Design of Metal-Organic Molecular Precursors for Atomic Layer Deposition

Jan Gerkens

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Georg-August-Universität Göttingen

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Jan Gerkens
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Betreuungsausschuss
Prof. Dr. Sven Schneider
Institut für Anorganische Chemie, Georg-August-Universität Göttingen
Prof. Dr. Franc Meyer
Institut für Anorganische Chemie, Georg-August-Universität Göttingen

Mitglieder der Prüfungskommission
Referent: Prof. Dr. Sven Schneider
Institut für Anorganische Chemie, Georg-August-Universität Göttingen
Korreferent: Prof. Dr. Franc Meyer
Institut für Anorganische Chemie, Georg-August-Universität Göttingen

Weitere Mitglieder der Prüfungskommission
Prof. Dr. Manuel Alcarazo
Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen
Dr. Oliver Bünermann
Institut für Physikalische Chemie, Georg-August-Universität Göttingen
Jun.-Prof. Dr. Nathalie Kunkel
Institut für Anorganische Chemie, Georg-August-Universität Göttingen
Dr. Christian Sindlinger
Institut für Anorganische Chemie, Georg-August-Universität Göttingen

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Abbreviations

ALD	atomic layer deposition
AFM	atomic force microscopy
C_6D_6	benzene-d6
CVD	chemical Vapor Deposition
EDX	energy dispersive X-ray spectroscopy
Et_2O	diethyl ether
h	hour
^{i}Pr	iso-propyl group
GPC	growth per cycle
Me	methyl
HER	hydrogen evolution reaction
HMDS	bis(trimethylsilyl)amine
n-BuLi	n-buthyllithium
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
RT	room temperature
SEM	Scanning electron microscope
^{t}Bu	tert-Butyl group
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMS	trimethylsilyl group
TMP	2,2,6,6-tetramethylpiperidine
TMPLi	lithium 2,2,6,6-tetramethylpiperidide
XPS	X-ray photoelectron spectroscopy

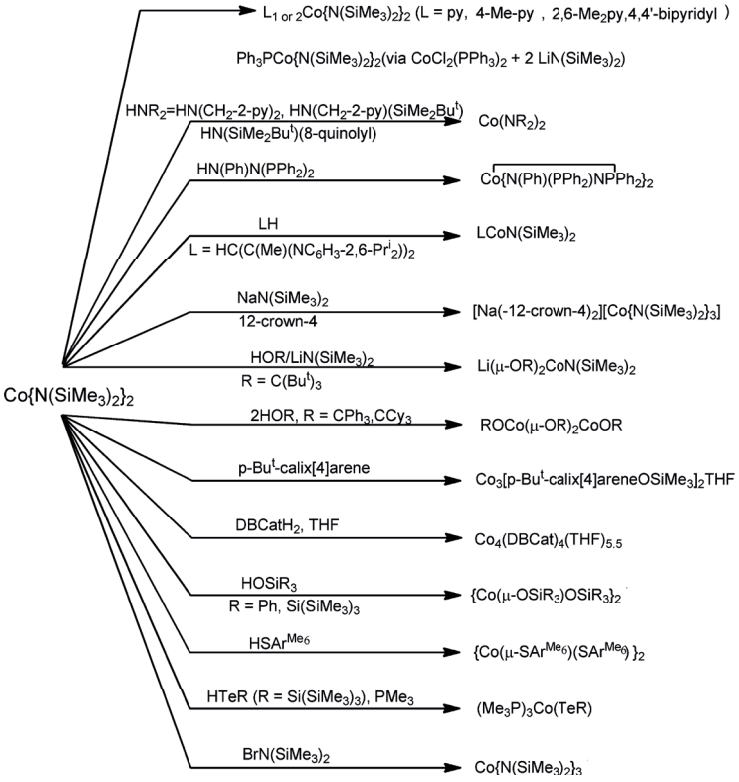
1 Introduction

1.1 The Versatile Chemistry of Low-coordinate Transition Metal Amides

Transition metal amido complexes have a tremendous span of reactivity and possible applications. Bulky amido ligands allow to stabilize open-shell transition metal complexes with unusual coordination environments and low coordination numbers. This provided the basis for the investigation of several phenomena in coordination chemistry.[1] After the first description of titanium tetrakis(diphenylamide) as one of the first transition metal amides in 1934, it took until 1959 to observe a true development in transition metal amide chemistry.[2] Bradley and Thomas started a series of reports of dialkylamides of early transition metals with a rare coordination numbers between three and five ($M(NMe_2)_n$, M = Ti^{IV}, Zr^{IV}, Nb^{IV-V}, Ta^{V}, Mo^{III-IV}, etc.).[3] It was not possible at that time to isolate amide complexes of late transition metals ions (e.g. Fe, Co, Ni), though. In 1961 Bürger and Wannagat introduced the bulky $–N(SiMe_3)_2$ (HMDS) ligand,[4] which allowed the isolation of low coordinate metal amides of late transition metals with coordination numbers of two and three for the first time.[5,6] After the report for the preparation of two-coordinate complexes $[Mn(N(SiMe_3)_2)_2]$, $[Fe(N(SiMe_3)_2)_2]$, $[Co(N(SiMe_3)_2)_2]$ and $[Ni(N(SiMe_3)_2)_2]$,[5,6] focus of transition metal chemistry turned to the examination of three-coordinate amido complexes, including the report of several lanthanide containing compounds.[7,8] The group of Power has heavily investigated strictly two-coordinated transition metal complexes since the 1980's, including the publication of solid state structures of two-coordinated iron amido complexes.[8]

Many metal amido complexes are highly reactive. This is expressed by their exceptional sensitivity towards moisture and oxygen. Mostly sterically demanding alkyl- and silylamides are used as ligands in order to provide steric shielding. This makes metal amido complexes highly soluble in aprotic hydrocarbon solvents, rendering this compound class a versatile source for hydrocarbon soluble metal ions. Insertion reactions into the M−N bond or M−N bond cleavage reactions with protic molecules are mostly observed. The reactivity of amido complexes was also used to activate small molecules like N_2 or CO.[9] In 1995, Cummins and coworkers reported a planar three-coordinate Mo^{III} complex with bulky amido ligands, which was able to activate N_2.[10]

Since then, multidentate amido ligands like pincer ligands and podants have been used to investigate and tune the reactivity of transition metal complexes.[11] The rich coordination chemistry of metal amides is exemplified in Scheme 1.1, where possible reactions of the low-coordinate cobalt complex $[Co(N(SiMe_3)_2)_2]$ (**1**) are presented.



Scheme 1.1 Possible reactions with Cobalt silylamido complex $[Co(N(SiMe_3)_2)_2]$ (1).[9] Adapted with permission from ref. 9. Copyright 2012 American Chemical Society.

In the solid state, the nonpolar coordination environment causes high volatility. Many transition silylamides can be sublimed at temperatures below 100 °C at 0.01 mbar. For this reason, metal amides are used as precursors in several depositions techniques like atomic layer deposition.[1,12] In transition metal complexes coordinated by two bulky silyl amides, most of the spin-orbit coupling remains

unquenched, resulting a high magnetic anisotropy and other interesting magnetic properties of these compounds. The coordination geometry also has a high impact on their magnetic properties.[9,13–15] Therefore, the magnetic properties of low coordinate transition metal amido complexes returned into the scientific focus, when single molecular magnetism was reported (see Section 1.2.2).[16,17]

In the following chapters, fundamental concepts and possible applications for transition metal amide complexes will be presented. First, fundamental concepts of metal amides like their coordination chemistry and their magnetic properties will be highlighted. In the second section, focus will be on the application of transition metal compounds deposition techniques and electrocatalysis.

Bonding Situation in Transition Metal Amido Complexes

Amido ligands are considered as both strong σ- and π-donors. The coordination geometry at the nitrogen atom can either be pyramidal or trigonal planar. In the first case, π-overlap between the nitrogen lone pair and valence orbitals of the metal center is hindered (see Figure 1.1, right). Most transition metal amide complexes show a planar coordination geometry at the nitrogen atom, pointing towards sp^2-hybridization. In this case, π-bonding is achieved via the interaction of the p-orbital lone pair of the nitrogen atom and vacant valence d-orbitals at the metal center (see Figure 1.1, left). It should to be noted that the inversion barrier for pyramidal coordinated nitrogen ligands is usually low, which may let them appear in a quasi-planar coordination sphere. Distinguishing the electronic situation of the nitrogen atom on the basis of its coordination chemistry can therefore lead to misjudgments [1]

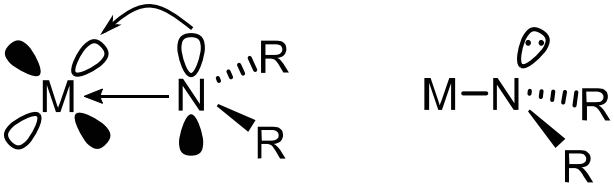


Figure 1.1 Left: Trigonal planar coordination geometry of the nitrogen atom enables π-donation of the amido ligand p-lone pair in a vacant metal d-orbital. Right: Pyramidal coordination geometry at the nitrogen atom hinders π-interaction between ligand and metal orbitals.[1]

As mentioned above, only alkylamido complexes of early transition metals could be isolated. When using silylamides, isolation of silylamido complexes of late transition metals is possible, though. Many attempts to rationalize these observations have been made.[1] One addresses the mismatch of "soft" metal centers and "hard" amido ligands.[18] In another attempts it was assumed, that the strong σ- and π-donor abilities of amido ligands lead to electronic repulsion with a late transition metal centers were the valence orbitals are already occupied, preventing the formation of late transition metal alkylamido complexes.[3] However, Bercaw and coworkers showed that the bond energy between metal centers and amido ligands not weaker as it is expected from their corresponding nitrogen−hydrogen bonding dissociation energies.[19] The distinction between the stability of alkyl- and silylamido transition metal complexes can be rationalized by hyperconjugation involving silicon and nitrogen orbitals. This so-called α-silicon effect stabilizes the negative charge of the amido ligand.[20] Silylamides are also considered to be weak π-acceptors, due to the mixing with vacant π-antibonding NSi_2 orbitals.[1]

1.2 Molecular Magnetism of Low-Valent Transition Metal Compounds

The stabilization of low coordination numbers with sterically demanding amido lignands allow to investigate unusual coordination environments, like linear or trigonal-planar coordination. These low coordination numbers go mostly in hand with interesting electronic and magnetic properties of the coordinated metal center.[9] Recently, the magnetic properties of low-coordinate transition metal complexes gained much attention.[17,21–24] Linear coordination of transition metal complexes can lead to a high degree of magnetic anisotropy, rendering these molecules a so-called single molecule magnet (vide infra). To understand the correlation between the coordination geometry of transition metal complexes and their magnetic properties, a brief introduction into the field of molecular magnetism will follow.

1.2.1 Origins of Molecular Magnetism

The finding of a hysteresis in the magnetization of a single molecule opened a new field of research, dealing with so-called single ion or single molecule magnets (SIM / SMM). The rise of molecular magnetism can be traced back to the report of a polynuclear Mn_{12} cluster in 1993 which exhibits magnetic hysteresis at low temperatures.[25]

Magnetic hysteresis is observable when a molecule shows magnetic anisotropy, which describes the preferred orientation of a spin in a system.[22] As a result of magnetic anisotropy, the system exhibits a barrier for the re-orientation of its magnetization. When a molecules spin is S > ½ and the symmetry is low (which is the case in low coordinate amido complexes) a separation of excited states may occur, which then mix through spin-orbit coupling.[21,26] This phenomenon is called zero-field splitting (ZFS) and can be expressed via the following Hamiltonian:

$$\hat{H} = D\left(\hat{S}_z^2 - \frac{S(S+1)}{3}\right) + E(\hat{S}_x^2 - \hat{S}_y^2)$$

D is defined as the axial and E as the rhombic ZFS parameter, while $\hat{S}$ describes the spin projection along a given axis. Spin-orbit coupling (SOC) is distinguished in first order spin-orbit coupling (in-state spin-orbit coupling) and second order spin-orbit coupling (out-of-state spin-orbit coupling).[27] First order SOC is caused by the direct mixing of spin and angular momentum in the electronic ground state of a system, while second order SOC arises from mixing of the ground state (with no first order SOC) with excited states which possess first order SOC.[17,26] As illustrated in Figure 1.2, negative axial ZFS leads to the splitting of an $S = 2$ state into its constituent M_S levels. Simply speaking, ZFS is based on lifting the degeneracy of 2S+1 microstates into magnetic spin states $\pm M_s$ in the absence of an external magnetic field. The magnitude that arises from ZFS, is given by the spin-orbit coupling parameter λ which is inverse proportional to the spin S [17,21].

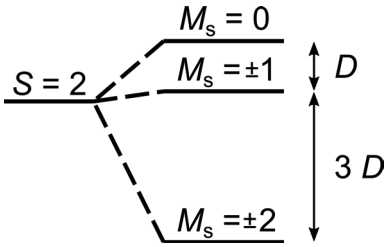


Figure 1.2 Effect of negative axial ZFS: splitting of an $S = 2$ state into M_S levels.[21]

As introduced before, the foundation of molecular magnetism is the occurrence of magnetic hysteresis of a spin system. So far, magnetic hysteresis is only observable at very low temperatures. The highest reported temperature at