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Volatility and High Thermal Stability in Mid-to-Late First-Row Transition-Metal Complexes Containing 1,2,5-Triazapentadienyl Ligands

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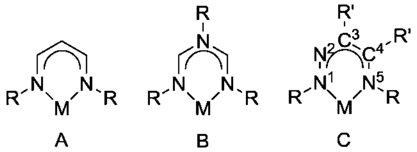
Supporting Information

ABSTRACT: Treatment of first-row transition-metal MCl_2 (M = Ni, Co, Fe, Mn, Cr) with 2 equiv of the potassium 1,2,5-triazapentadienyl salts K(tBuNNCHCHNR) (R = tBu, NMe_2) afforded $M(tBuNNCHCHNR)_2$ in 18−73% isolated yields after sublimation. The X-ray crystal structures of these compounds show monomeric, tetrahedral molecular geometries, and magnetic moment measurements are consistent with high-spin electronic configurations. Complexes with R = tBu sublime between 155 and 175 °C at 0.05 Torr and have decomposition temperatures that range from 280 to 310 °C, whereas complexes with R = NMe_2 sublime at 105 °C at 0.05 Torr but decompose between 181 and 225 °C. This work offers new nitrogen-rich ligands that are related to widely used β-diketiminate and 1,3,5-triazapentadienyl ligands and demonstrates new complexes with properties suitable for use in atomic-layer deposition.

Metal complexes containing β-diketiminate ligands have been widely explored.[1] The κ^2-coordination mode through the nitrogen atoms is most common (Chart 1, A), and the steric and electronic nature of the ligand can be tuned through variation of the nitrogen and carbon atom substituents. Recently, there have been many reports of late-transition-metal complexes containing related 1,3,5-triazapentadienyl ligands.[2,3] In addition to the terminal κ^2-coordination mode to the 1- and 5-nitrogen atoms (Chart 1, B), coordination of 1,3,5-triazapentadienyl ligands can also occur at the 3-nitrogen atom, leading to new terminal and bridging coordination modes.[2,3] Complexes containing the isomeric 1,2,5-triazapentadienyl ligands are rare (Chart 1, C) and are limited to a few nickel(II) and copper(II) complexes containing 1-phenyl, 3-acyl or 3-benzoyl, and 5-alkyl substituents,[4] although the 1,2,5-triazapentadienyl ligand core is also found within more complex chelating ligands.[5] Our laboratory is interested in the development of volatile and thermally stable first-row mid-to-late-transition-metal complexes that can be used for the atomic-layer deposition (ALD) growth of metallic transition-metal thin films. Such materials have many applications, including copper metallization, copper/manganese alloys for self-forming copper diffusion barriers, seed layers for copper metallization, and magnetic alloys.[6] We have reported the synthesis and properties of some main-group metal complexes that contain β-diketiminate ligands,[7] and others have examined the use of β-diketiminate complexes for the chemical vapor deposition (CVD) and ALD growth of copper metal films.[8] However, group 2 and copper complexes containing β-diketiminate ligands have generally low thermal stabilities and may not be appropriate for widespread use as ALD precursors.[8]

Chart 1. β-Diketiminate (A), 1,3,5-Triazapentadienyl (B), and 1,2,5-Triazapentadienyl (C) Ligands



Herein, we describe the synthesis, structure, volatility, and thermal stability of a series of nickel(II), cobalt(II), iron(II), manganese(II), and chromium(II) complexes that contain 1,2,5-triazapentadienyl ligands. These complexes adopt tetrahedral, monomeric structures, exhibit good volatilities and very high thermal stabilities, and thus have excellent properties for use as ALD precursors. Additionally, 1,2,5-triazapentadienyl ligands are easily prepared with a variety of nitrogen and carbon atom substituents and should uniquely complement the rapidly expanding chemistry of metal complexes with β-diketiminate and 1,3,5-triazapentadienyl ligands.[1−3]

The protonated ligand precursors containing two tBu or one tBu and one NMe_2 substituents on the 1- and 5-nitrogen atoms were prepared as described in the Supporting Information through stepwise treatment of glyoxal with $tBuNHNH_2$/$tBuNH_2$ or Me_2NNH_2/$tBuNHNH_2$.[9] Treatment of the protonated ligands with KH in tetrahydrofuran (THF), followed by the addition of anhydrous MCl_2, afforded complexes **1−9** upon sublimation (Scheme 1).[9] These complexes were characterized by spectral and analytical

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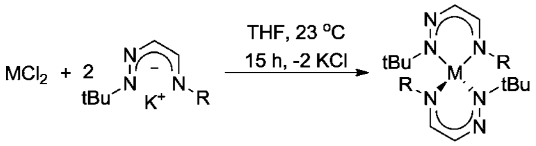
Scheme 1. Synthesis of 1−9



1, M = Ni, R = tBu, 35%
2, M = Co, R = tBu, 57%
3, M = Fe, R = tBu, 73%
4, M = Mn, R = tBu, 54%
5, M = Cr, R = tBu, 55%
6, M = Ni, R = NMe_2, 23%
7, M = Co, R = NMe_2, 27%
8, M = Fe, R = NMe_2, 18%
9, M = Mn, R = NMe_2, 32%

methods and by X-ray crystallography, as described below. All of the new complexes are paramagnetic in solution and exhibited very broad resonances in the ^{1}H NMR spectra. Magnetic moments for **1**−**9** in the solid state and in solution were consistent with high-spin tetrahedral geometries.

X-ray crystal structures of **1**−**7** were determined. Complexes **1**−**5** exhibit merohedral twinning, which leads to an inherent 50/50 occupancy of the core 2-nitrogen/4-carbon atoms. Such disorder is not present in **6** and **7** because of asymmetric ligand substitution, and the structure of **6** described herein presents typical structural features for **1**−**7** (Figure 1).[9] Complex **6** is monomeric and four-coordinate, contains κ^2-1,2,5-triazapentadienyl ligands bound through the 1- and 5-nitrogen atoms, and has distorted tetrahedral geometry about the nickel ion, as exemplified by the 84.0° angle between the best planes of the NiN_3C_2 groups. The Ni−N bond lengths range between 1.932(3) and 1.969(3) Å, which are similar to other high-spin tetrahedral nickel(II) complexes containing κ^2-β-diketiminate ligands.[10] The intraligand N−Ni−N angles are 92.7(1) and 92.8(1)°, while the corresponding interligand angles range between 112.3(1) and 122.0(1)°. Within the NiN_3C_2 ligand cores, the N−N bond lengths are 1.314(4) and 1.307(4) Å, the N−C distances are between 1.304(5) and 1.322(5), and the C−C bond lengths are 1.414(2) and 1.415(2) Å. These values are between N−N, C−N, and C−C single and double bonds and suggest delocalized, monoanionic 1,2,5-triazapentadienyl ligands.

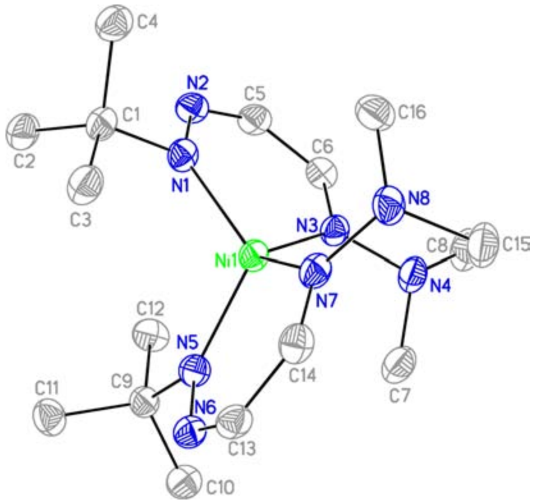


Figure 1. Perspective views of **6** with thermal ellipsoids at the 50% level. Selected bond lengths (Å) and angles (deg): Ni−N1 1.932(3), Ni−N3 1.969(3), Ni−N5 1.949(3), Ni−N7 1.952(3), N1−N2 1.314(4), N2−C5 1.319(5), C5−C6 1.415(5), C6−N3 1.304(4), N5−N6 1.307(4), N6−C13 1.322(5), C13−C14 1.414(5), C14−N7 1.309(5); N1−Ni−N3 92.8(1), N1−Ni−N5 117.7(1), N1−Ni−N7 122.03(1), N3−Ni−N5 121.8(1), N3−Ni−N7 112.3(1), N5−Ni−N7 92.7(1).

To assess the suitability of **1**−**9** for use as CVD and ALD precursors, their volatilities and thermal stabilities were determined by preparation sublimation experiments, solid-state decomposition point measurements, and thermogravimetric analysis (TGA).[9] Complexes **1**−**5** sublime on ~0.5 g scales over 2−3 h with <2% nonvolatile residues between 155 and 175 °C at 0.05 Torr, whereas the *N*-dimethylamino complexes **6**−**9** sublime at 105 °C under similar conditions (Table 1). We have previously demonstrated that magnesium and calcium β-diketiminate complexes containing *N*-dimethylamino groups sublime at considerably lower temperatures than analogous complexes containing *tert*-butyl or isopropyl substituents.[7a,b] The lower sublimation temperatures in the former complexes were attributed to intermolecular lone pair−lone pair repulsions between the nonbonded dimethylamino groups, which lowers the lattice energies and thereby increases the volatilities. Complexes **6**−**9** have melting points that are close to the sublimation temperatures; hence, these complexes evaporate from the liquid state. Liquid precursors are highly desirable in CVD and ALD to promote steady vapor-phase delivery and to avoid particle incorporation into the growing films.[11] The solid-state decomposition temperatures of **1**−**5** range between 280 and 310 °C, which are extraordinarily high for complexes containing these elements. High thermal stability is desirable for ALD precursors because thermal decomposition of the precursor usually signals loss of the self-limited growth mechanism and the onset of CVD-like growth.[11,12] Complexes **6**−**9** have decomposition temperatures that range between 181 and 225 °C, which are much lower than those of **1**−**5**. However, **6**−**9** have much lower sublimation temperatures than **1**−**5**, and their decomposition points are still high enough to be useful in the ALD growth of transition-metal thin films.[8b,12] The TGA data for **1**−**4** showed single-step weight losses and residues of <10% upon reaching 300 °C, **5** gave poor behavior likely because of its extreme air sensitivity, and **6**−**9** showed single-step weight losses up to about the decomposition temperatures that are shown in Table 1.[9]

Table 1. Sublimation and Thermal Stability Data for 1−9

compound	sublimation temp (°C)	melting point (°C)	decomposition point (°C)
1	155	262	290
2	160	260	296
3	175	275	310
4	165	284	310
5	165	257	280
6	105	99	188
7	105	105	225
8	105	106	181
9	105	108	200

To assess its initial viability for use in ALD film growth, **6** was treated with anhydrous hydrazine in THF at 23 °C. A metallic black precipitate was observed within 0.25 h. The precipitate stuck to the magnetic stir bar, and a powder X-ray diffraction spectrum indicated the formation of nickel metal. Hence, **6** is reduced rapidly by hydrazine, and this chemistry may lead to a nickel ALD process. Previous reports have shown that solution reactions are useful in screening precursor pairs for transition-metal ALD processes.[8b,c,12]

The present study demonstrates that metal complexes containing 1,2,5-triazapentadienyl ligands are easily prepared. The synthetic approach to the ligand precursors is inherently flexible and should allow incorporation of a broad range of ligand-core nitrogen and carbon atom substituents. Complexes containing 1,2,5-triazapentadienyl ligands should be electronically distinct from those with β-diketiminate and 1,3,5-triazapentadienyl ligands because the 1-nitrogen atom is bonded to an electronegative nitrogen atom in the former. In addition to the unique characteristics of 1,2,5-triazapentadienyl ligands, we have documented that first-row mid-to-late-transition-metal(II) complexes are monomeric and volatile and have very high thermal decomposition temperatures. As a comparison, the nickel(II) amidinate complex $\mathrm{Ni(iPrNCMeNiPr)_2}$ undergoes solid-state decomposition at about 180 °C,[13,14] whereas the nickel complex **1** decomposes at 290 °C. Additionally, **1−9** do not contain oxygen atoms and have only metal−nitrogen bonds, which tend to be more reactive than metal−oxygen bonds in ALD film growth processes.[11,13] These properties make **1−9** very attractive precursor candidates for use in ALD, as exemplified by the rapid reduction of **6** to nickel metal upon treatment with hydrazine. Film growth studies with **6** and related complexes will be reported separately.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures and analytical and spectroscopic data for **1−9** and X-ray crystallographic data for **6** and **7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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