Nitrides of the transition metals of groups 7-11 possess desirable properties, such as higher hardness and saturation magnetization than the corresponding metals. In order to develop new chemical vapor deposition (CVD) precursors for late transition metal nitrides, we have explored the synthesis, characterization, and CVD of late transition metal complexes of the sterically demanding ligands di(tert-butyl)amide and 2,2,6,6-tetramethylpiperidine.

Treatment of MnBr₂(thf)₂, FeBr₂(dme), CoBr₂(dme), and NiBr₂(dme) with two equivalents of LiN(t-Bu)₂ in pentane, followed by sublimation in static vacuum, affords the two-coordinate compounds M[N(t-Bu)₂]₂ (M = Mn, Fe, Co, Ni) previously reported by our group. Low-temperature CVD from the reaction between these two-coordinate M[N(t-Bu)₂]₂ compounds and ammonia affords manganese, iron, cobalt, and nickel nitride thin films. Deposition rates as high as 18 nm/min have been observed for cobalt nitride, and deposition temperatures as low as 25 °C have been observed for iron nitride. The XPS binding energies confirm that the nitrogen is present as nitride in all cases. The M:N ratio in the deposited films decreases from Mn (2.5) to Fe (4) to Co (4.6-6) to Ni (9). Carbon contamination in the films is minimal for the manganese, iron, and cobalt nitride films, but similar to the nitrogen content in the nickel nitride films. Comparison of the growth onset temperatures with the decomposition temperatures of the compounds M(NH₂)₂ supports the intermediacy in the film growth of the latter species, which are the expected products of transamination of M[N(t-Bu)₂]₂ compounds with NH₃.

These M[N(t-Bu)₂]₂ compounds have several other interesting features. Previous work has established that the iron and manganese compounds have linear N-M-N angles, whereas the cobalt and nickel compounds are bent. The iron and cobalt compounds have large orbital

![Splitting diagram for d-orbitals in a D₂d amido compound, and relative energies of the triplet states of a d² ion as a function of ligand field strength (units of e₀; eₙy = 0.4 eₙx = 0.24 e₀).](image-url)
angular momentum contributions to their magnetic moments, whereas the manganese and nickel compounds do not. In order to understand these properties, the electronic structures of these compounds have been described using the Angular Overlap Model (AOM). Two general conclusions help rationalize the previously observed molecular properties of these and other two-coordinate compounds: (1) The potential energy surfaces for two-coordinate compounds are nearly flat, varying only a few kcal/mol even with 30° changes in the N-M-N angle, and (2) the ground state configurations for two-coordinate d² and d³ (and therefore also d⁷ and d⁸) compounds experience strong electron-electron repulsion and extensive state mixing. Figure 1 shows the d-orbital splitting diagram and triplet portion of the d² two-coordinate Tanabe-Sugano diagram for an idealized M[N(t-Bu)₂]₂ compound (D₂d symmetry). For reasonable ligand field strengths (eₛ ≤ 10 B), the ground state is not the expected δ² state, but rather a δπ state. This arises because the δ² configuration confines the two β-spin electrons to a single plane, which incurs an energetic penalty larger than the cost of promoting an electron to the δπ state.

Treatment of MnBr₂(θf)₂, FeBr₂(dme), and CoBr₂(dme) with two equivalents of lithium 2,2,6,6-tetramethylpiperidide, Li(tmp), in pentane, followed by sublimation in static vacuum, affords the new compounds M(tmp)₂ (M = Mn, Fe, Co). The heteroleptic, dinuclear three-coordinate compounds Fe₂(tmp)₃(OEt) and [Li(dme)][CoBr(tmp)₂] have also been isolated. Crystallographic studies of Fe(tmp)₂ demonstrate that the tmp ligand, which is the cyclic analog of di(tert-butyl)amide with a slightly compressed C-N-C angle, can also enforce two-coordination (Figure 2). The Fe-N bonds are similar to those in the linear compound Fe[N(t-Bu)₂]₂, although the N-Fe-N angle of 173° and ligand dihedral angle of 73° are smaller. Fe(tmp)₂ might therefore be expected to have a less degenerate ground state. Instead, the room-temperature magnetic moment of 5.91 μₜ suggests the ground state of Fe(tmp)₂ is more degenerate than that of Fe[N(t-Bu)₂]₂ (μ_eff = 5.55 μₜ). This conclusion is corroborated by zero-field hyperfine splitting of the Mössbauer spectrum of Fe(tmp)₂ at 4.2 K (Figure 2). The very large internal hyperfine field, H_INT ≈ 135 T, is the second-largest field reported to date for any iron compound, corresponding to an orbital field Hₗ of ≈ 186 T. This orbital field exceeds that of Fe[N(t-Bu)₂]₂ by ca. 30 T. AOM calculations suggest that the splitting between the essentially non-bonding xy and x²-y² d-orbitals is controlled by weak interactions (δ-bonding or Fe⋯H-C interactions) instead of by the bend angle. A consequence of the 7° smaller dihedral angle and compressed C-N-C angle in Fe(tmp)₂ is weakening of these interactions and greater degeneracy of the ground state, as observed experimentally.

Figure 2. X-ray crystallographic structure of the major disorder component (30 % probability density surfaces, H atoms omitted) and zero- and applied-field Mössbauer spectra of Fe(tmp)₂.
Treatment of TiCl₄ with two equivalents of H(tmp) affords the new compound Ti₂Cl₆(tmp)₂. In contrast, treatment of TiCl₄ or TiCl₄(thf)₂ with three equivalents of Li(tmp) induces ring-opening dealkylation of one tmp ligand and formation of a 1,1,5-trimethyl-5-hexenylimido ligand. A similar reaction is known for the di(tert-butyl)amido ligand.³ IR spectroscopic studies demonstrate that the tmp ligand undergoes ring-opening dealkylation at early transition metal centers including Ti(III), Ti(IV), Hf(IV), V(III), Nb(III), Nb(V), and Mo(III), but not Cr(III). The evidence is consistent with a γ-deprotonation mechanism in which the first two equivalents of Li(tmp) install two tmp groups on the metal center, but a third equivalent of Li(tmp) results in deprotonation of one of these two now-coordinated groups. The resulting carbanion undergoes a rearrangement to afford an imido ligand and an olefin (the latter remaining bound to the imide through the tmp methylene units). We conclude that the synthesis of early transition metal tmp and di(tert-butyl)amido compounds is hampered by the high electropositivity of these metals, which activates the methyl protons towards γ-deprotonation.

References


