapter IV describes the reaction of L^tBuCoCH3 with Me3SnF to give a rare example of partially fluorinated cobalt tin fluoride complex [L^tBuCo(μ-F)2]2SnMe2·2Et2O and its transformation to a four-coordinate cobalt fluoride pyridine adduct L^tBuCoF(py). The reason for their lack of catalytic hydrodefluorination activity was examined.
Chapter V describes the synthesis of two unusual iron(I) alkyl complexes of \( {\text{L}}^{{\text{t}}^{{\text{Bu}}}}_{} \), \([{\text{KL}}^{{\text{t}}^{{\text{Bu}}}}_{} {\text{FeCH}}_3]_2 \) and \([{\text{KL}}^{{\text{t}}^{{\text{Bu}}}}_{} {\text{FePh}}_2{\text{Et}}_2{\text{O}}] \). Their catalytic suitability for aryl-alkyl cross coupling reactions are discussed.

I.5. References


3 (a) There are short Fe-Fe contacts of 2.65 ± 0.04 Å in the FeMoco that probably modify the behavior of iron: Mayer, S. M.; Lawson, D. M.; Gormal, C. A.; Roe, S. M.; Smith, B. E. *J. Mol. Biol.* 1999, 292, 871-891. (b) A very recent paper presents evidence that there is a fourth ligand coordinated to these iron atoms: Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* 2002, 297, 1696-1700.


5 (a) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Science **2003**, *301*, 935.


127, 15191-15200. (g) Curley, J. J.; Cook, T. R.; Reece, S. Y.; Muller, P.; 


16 (a) Holland, P. L.; Tolman, W. B. J. Am. Chem. Soc. 1999, 121, 7270-7271. (b) 
Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. 
C.; Roesky, H. W.; Magull, J.; Bencini, A.; Caneschi, A.; Gatteschi, D. J. Am. 
Rzepa, H. S.; White, A. J. P.; Williams, D. J. J. Am. Chem. Soc. 2006, 128, 
129, 8436-8437. (g) York, J. T.; Llobet, A.; Cramer, C. J.; Tolman, W. B. J. Am. 
2779-2781.

17 (a) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S. I.; Yun, H. S.; Lee, 
H.; Park, Y. W. J. Am. Chem. Soc. 2005, 127, 3031-3037. (b) Yao, Y. M.; Zhang, 
Z. Q.; Peng, H. M.; Zhang, Y.; Shen, Q.; Lin, J. Inorg. Chem. 2006, 45,

