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13. ABSTRACT (Maximum 200 words) The goal of this proposal was to synthesize new lanthanide and other source compounds for use in chemical vapor deposition and related processes using molecular precursors and to evaluate these compounds in materials growth processes. Specific objectives included the synthesis and characterization of lanthanide complexes that can be used to dope nitride and sulfide materials, materials growth using these precursors, and the synthesis and characterization of volatile, multimetallic first row transition metal complexes that can be used for as dopant precursors for magnetic semiconductor materials such as GaN:Mn or GaN:Cr. In addition, several new classes of potential film growth precursors for the group 2 elements magnesium, calcium, strontium, and barium were developed.			
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**(1) Statement of the Problem Studied**

The goal of this proposal was to synthesize new lanthanide and other source compounds for use in chemical vapor deposition and related processes using molecular precursors and to evaluate these compounds in materials growth processes. Specific objectives included the synthesis and characterization of lanthanide complexes that can be used to dope nitride and sulfide materials, materials growth using these precursors, and the synthesis and characterization of volatile, multimetallic first row transition metal complexes that can be used for as dopant precursors for magnetic semiconductor materials such as GaN:Mn or GaN:Cr. In addition, several new classes of potential film growth precursors for the group 2 elements magnesium, calcium, strontium, and barium were developed.

**(2) Summary of the Most Important Results**

We have developed a new class of volatile lanthanide complexes that can be used for the growth of lanthanide-containing semiconductor materials. Treatment of di-*tert*-butylcarbodiimide or diisopropylcarbodiimide with methyllithium afforded lithium amidinate salts, which react with lanthanide trichlorides to afford the lanthanide tris(amidinate) complexes in 16-77% yields. Crystal structures of representative examples reveal monomeric complexes and no neutral Lewis bases are coordinated to the metal centers. Importantly, Er(tBuNC(CH<sub>3</sub>)NtBu)<sub>3</sub> begins to sublime at 90 °C (10<sup>-3</sup> torr), and there was <0.5% residue after preparative sublimation. The other complexes sublime at similar temperatures and pressures without decomposition. Accordingly, the new lanthanide amidinate complexes are substantially more volatile than our previous erbium pyrazolato source compounds, which in turn, are more volatile than Cp<sub>3</sub>Er (sublimes 180-190 °C (10<sup>-3</sup> torr)).

We had the idea that volatile lanthanide complexes containing nitrogen-rich ligands might decompose more efficiently (to dinitrogen and other volatile carbon-containing fragments) than related ligands with lower nitrogen content. To address this possibility, we examined the reaction of selected LnCp<sub>3</sub> with 2-amino-4,6-dimethylpyridine and 3-amino-5,6-dimethyl-1,2,4-triazine. These reactions resulted in complexes of the formula {Cp<sub>2</sub>Ln(NHHet)}<sub>2</sub>, where Ln = lanthanide(III) and Het = substituted pyridine or triazine. These new complexes were characterized by spectral and analytical data, as well as by X-ray crystallography. Under no conditions was it possible to eliminate more than one cyclopentadienyl ligands from LnCp<sub>3</sub>, and only {Cp<sub>2</sub>Ln(NHHet)}<sub>2</sub> were isolated. In addition, {Cp<sub>2</sub>Ln(NHHet)}<sub>2</sub> were not volatile and instead decomposed at ~200 °C under nitrogen. This chemistry was not pursued further, but a paper describing the results is currently being written.

In collaborative work with Professor Jeff Coffey of Texas Christian University, the growth and properties of Er-doped silicon nanocrystals were investigated using our new precursor Er(tBuNC(CH<sub>3</sub>)NtBu)<sub>3</sub>. Previous work from the Coffey group using the gas phase pyrolysis of disilane at 1000 °C in the presence of Er(tmhd)<sub>3</sub> (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato) as an Er source typically yielded Si nanocrystals with 1-2% Er, depending on oven length. Experiments under identical growth conditions using Er(tBuNC(CH<sub>3</sub>)NtBu)<sub>3</sub> as the Er precursor demonstrated that much higher loadings of Er<sup>3+</sup> were obtained in the silicon nanocrystals, with values up to 20% Er being detected by selected area EDAX measurements of the Si nanocrystals. Rare earth concentration clearly impacts optimal emission intensity (excited either optically or electrically), since it is necessary to go well beyond a threshold value for efficient detection. However, if the local concentration is too high, energy transfer between Er centers increases non-radiative channels for relaxation. The 2-10 nm Si nanocrystals prepared using Er(tBuNC(CH<sub>3</sub>)NtBu)<sub>3</sub> exhibited the expected Si cubic unit cell structure and also the desired near IR luminescence associated with the Er centers at 1540 nm. Excitation wavelength studies confirm that the emission mechanism is mediated by energy transfer from the silicon electron/hole pairs. A full paper describing part of this work recently appeared (*Nanotechnology* **2004**,

15, 643-647). Additional results relating to analysis of the Er sites by EXAFS have been obtained, and a second full paper is being written.

A sample of  $\text{Er}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_3$  was sent to the laboratories of Professor Lauri Niinistö at the Helsinki University of Technology for evaluation as a precursor for the growth of  $\text{Er}_2\text{O}_3$  films using atomic layer deposition (ALD).  $\text{ErCp}_3$  is currently used for the growth of  $\text{Er}_2\text{O}_3$  films, but the strong metal-carbon bonds in this precursor lead to significant carbonate formation when ozone as the oxygen source. It was our hypothesis that the lack of metal-carbon bonds in  $\text{Er}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_3$  would lead to low carbon content  $\text{Er}_2\text{O}_3$  films with use of ozone as a co-reactant. A complete deposition study has been carried out. The ALD of  $\text{Er}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_3$  with ozone affords high quality  $\text{Er}_2\text{O}_3$  thin films in the temperature range of 225-275 °C. Interestingly, the growth rate increases with temperature within this deposition window, suggesting that  $\text{Er}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_3$  is undergoing decomposition and is not giving true ALD growth. However, excellent quality films resulted despite the decomposition of  $\text{Er}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_3$ . The films were amorphous by X-ray diffraction, and were identified as  $\text{Er}_2\text{O}_3$  by time of flight/elastic recoil detection analysis using  $^{127}\text{I}$  atoms. Carbon content in the films (presumably as carbonate) was 3.1% from time of flight/elastic recoil detection analysis.  $\text{Er}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_3$  has several advantages over the traditional precursors  $\text{ErCp}_3$  and  $\text{Er}(\text{tmhd})_3$ , including much higher vapor pressure, higher film growth rates, and low carbonate content in the films. A paper describing the deposition work as well as the synthesis of the precursors is currently being written.

We sent a 7.5 g sample of high purity  $\text{Eu}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_3$  to Professor Andrew J. Steckl at the University of Cincinnati. The intent was to use this precursor in the growth of Eu-doped GaN and to assess the red luminescence of these films. However, Professor Steckl lost funding for his GaN work, and informed us that he would not be able to carry out the research. Thus, this work was not pursued any further.

Lanthanide-doped metal sulfide materials have are of significant interest for full color displays and as far-infrared emitting materials. Chemical vapor deposition is an attractive method for the growth of these materials, but routes to date have employed oxygen-based precursors in combination with hydrogen sulfide. Such deposition routes yield materials that are contaminated heavily with oxygen, and it is well known that the crystallinity and presence of impurities can affect the luminescence efficiency of the lanthanide ions. Effort in the grant period was directed toward the development of volatile lanthanide complexes with sulfur-based ligands, which might serve as film growth precursors to high purity metal sulfide materials. Xanthate ligands have yielded complexes with lanthanide-sulfur bonds. Treatment of  $\text{LnCl}_3$  with  $\text{K}[\text{S}_2\text{COiPr}]$  in tetrahydrofuran at ambient temperature afforded the xanthate complexes  $\text{Ln}(\text{S}_2\text{COiPr})_3(\text{THF})_2$  and  $\{\text{Ln}(\text{S}_2\text{COiPr})_2(\mu\text{-OiPr})(\text{THF})\}_2$  as crystalline solids.  $\text{Er}(\text{S}_2\text{COiPr})_3(\text{THF})_2$  sublimates at 180 °C/0.05 torr. Crystal structures of  $\text{Ln}(\text{S}_2\text{COiPr})_3(\text{THF})_2$  revealed monomeric structures with two tetrahydrofuran ligands. By contrast,  $\{\text{Y}(\text{S}_2\text{COiPr})_2(\mu\text{-OiPr})(\text{THF})\}_2$  crystallized as the dimeric isopropoxide complex, which apparently formed by extrusion of carbon disulfide from a structure related to  $\text{Ln}(\text{S}_2\text{COiPr})_3(\text{THF})_2$ . A manuscript on these complexes is being written.

There is considerable current interest in the growth of Mn(II)-doped GaN films for Spintronics applications. A recent theoretical study predicted that small Mn clusters in GaN are responsible for the high magnetic ordering temperatures in GaN:Mn. To date, GaN:Mn films that show high magnetic ordering temperatures (<940 K) have been grown by PVD techniques, where small metal clusters might be incorporated into the growing film. However, magnetic ordering temperatures have ranged from below 100 K up to 940 K, and there is not a clear picture to date about how the nanoscale structure contributes to the magnetic ordering temperatures. To address the theoretical predictions, we have synthesized and characterized a series of first row transition metal(II) amidinate complexes of the empirical formula  $\text{M}(\text{RNC}(\text{CH}_3)\text{NR}')_2$ , where  $\text{M} = \text{Mn, Fe, Co, Ni}$  and  $\text{R, R}' = \text{small alkyl groups}$ . When  $\text{R} = \text{R}' = \text{tBu}$ , monomeric, four-coordinate complexes are obtained for all M. These compounds contain all-nitrogen coordination spheres, sublime rapidly without decomposition between 50-60 °C ( $10^{-3}$  torr), and are excellent dopant source candidates for compound semiconductors. When  $\text{R} = \text{R}' = \text{iPr}$ , dimeric complexes of the formula  $\text{M}_2(\eta^2\text{-iPrNC}(\text{CH}_3)\text{NiPr})_2(\mu_2\text{-iPrNC}(\text{CH}_3)\text{NiPr})_2$  are obtained for  $\text{M} = \text{Mn, Fe, Co, and Ni}$ . These dimeric complexes sublime at about 80-100 °C ( $10^{-3}$  torr). The higher sublimation temperatures for the

dimeric complexes, compared to the monomeric complexes, suggest that the dimeric complexes sublime as intact dimers.

We have recently published a paper describing the synthesis and characterization of the Cr(II) amidinate complexes  $[\text{Cr}(\text{RNC}(\text{CH}_3)\text{NR}')_2]_x$ , where  $x = 1$  or  $2$  (*J. Am. Chem. Soc.* **2003**, *125*, 7774-7775).  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  exhibits a very different structure than the other dimeric amidinate complexes that we have studied. It contains a metal-metal quadruple bond, with a Cr-Cr bond distance of 1.9601 Å. It is diamagnetic in the solid state, but paramagnetic in solution. NMR studies suggest that the paramagnetism in solution arises from dissociation of  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  into monomeric  $\text{Cr}(\eta^2\text{-tBuNC}(\text{CH}_3)\text{NEt})_2$ . Dissociation to monomers was confirmed using the Evans' Method solution magnetic moment measurements and a freezing point depression molecular weight measurement. The combined results suggest that the Cr-Cr bond strength in  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  is weak and cannot exceed the difference in solvation energies between the dimer and two monomers, plus any increase in Cr-N bond strengths in the monomers. This work is extremely significant from several perspectives. Traditional wisdom in the inorganic literature generally assumes that Cr-Cr quadruple bonds are strong and persist in solution and the solid state. However, our results suggest that Cr-Cr bonds are actually weak and that it is simply the bridging ligands that hold the two Cr atoms in close proximity.  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  sublimes without decomposition at 90 °C ( $10^{-3}$  torr), while monomeric  $\text{Cr}(\text{iPrNC}(\text{CH}_3)\text{NiPr})_2$  and  $\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$  sublime at 50 °C ( $10^{-3}$  torr). Such a difference in sublimation temperatures suggests that  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  may sublime as a dimeric species. Thus,  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  may serve as a film growth precursor that can seed semiconductor films with  $\text{Cr}_2$  magnetic sites. As noted above, a recent theoretical study has suggested that small metal clusters in GaN films should be responsible for the high magnetic moments. Cr-doped GaN films have been demonstrated to have magnetic ordering temperatures that are above 400 K, so  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  is a potentially significant precursor.

Complexes containing Mo-Mo multiple bonds are thought to have much stronger metal-metal bonds than complexes containing Cr-Cr bonds. Since we discovered that the metal-metal bond in  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$  is unexpectedly weak, we are exploring the synthesis of analogous Mo complexes to assess the bond strength in these systems. Treatment of  $\text{Mo}_2(\text{OAc})_4$  with excess lithium amidinates  $\text{Li}[\text{RNC}(\text{CH}_3)\text{NR}']$  afforded the partially exchanged complex  $\text{Mo}_2(\text{OAc})_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_2$ , the desired dimer  $\text{Mo}_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_4$ , or monomeric  $\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$  depending upon the steric bulk of the nitrogen substituents and the reaction conditions.  $\text{Mo}_2(\text{OAc})_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_2$  was obtained when the reaction was run at ambient temperature, while  $\text{Mo}_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_4$  and  $\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$  resulted when the reactions were conducted in refluxing tetrahydrofuran. A crystal structure of  $\text{Mo}_2(\text{OAc})_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_2$  revealed a dimer with four bridging ligands, a Mo-Mo bond length of 2.06 Å, and trans-acetato ligands within the dimer. The  $^1\text{H}$  NMR spectrum of  $\text{Mo}_2(\text{OAc})_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_2$  gave sharp resonances consistent with diamagnetic complexes, suggesting that a dimeric structure is maintained in solution. A crystal structure was obtained for  $\text{Mo}_2(\text{tBuNC}(\text{CH}_3)\text{NEt})_4$ . The overall structure was very similar to the Cr analog, and the Mo-Mo bond distance was 2.07 Å. The  $^1\text{H}$  NMR spectrum afforded sharp resonances, consistent with retention of a dimeric structure in solution. Treatment of  $\text{Mo}_2(\text{OAc})_4$  with excess  $\text{Li}[\text{tBuNC}(\text{CH}_3)\text{NtBu}]$  afforded a complex  $\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$  consistent with the formulation  $[\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2]_x$ . To date, we have not been able to grow single crystals of  $\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$ , so its solid state structure remains unknown. The  $^1\text{H}$  NMR spectrum of  $\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$  afforded very broad resonances, which is consistent with monomeric, paramagnetic  $\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$ . Other structures are also possible (e.g., a dimer with a low-lying triplet electronic state), and work is ongoing to understand these complexes. It is possible that  $\text{Mo}(\text{tBuNC}(\text{CH}_3)\text{NtBu})_2$  exists as a dimer in the solid state and as a monomer in solution, like  $[\text{Cr}(\text{tBuNC}(\text{CH}_3)\text{NEt})_2]_2$ . If this turns out to be the case, it will indicate that even Mo-Mo bonds have low bond strengths. These studies are providing a knowledge base to understand the tendency of certain transition metals to undergo clustering, which is directly relevant to the growth of magnetic semiconductor materials. These studies are continuing into the P.I.'s current ARO grant, and several manuscripts will be written in the near future.

To provide precursors for the growth of group 2 metal sulfide host materials for lanthanide light emitting centers, we sought to prepare volatile group 2 compounds that do not contain oxygen atoms and which might react with hydrogen sulfide to afford high purity sulfide materials. In particular, we felt that

nitrogen donor ligands might serve this role through protonation of the metal-nitrogen bonds by the acidic H-S bond. The ultimate goal was to prepare heavier group 2 precursors, as outlined below, since CaS and SrS are common hosts for lanthanide-doped far infrared emitting materials. We have extensive experience with Mg chemistry, and thus carried out a feasibility study prior to moving to the heavier group 2 elements (*Organometallics* **2004**, *23*, 3488-3495).  $\beta$ -Diketiminato ligands, as outlined in this section, are promising ligands for the development of film growth precursors, since complexes containing these ligands should have strong metal-nitrogen bonds and weak interactions with the carbon atoms of the ligand backbone. In addition, complexes with  $\beta$ -diketiminato ligands that we describe in this section are volatile in analogy with  $\beta$ -diketonato complexes. Most  $\beta$ -diketiminato ligands reported to date contain bulky aromatic groups on the nitrogen atoms, which would reduce volatility through  $\pi$ -stacking interactions in the solid state and by very large molecular weights. We sought to increase volatility through use of the alkyl-substituted  $\beta$ -diketiminato ligand precursors. Complexes were prepared by protonolysis reactions (from  $[\text{MgCp}(\text{CH}_3)(\text{OEt}_2)_2]_2$  or  $\text{MgBu}_2$ ) or by salt metathesis reactions. The coordination chemistry was more complicated than expected. In  $\text{MgCp}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})$ , the  $\beta$ -diketiminato ligand bonds to the Mg ion in a  $\pi$ -fashion, to form a metallocene-like structure.  $\text{MgCp}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})$  is very volatile, and sublimates at the same temperature and pressure as  $\text{MgCp}_2$ . The closely related  $\text{MgCp}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})(\text{OEt}_2)$  was isolated as a diethyl ether adduct, which slowly lost the coordinated diethyl ether to form mixtures of  $\text{Mg}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})_2$  and  $\text{MgCp}_2$ . There was no evidence for a stable species similar to  $\text{MgCp}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})$ . The pyridine adduct  $\text{MgCp}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})(\text{py})$  is stable, and was completely characterized. The  $\beta$ -diketiminato ligands in  $\text{MgCp}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})(\text{L})$  have the  $\eta^2$ -coordination mode. Complexes  $\text{Mg}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})_2$  and  $\text{Mg}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})_2$  possess  $\eta^2$ - $\beta$ -diketiminato ligands. The biggest surprise from this study was documentation of the unusual  $\pi$ -coordination mode in  $\text{MgCp}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})$ . We believe that this coordination mode arises from steric effects associated with the *tert*-butyl substituents, since formation of an  $\eta^2$ - $\beta$ -diketiminato ligand in  $\text{MgCp}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})$  would lead to unfavorable steric repulsions between the *tert*-butyl groups and the cyclopentadienyl ligand. The volatility of  $\text{MgCp}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})$  and the poor donor characteristics of the carbon atoms in the  $\pi$ - $\beta$ -diketiminato ligand suggest that complexes incorporating this ligand might make good film growth precursors.

One of the goals of our project was to prepare volatile precursors that could be used for the growth of oxygen-free CaS and SrS films. Given the surprising formation of  $\text{MgCp}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})$ , we felt that  $\pi$ - $\beta$ -diketiminato ligands might lead to volatile, oxygen-free Ca, Sr, and Ba complexes that might serve as precursors to sulfide phases. The anionic nitrogen donor ligands should react with hydrogen sulfide in a CVD process to form the metal sulfides, and such processes should be exothermic and facile. The formation of Ca, Sr, and Ba complexes containing  $\beta$ -diketiminato ligands was therefore examined through protonolysis reactions using  $\text{M}(\text{N}(\text{SiMe}_3)_2)_2(\text{THF})_2$ . These procedures resulted in the isolation of Ca, Sr, and Ba complexes containing  $\beta$ -diketiminato ligands. In  $\text{M}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})_2$ , metallocene-type structures with  $\eta^5$ - $\beta$ -diketiminato ligands were obtained. These complexes sublime rapidly (<1 h on a 1.0 g scale) without decomposition between 115 (Ca, Sr) and 150 (Ba) °C (0.1 torr). This is an extremely low sublimation temperature for a Ba complex, and indicates an unusually high vapor pressure.  $\text{Ca}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})_2$  exhibits  $\eta^2$ - $\beta$ -diketiminato ligands, while the Ba complex  $\{\text{Ba}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})_2\}_2$  adopts an unusual dimeric structure with bridging  $\eta^5$ - $\beta$ -diketiminato ligands. Complexes  $\text{Ca}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})_2$  and  $\{\text{Ba}(\text{iPrNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NiPr})_2\}_2$  sublime at 135 and 180 °C (0.1 torr), respectively, and the rates of sublimation are noticeably slower than those of  $\text{M}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})_2$ . A paper describing these results appeared recently (*Organometallics* **2004**, *23*, 4995-5002).

In attempted salt metathesis routes to  $\text{M}(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})_2$  (from  $\text{MI}_2$  and the potassium salts of the  $\beta$ -diketiminato ligands), partially substituted byproducts of the formula  $\text{M}_x(\text{tBuNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NtBu})_y(\text{I})_z$  were isolated and fully characterized. These complexes could be obtained in high yields with proper stoichiometries in the syntheses. When  $\text{M} = \text{Sr}$ , a dimeric complex

[Sr(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)(I)(THF)]<sub>2</sub> with an M<sub>2</sub>I<sub>2</sub> core and terminal η<sup>5</sup>-β-diketiminato ligands was isolated. When M = Ba, a tetrameric complex Ba<sub>4</sub>(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)<sub>6</sub>(I)<sub>2</sub> with bridging iodide and bridging η<sup>5</sup>-β-diketiminato ligands was obtained. The overall structure of Ba<sub>4</sub>(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)<sub>6</sub>(I)<sub>2</sub> was a molecular square. Treatment of [Sr(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)(I)(THF)]<sub>2</sub> with potassium 3,5-di-tert-butylpyrazolate (2 equivalents) afforded a dimeric structure [Sr(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)(tBu<sub>2</sub>pz)]<sub>2</sub> that contains terminal η<sup>5</sup>-β-diketiminato and bridging μ:η<sup>2</sup>,η<sup>5</sup>-pyrazolato ligands. [Sr(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)(tBu<sub>2</sub>pz)]<sub>2</sub> and the isostructural Ba species were alternatively obtained from the equimolar reaction of M(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>(THF)<sub>2</sub>, the parent β-diketimine, and 3,5-di-tert-butylpyrazole. The η<sup>5</sup>-coordination mode for a pyrazolato ligand is extremely rare. Finally, treatment of [Sr(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)(I)(THF)]<sub>2</sub> with sodium cyclooctatetraenide afforded the triple decker complex {[Sr(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)]<sub>2</sub>[μ-COT]}. Triple decker sandwich complexes of the group 2 elements are rare. Similar triple decker complexes of Mg, Ca, and Ba were also obtained. Three manuscripts resulting from this work are currently being written.

The final class of complexes that have been prepared is of the formula M(3,5-di-tert-butylpyrazolate)<sub>2</sub>(L), where M = Sr or Ba and L = triglyme or pentamethyldiethylene triamine. These complexes contain η<sup>2</sup>-pyrazolato ligands, and the neutral nitrogen or oxygen donor ligands saturate the coordination spheres. These complexes are analogs of well known volatile β-diketetonato complexes that have been widely used to grow films containing Sr or Ba ions. Unfortunately, M(3,5-di-tert-butylpyrazolate)<sub>2</sub>(L) are not volatile, and instead decompose upon heating to >200 °C. A paper describing this chemistry has been submitted, and positive reviews were obtained. A revised manuscript was submitted, and should be accepted.

We prepared a 10 g sample of Ba(tBuNC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)NtBu)<sub>2</sub>, and submitted it to the laboratory of Professor David G. Goodwin at the California Institute of Technology for initial film deposition trials of BaTiO<sub>3</sub>.

### (3) Listing of All Publications and Technical Reports Supported Under This Grant or Contract.

#### (a) Papers published in peer-reviewed journals

“A Weak, Short Metal-Metal Bond in a Chromium(II) Amidinate Complex,” A.R. Sadique, M.J. Heeg, and C.H. Winter, *J. Am. Chem. Soc.* **2003**, *125*, 7774-7775.

“Rare Earth Doped Silicon Nanocrystals Derived from an Erbium Amidinate Precursor,” J. Ji, R.A. Senter, L.R. Tessler, D. Back, C.H. Winter, and J.L. Coffey, *Nanotechnology* **2004**, *15*, 643-647.

“Factors that Influence π- Versus η<sup>2</sup>-Coordination of β-Diketiminato Ligands in Magnesium Complexes,” H. M. El-Kaderi, A. Xia, M.J. Heeg, and C.H. Winter, *Organometallics* **2004**, *23*, 3488-3495.

“Sandwich Complexes of the Heavier Alkaline Earth Metals Containing η<sup>5</sup>-β-Diketiminato Ligand Sets,” H. M. El-Kaderi, M.J. Heeg, and C.H. Winter, *Organometallics* **2004**, *23*, 4995-5002.

#### (b) Papers published in non-peer-reviewed journals or in conference proceedings

“Metallic Materials Deposition: Metal-Organic Precursors,” C. H. Winter, W. Zheng, and H. M. El-Kaderi, *Encyclopedia of Inorganic Chemistry*, Wiley: Chichester, **2004**, in press (review article on metalorganic film growth precursors).

#### (c) Papers presented at meetings, but not published in conference proceedings

“Synthesis, Structure, and Unusual Reactivity of Magnesium Amidinate Complexes,” A.R. Sadique, M.J. Heeg, and C.H. Winter, 222<sup>nd</sup> National Meeting of the American Chemical Society, Chicago, Illinois, August 26-30, 2001, Abstract #INOR-150.

“Design of Volatile Precursors for Transition Metal-Containing Thin Films,” C. H. Winter, ONR Workshop on Epitaxial Heterogeneous Interfaces—Formation & Stability, Fish Camp, California May 4-8, 2003; *Scene-Setter Talk*.

“A Weak, Short Metal-Metal Bond in a Chromium(II) Amidinate Complex,” C.H. Winter, A.R. Sadique, and M.J. Heeg, Gordon Conference on Inorganic Chemistry, Salve Regina University, Newport, Rhode Island, July 13-18, 2003.

“ $\eta^5$ -Coordination of  $\beta$ -Diketiminato Ligands to the Heavier Group 2 Elements,” C.H. Winter, H. El-Kaderi, and M.J. Heeg, Gordon Conference on Inorganic Chemistry, Salve Regina University, Newport, Rhode Island, July 13-18, 2003.

“Synthesis, Structure, and Atomic Layer Deposition Film Growth Studies of Tris(amidinate)lanthanide(III) Precursors,” C. L. Dezelah IV, D. Back, H. M. El-Kaderi, M. J. Heeg, C. H. Winter, J. Päiväsäari, M. Putkonen, and L. Niinistö, ALD 2004, Helsinki, Finland, August 16-18, 2004, Poster #8.

“Sandwich Complexes of the Group 2 Elements Containing  $\beta$ -Diketiminato Ligands,” H. M. El-Kaderi, M. J. Heeg, and C. H. Winter, 37<sup>th</sup> Inorganic Discussion Weekend, Queens University, Kingston, Ontario, November 6-7, 2004, Talk #B08.

“New Dimolybdenum(II) Complexes Containing Short Metal-Metal Distances: Is Short Necessarily Strong?,” O. M. El-Kadri, A. R. Sadique, M. J. Heeg, and C. H. Winter, 37<sup>th</sup> Inorganic Discussion Weekend, Queens University, Kingston, Ontario, November 6-7, 2004, poster presentation.

*(d) Manuscripts submitted, but not published*

“Synthesis, Structure, and Properties of Monomeric Strontium and Barium Complexes Containing Terminal  $\eta^2$ -3,5-Di-*tert*-butylpyrazolato Ligands,” H. M. El-Kaderi, M.J. Heeg, and C.H. Winter, *Polyhedron* **2004**, *23*, positive reviews obtained, revised manuscript submitted 12/8/04.

*(e) Technical reports submitted to ARO*

This report.

#### **(4) List of All Participating Scientific Personnel Showing Any Advanced Degrees Earned By Them While Employed on the Project**

Charles H. Winter, Principal Investigator  
Dwayne Back, Graduate Research Assistant  
Azwana R. Sadique, Graduate Research Assistant

Hani M. El-Kaderi, Graduate Research Assistant  
Likitha Seneviratne, Graduate Research Assistant

Degrees earned by personnel employed on this project:

Azwana R. Sadique, Ph.D. in Chemistry, March 2003, Wayne State University. Thesis title: "Amidinate Complexes of Magnesium and First Row Metals: Source Compounds for Semiconductor Films"

**(5) Report of Inventions (by title only)**

No patent applications resulting from this project have been submitted.

**(6) Bibliography**

No literature cited other than the publications noted above.