

Syntheses, properties, and reactions of transition metal complexes of di(*tert*-butyl)amide and 2,2,6,6-tetramethylpiperidine

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Nitrides of the transition metals of groups 7-11 possess desirable properties, such as higher hardness and saturation magnetization than the corresponding metals.^{1, 2} These nitrides have realized and potential applications in tool coatings and magnetic recording media.¹ 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 $\text{MnBr}_2(\text{thf})_2$, $\text{FeBr}_2(\text{dme})$, $\text{CoBr}_2(\text{dme})$, and $\text{NiBr}_2(\text{dme})$ with two equivalents of $\text{LiN}(t\text{-Bu})_2$ in pentane, followed by sublimation in static vacuum, affords the two-coordinate compounds $\text{M}[\text{N}(t\text{-Bu})_2]_2$ ($\text{M} = \text{Mn, Fe, Co, Ni}$) previously reported by our group.^{3, 4} Low-temperature CVD from the reaction between these two-coordinate $\text{M}[\text{N}(t\text{-Bu})_2]_2$ compounds and ammonia affords manganese,⁵ 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 $\text{M}(\text{NH}_2)_2$ supports the intermediacy in the film growth of the latter species, which are the expected products of transamination of $\text{M}[\text{N}(t\text{-Bu})_2]_2$ compounds with NH_3 .

These $\text{M}[\text{N}(t\text{-Bu})_2]_2$ 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.³ The iron and cobalt compounds have large orbital

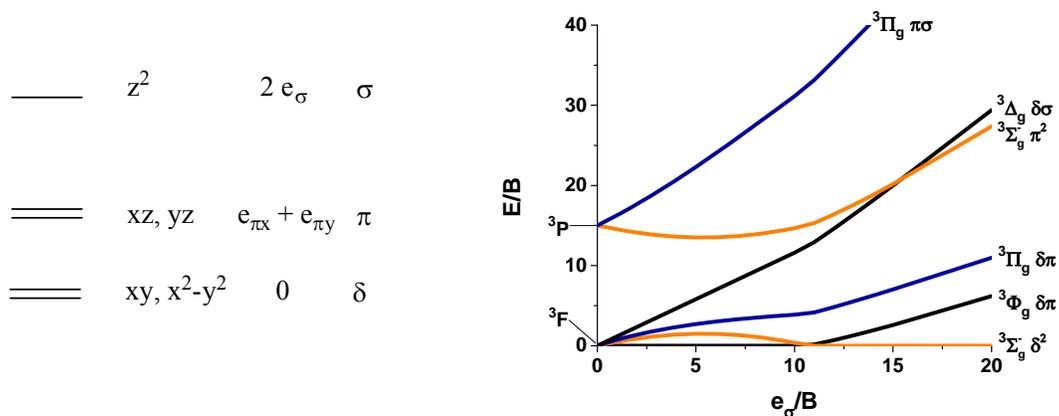


Figure 1. Splitting diagram for d-orbitals in a D_{2d} amido compound, and relative energies of the triplet states of a d^2 ion as a function of ligand field strength (units of e_σ ; $e_{\pi y} = 0.4 e_{\pi x} = 0.24 e_\sigma$).

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 other⁶ 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 d^2 and d^3 (and therefore also d^7 and d^8) compounds experience strong electron-electron repulsion and extensive state mixing. Figure 1 shows the d-orbital splitting diagram and triplet portion of the d^2 two-coordinate Tanabe-Sugano diagram for an idealized $M[N(t\text{-Bu})_2]_2$ compound (D_{2d} symmetry). For reasonable ligand field strengths ($e_\sigma \leq 10 B$), the ground state is not the expected δ^2 state, but rather a $\delta\pi$ state. This arises because the δ^2 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 $\delta\pi$ state.

Treatment of $\text{MnBr}_2(\text{thf})_2$, $\text{FeBr}_2(\text{dme})$, and $\text{CoBr}_2(\text{dme})$ with two equivalents of lithium 2,2,6,6-tetramethylpiperidide, $\text{Li}(\text{tmp})$, in pentane, followed by sublimation in static vacuum, affords the new compounds $M(\text{tmp})_2$ ($M = \text{Mn}, \text{Fe}, \text{Co}$). The heteroleptic, dinuclear three-coordinate compounds $\text{Fe}_2(\text{tmp})_3(\text{OEt})$ and $[\text{Li}(\text{dme})][\text{CoBr}(\text{tmp})_2]$ have also been isolated. Crystallographic studies of $\text{Fe}(\text{tmp})_2$ 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 $\text{Fe}[N(t\text{-Bu})_2]_2$, although the N-Fe-N angle of 173° and ligand dihedral angle of 73° are smaller. $\text{Fe}(\text{tmp})_2$ might therefore be expected to have a less degenerate ground state. Instead, the room-temperature magnetic moment of 5.91 μ_B suggests the ground state of $\text{Fe}(\text{tmp})_2$ is more degenerate than that of $\text{Fe}[N(t\text{-Bu})_2]_2$ ($\mu_{\text{eff}} = 5.55 \mu_B^4$). This conclusion is corroborated by zero-field hyperfine splitting of the Mössbauer spectrum of $\text{Fe}(\text{tmp})_2$ at 4.2 K (Figure 2). The very large internal hyperfine field, $H_{\text{INT}} \approx 135 \text{ T}$, is the second-largest field reported to date for any iron compound,^{4, 7, 8} corresponding to an orbital field H_L of $\approx 186 \text{ T}$. This orbital field exceeds that of $\text{Fe}[N(t\text{-Bu})_2]_2$ by ca. 30 T. AOM calculations suggest that the splitting between the essentially non-bonding xy and x^2-y^2 d-orbitals is controlled by weak interactions (δ -bonding or $\text{Fe}\cdots\text{H-C}$ interactions) instead of by the bend angle. A consequence of the 7° smaller dihedral angle and compressed C-N-C angle in $\text{Fe}(\text{tmp})_2$ is weakening of these interactions and greater degeneracy of the ground state, as observed experimentally.

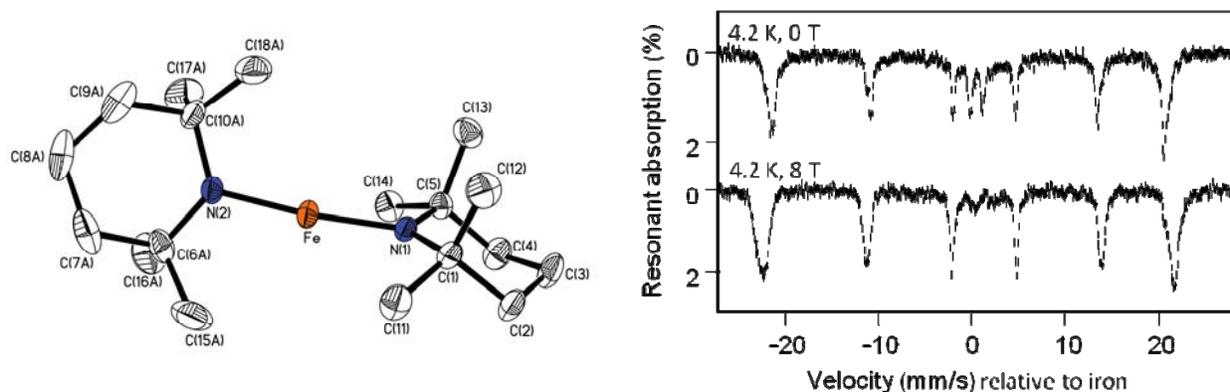


Figure 2. X-ray crystallographic structure of the major disorder component (30 % probability density surfaces, H atoms omitted) and zero- and applied-field Mössbauer spectra of $\text{Fe}(\text{tmp})_2$.

Treatment of TiCl_4 with two equivalents of $\text{H}(\text{tmp})$ affords the new compound $\text{Ti}_2\text{Cl}_6(\text{tmp})_2$. In contrast, treatment of TiCl_4 or $\text{TiCl}_4(\text{thf})_2$ with three equivalents of $\text{Li}(\text{tmp})$ 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 $\text{Li}(\text{tmp})$ install two tmp groups on the metal center, but a third equivalent of $\text{Li}(\text{tmp})$ 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)amide compounds is hampered by the high electropositivity of these metals, which activates the methyl protons towards γ -deprotonation.

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