

**Synthesis and Characterization of Two “Tied-back”
Lithium Ketimides and Isolation of a Ketimide-bridged
[Cr₂]⁶⁺ Dimer with Strong Antiferromagnetic Coupling**

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Abstract

Reaction of 1 equiv of $\text{KN}(\text{SiMe}_3)_2$ with 9-fluorenone results in the formation of $(\text{Me}_3\text{Si})\text{N}=\text{C}_{13}\text{H}_8$ (**1**) in high yield after work-up. Addition of 1 equiv of phenol to **1** results in rapid desilylation and formation of 9-fluorenone imine, $\text{HN}=\text{C}_{13}\text{H}_8$ (**2**). Subsequent reaction of **2** with 1 equiv of LiN^iPr_2 results in deprotonation and formation of $[\text{Li}(\text{Et}_2\text{O})]_4[\text{N}=\text{C}_{13}\text{H}_8]_4$ (**3**) in good yield. Reaction of 1 equiv of $\text{KN}(\text{SiMe}_3)_2$ with 2-adamantanone for 7 d at room temperature results in the formation of $(\text{Me}_3\text{Si})\text{N}=\text{C}_{10}\text{H}_{14}$ (**4**) in good yield. Dissolution of **4** in neat MeOH results in rapid desilylation concomitant with formation of 2-adamantanone imine, $\text{HN}=\text{C}_{10}\text{H}_{14}$ (**5**). Subsequent reaction of **5** with 1 equiv of LiN^iPr_2 results in formation of $[\text{Li}(\text{THF})]_4[\text{N}=\text{C}_{10}\text{H}_{14}]_4$ (**6**). Both **3** and **6** were characterized by X-ray crystallography. Finally, reaction of CrCl_3 with 3.5 equiv of **6** results in formation of the $[\text{Cr}_2]^{6+}$ dimer, $[\text{Li}][\text{Cr}_2(\text{N}=\text{C}_{10}\text{H}_{14})_7]$ (**7**), which can be isolated in modest yield after work up. Complex **7** features a Cr-Cr bond length of 2.653(2) Å. Additionally, solid-state magnetic susceptibility measurements reveal strong antiferromagnetic coupling between the two Cr centers, with $J = -200 \text{ cm}^{-1}$.

Introduction

The ketimide ligand (e.g., $[\text{N}=\text{CR}_2]^-$) is an emerging ligand class known for imparting unusual properties upon metal centers. For example, the tetra(ketimide) complexes $\text{M}^{\text{IV}}(\text{N}=\text{C}^t\text{Bu}_2)_4$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$) all feature D_{2d} squashed-tetrahedral geometries,¹⁻⁵ while $\text{Pt}^{\text{II}}(\text{N}=\text{C}^t\text{Bu}_2)_2$ represents an extremely rare example of a linear Pt(II) coordination complex.⁶ These unique properties are a consequence, in part, of the ketimide ligand's ability to simultaneously engage in σ -donating, π -donating and π -accepting behavior. In this regard, the squashed-tetrahedral geometries observed for $\text{M}(\text{N}=\text{C}^t\text{Bu}_2)_4$ are thought to be a consequence of the ketimide ligand maximizing its ability to both π -donate and π -accept.^{3, 7} This combination of interactions also results in a highly covalent metal-ketimide bond, which is reflected in a number of physicochemical studies.^{3, 7} For example, EPR spectral studies of $\text{M}(\text{N}=\text{C}^t\text{Bu}_2)_4$ ($\text{M} = \text{V}, \text{Nb}, \text{Ta}$) reveal large ^{14}N hyperfine coupling, consistent with high degree of M-N orbital overlap.⁷ Similarly, the incredibly short Pt-N bond lengths observed in $\text{Pt}(\text{N}=\text{C}^t\text{Bu}_2)_2$, along with a linear Pt-N-C angle, are suggestive of a large degree of Pt-N π -donation.⁶ This strong donor ability has made the ketimide ligand attractive for other applications, as well, including the stabilization of high oxidation states, such as Nb(V), Ce(IV), U(V), and U(VI),⁸⁻¹¹ and as a supporting ligand for olefin polymerization and olefin metathesis catalysts.¹²⁻²⁸ The ketimide ligand has also been used to support inverse sandwich arene complexes of the actinides.²⁹⁻³¹

Of particular importance to this work, the ketimide ligand has proven to be exceptionally effective at stabilizing metal-metal interactions, as evidenced by the isolation of $[\text{Li}(\text{12-crown-4})_2][\text{M}_2(\text{N}=\text{C}^t\text{Bu}_2)_5]$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$),³² the Pd_7 nanocluster, $[\text{Pd}_7(\text{N}=\text{C}^t\text{Bu}_2)_6]$,³³ $[\text{Cu}(\text{N}=\text{C}^t\text{Bu}_2)]_4$,³⁴ and the tetrametallic iron cluster, $[\text{Fe}_4(\text{N}=\text{CPh}_2)_6]$.³⁵ The latter species features strong ferromagnetic coupling between its four Fe centers, which results in an $S = 7$ spin ground state. It is also a single-molecule magnet with a relaxation barrier of $U_{\text{eff}} = 29 \text{ cm}^{-1}$.

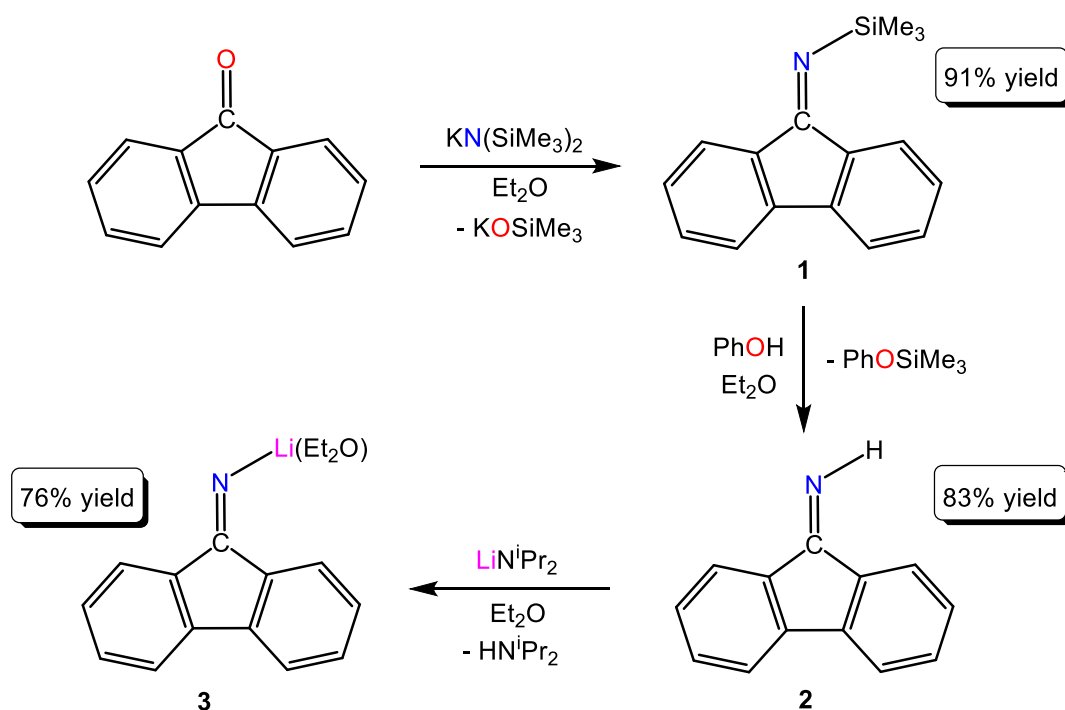
Despite these promising results, the number of reported ketimide ligands is relatively small,³⁶⁻⁴⁵ and only a few monodentate ketimide frameworks have seen widespread usage, including bis(*tert*-butyl)ketimide, $[\text{N}=\text{C}^t\text{Bu}_2]^-$,^{1-4, 7, 32, 46-48} diphenylketimide, $[\text{N}=\text{CPh}_2]^-$,^{18, 22, 37, 40, 49-71} and *tert*-butylphenylketimide, $[\text{N}=\text{C}(\text{Ph})^t\text{Bu}]^-$.^{9, 11, 72-75} Moreover, these examples span a relatively narrow region of steric and electronic space. Thus, further progress in ketimide-supported coordination chemistry would benefit from the synthesis of new ketimide ligand architectures with a diverse array of steric and electronic properties.

Herein, we report the synthesis and characterization of lithium fluorenyl ketimide and lithium 2-adamantyl ketimide. These two lithium ketimides were targeted because they offer much different steric and electronic profiles than ketimide ligands commonly employed in the past. Additionally, their “tied-back” structures should impart increased thermodynamic and kinetic stability onto the ketimide fragment relative to that observed for commonly-employed bis(*tert*-butyl) ketimide ligand,

[N=C^tBu₂]⁻, which is susceptible to oxidation (and an accompanying C-C bond homolysis) when bound to high-valent mid and late transition metal ions.²⁻⁴ Additionally, we describe a preliminary reactivity study of lithium 2-adamantyl ketimide with CrCl₃.

Results and Discussion

To access the desired imines, we chose to employ a synthetic route first developed by Rochow and co-workers in 1963.⁷⁶ Specifically, they discovered that reaction of a non-enolizable ketone with NaN(SiMe₃)₂ resulted in formation of an *N*-silyl imine and NaOSiMe₃. LiN(SiMe₃)₂ can also be used to generate *N*-silyl imines.⁷⁷ Importantly, this strategy works for wide variety of ketones, including sterically bulky ketones. Moreover, and unlike condensation reactions with NH₃, this strategy can be performed under anhydrous conditions. Because of the enhanced driving force inherent in Si-O bond formation, this procedure also avoids the low yields often found for NH₃ condensations, which often do not go to completion.⁷⁸



Scheme 1. Synthesis of compounds **1**, **2**, and **3**.

Thus, addition of 1 equiv of $\text{KN}(\text{SiMe}_3)_2$ to a stirring solution of 9-fluorenone in hexanes for 10 min results in the formation of $(\text{Me}_3\text{Si})\text{N}=\text{C}_{13}\text{H}_8$ (**1**), which is obtained as a yellow oil in 91% yield upon work-up (Scheme 1). This procedure represents an improvement over the original reaction conditions, which employed $\text{NaN}(\text{SiMe}_3)_2$ as the nitrogen source.⁷⁶ The decreased solubility of the KO^tBu vs. NaO^tBu facilitates the separation of the silylimine from the salt by-product, making the work-up substantially easier.

The ^1H NMR spectrum of **1** in C_6D_6 exhibits a single resonance at 0.46 ppm assignable to methyl protons of the silyl group and four aryl resonances at 7.73 ppm, 7.25 ppm, 7.09 ppm, and 7.00 ppm assignable to the four expected aryl environments.

The ^{13}C NMR spectrum of **1** in C_6D_6 exhibits a single resonance at 1.36 ppm, assignable to the methyl carbons of SiMe_3 , and seven aromatic ^{13}C resonances, assignable to the fluorenyl group (Figure S3). Most notable of these is the resonance assignable to the imine $\text{N}=\text{C}$ carbon at 169.9 ppm. This value is in line with other $\text{N}=\text{C}$ chemical shifts.^{6, 34, 79}

Given our desire to develop an anhydrous synthetic procedure for **3**,⁸⁰ we chose phenol as a stoichiometric proton source to effect the desilylation of **1**, instead of H_2O as described in the original protocol. Thus, addition of 1 equiv of phenol to **1** in hexanes results in immediate precipitation of $\text{HN}=\text{C}_{13}\text{H}_8$ (**2**), as a bright yellow powder. Compound **2** can be isolated in 83% yield after work-up. It is very soluble in THF, moderately soluble in diethyl ether, and insoluble in hexanes and pentane. Interestingly, **2** can also be prepared via a $\text{Sc}(\text{OTf})_3$ -catalyzed condensation from 9-fluorenone and $\text{HN}(\text{SiMe}_3)_2$.⁸¹

The ^1H NMR spectrum of **2** in $\text{THF-}d_8$ features five aryl C-H resonances. These resonances are present in a 1:1:2:2:2 ratio and are consistent with eight unique CH environments (three of the peaks consist of overlapping signals) (Figure S4). The imine proton environment is observed at 11.04 ppm, and confirms the removal of the SiMe_3 protecting group. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits 13 distinct carbon resonances, consistent with the C_s symmetry observed in the solid-state. Of particular note, the resonance assignable to the imine $\text{N}=\text{C}$ carbon was found at 172.7 ppm,

which is similar to the value observed for **1**. Compound **2** was also characterized by X-ray crystallography (see SI for details).

Addition of 1 equiv of LiN^iPr_2 to an Et_2O solution of **2** results in the formation of a deep blue solution, from which a deep blue-green precipitate slowly deposits. This deep blue-green solid was identified as $[\text{Li}(\text{Et}_2\text{O})]_4[\text{N}=\text{C}_{13}\text{H}_8]_4$ (**3**) by ^1H NMR spectroscopic and X-ray crystallographic characterization (Scheme 1). While complex **3** is only modestly soluble in ethereal solutions, single crystals suitable for X-ray diffraction could be obtained by storage of a dilute Et_2O solution at $-25\text{ }^\circ\text{C}$ for 24 h. When crystallized in this fashion, complex **3** crystallizes in the triclinic space group $\text{P}\bar{1}$ as a diethyl ether solvate, $\mathbf{3}\cdot\text{Et}_2\text{O}$. In the solid-state, complex **3** exists as a tetramer, forming a distorted Li_4N_4 cubane core (Figure 1). For comparison, the other structurally characterized alkali metal ketimides also form oligomers in the solid-state, including $[\text{Li}]_6[\text{N}=\text{C}^t\text{Bu}_2]_6$, $[\text{Li}]_6[\text{N}=\text{C}(\text{NMe}_2)_2]_6$, and $[\text{Na}]_6[\text{N}=\text{C}(\text{Ph})(\text{Ad})]_6$.^{72, 79, 82} The average N-C bond length is 1.259 Å and is within the accepted range of N=C distances for this class of materials.^{72, 79, 82-85} Each Li cation features a tetrahedral coordination environment that consists of three ketimide nitrogen atoms and one diethyl ether oxygen atom. The average Li-O and Li-N distances are 2.046 Å and 2.076 Å, respectively. Interestingly, a handful of fluorenyl ketimide complexes have appeared in the literature,⁸⁶⁻⁸⁹ but none were prepared by salt metathesis with a fluorenyl ketimide salt.

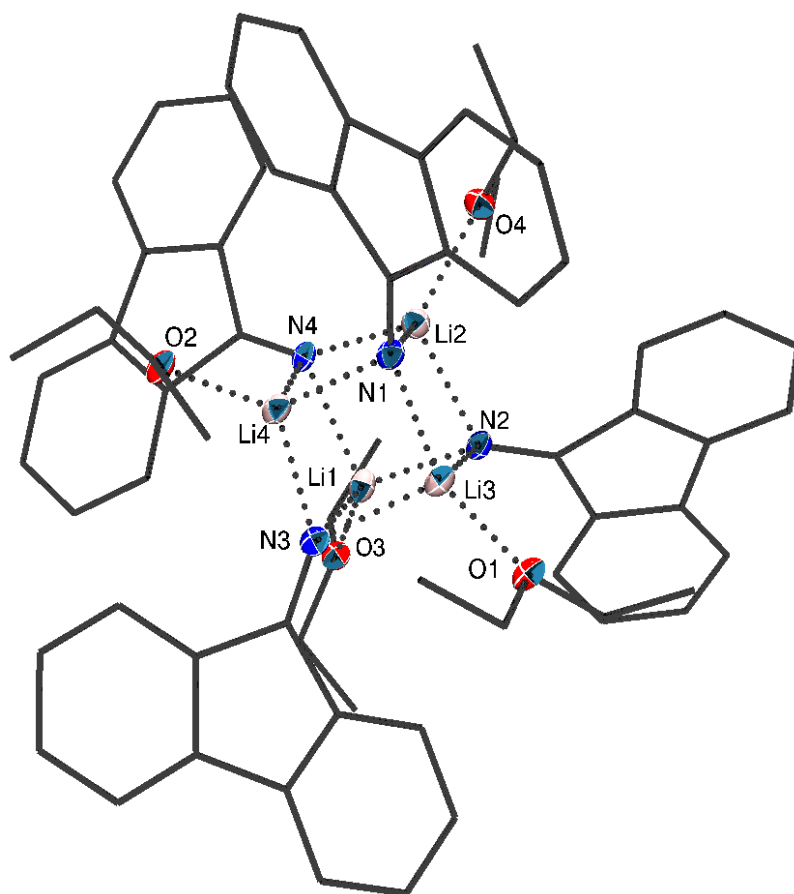


Figure 1. Solid-state molecular structure of $[\text{Li}(\text{Et}_2\text{O})]_4[\text{N}=\text{C}_{10}\text{H}_8]_4 \cdot \text{Et}_2\text{O}$ (**3**· Et_2O) with 50% probability ellipsoids for non-carbon atoms. Hydrogen atoms and Et_2O solvate molecule have been excluded for clarity. Selected bond lengths (Å) and angles (°): $\text{N1}-\text{C1} = 1.262(2)$, $\text{N2}-\text{C14} = 1.258(2)$, $\text{N3}-\text{C27} = 1.259(2)$, $\text{N4}-\text{C40} = 1.256(2)$, $\text{Li2}-\text{O4} = 2.050(3)$, $\text{Li1}-\text{O3} = 2.025(3)$, $\text{Li4}-\text{O2} = 2.031(3)$, $\text{Li3}-\text{O1} = 2.078(3)$, $\text{Li1}-\text{N2} = 1.996(3)$, $\text{Li2}-\text{N1} = 2.124(3)$, $\text{Li3}-\text{N2} = 2.106(3)$, $\text{Li4}-\text{N3} = 2.001(3)$.

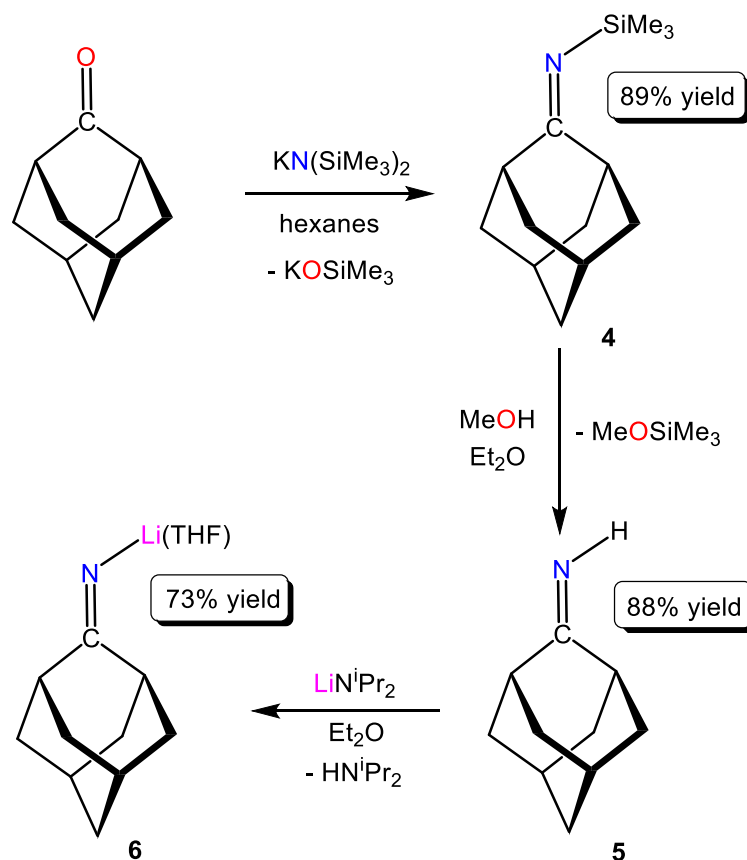
The ^1H NMR spectrum of **3** in $\text{THF}-d_8$ exhibits four aryl resonances at 7.73 ppm, 7.62 ppm, 7.22 ppm, and 7.06 ppm in a 1:1:1:1 ratio, consistent with the D_{2d} symmetry observed in the solid-state. Its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits 7 unique fluorenyl resonances, which is also consistent with solid-state molecular structure. The imine

N=C carbon resonance was observed at 166.4 ppm, which is similar to the shifts observed for **1** and **2**. Finally, the $^7\text{Li}\{^1\text{H}\}$ NMR of **6** features one sharp peak at 2.99 ppm which is assignable to the lone lithium environment (Figure S8).

We next endeavored to apply this synthetic procedure to the synthesis of an aliphatic “tied-back” ketimide salt. Thus, reaction of 1 equiv of $\text{KN}(\text{SiMe}_3)_2$ with 2-adamantanone in hexanes for 7 d at room temperature results in the formation of $(\text{Me}_3\text{Si})\text{N}=\text{C}_{10}\text{H}_{14}$ (**5**), which can be isolated as a colorless oil in 89% yield after work-up (Scheme 2). The reaction of 2-adamantanone with $\text{KN}(\text{SiMe}_3)_2$ is much slower than that of 9-fluorenone with $\text{KN}(\text{SiMe}_3)_2$, which we attribute to the lower electrophilicity of the carbonyl group in 2-adamantanone, as well as the greater steric bulk about the carbonyl carbon. However, it is notable that this synthetic approach still works for such a constrained and electron rich substrate.

The ^1H NMR spectrum of **4** in C_6D_6 exhibits five resonances in a 2:8:2:2:9 ratio, which is indicative of a C_{2v} symmetric molecule in solution, and suggests that the barrier of *E/Z* isomerization is relatively low.⁹⁰ Of particular note, the β -CH methine resonance exhibits a diagnostic downfield shift of 2.59 ppm, whereas the SiMe_3 resonance appears at 0.31 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in C_6D_6 exhibits 5 resonances assignable to the adamantyl skeleton, as anticipated. In particular, the imine N=C carbon resonance was observed at 190.7 ppm, which is somewhat upfield of the carbonyl resonance reported for 2-adamantanone (ca. 220 ppm).⁹¹ Finally, the trimethylsilyl group appears at 1.45 ppm in this spectrum.

Dissolution of **4** into neat MeOH immediately affords HN=C₁₀H₁₄ (**5**), which can be isolated as a white microcrystalline powder in 88% yield after work-up (Scheme 2). The ¹H NMR spectrum of **5** in C₆D₆ exhibits two distinct β-CH methine resonances, at 2.85 and 1.92 ppm, consistent with the expected C_s symmetry (Figure S11). The imine proton environment is observed at 8.63 ppm, and confirms the removal of the SiMe₃ protecting group. The ¹³C{¹H} NMR spectrum of **5** in C₆D₆ features an imine N=C carbon resonance at 187.5, while the two unique β-CH methine resonances are found at 46.6 and 41.6 ppm.



Scheme 2. Synthesis of [Li(THF)]₄[N=C₁₀H₁₄]₄ (**6**).

The addition of 1 equiv of LDA to an Et₂O solution of **5** results in the deposition of a white solid, which, after crystallization from THF/hexanes, was identified as [Li(THF)]₄[N=C₁₀H₁₄]₄ (**6**) by ¹H NMR spectroscopy and X-ray crystallography (Figure 2). This material was isolated in 73% yield. Complex **6** crystallizes in the tetragonal space group I4₁/a and lies on a special position, whereby three additional Li-ketimide fragments are generated by symmetry. As a result, complex **6** features a similar distorted Li₄N₄ cubane structure as was found in **3**. Each lithium cation is coordinated to three nitrogen atoms and one THF molecule (Li1–O1 = 2.031(3) Å). The Li–N bond length is 2.053(5) Å, while the C=N bond length is 1.257(3) Å. These metrical parameters are in line with those observed for complex **3** and other previously reported ketimide salts.^{82, 92}

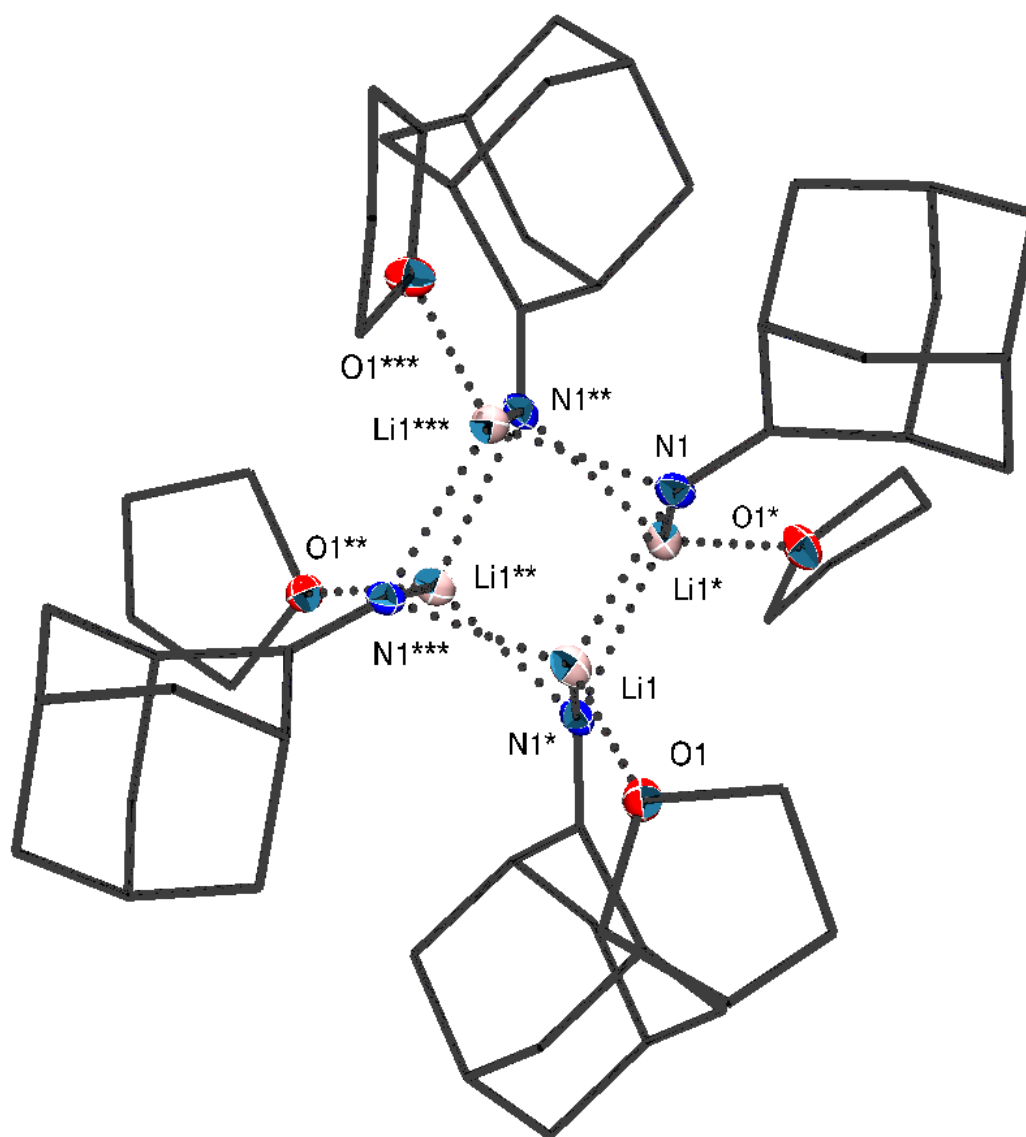


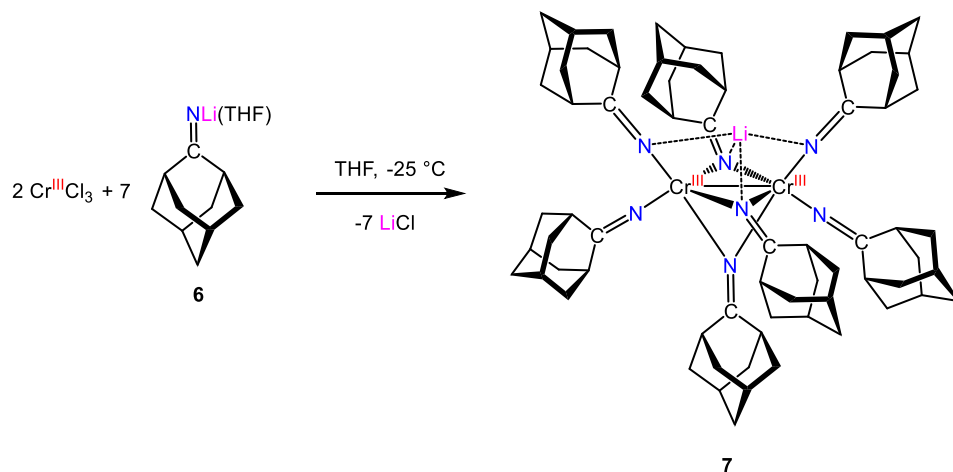
Figure 2. Solid-state molecular structure of $[\text{Li}(\text{THF})]_4[\text{N}=\text{C}_{10}\text{H}_{14}]_4$ (**6**) with 50% probability ellipsoids for non-carbon atoms. Hydrogen atoms have been excluded for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): $\text{Li1}-\text{N1} = 2.053(5)$, $\text{N1}-\text{C1} = 1.257(3)$, $\text{Li1}-\text{O1} = 2.031(3)$, $\text{O1}-\text{Li1}-\text{N1} = 108.9(2)$, $\text{Li1}-\text{N1}-\text{C1} = 143.1(2)$.

The ^1H NMR spectrum of **6** in $\text{THF-}d_8$ is consistent with the D_{2d} symmetry observed in the solid-state. In particular, only one $\beta\text{-CH}$ methine resonance is observed in this spectrum, at 1.97 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in $\text{THF-}d_8$ features a single $\beta\text{-CH}$ methine resonance at 53.02 ppm; however, the $\text{C}=\text{N}$ resonance could not be located, likely because it is too broad to be observed. The $^7\text{Li}\{^1\text{H}\}$ NMR spectrum of **6** features a single, sharp resonance at 0.16 ppm, which is assignable to the lone lithium environment (Figure S15).

Finally, we endeavored to perform a preliminary metal ligation study with 2-adamantyl ketimide. Thus, reaction of CrCl_3 with 3.5 equiv of **6** in cold THF results in formation of a deep brown solution. Work up of this reaction mixture, followed by crystallization from a mixture of pentane/benzene affords dark brown crystals of $[\text{Li}][\text{Cr}_2(\text{N}=\text{C}_{10}\text{H}_{14})_7]$ (**7**) in 43% yield (Scheme 3). Complex **7** is also the major product in the reactions of CrCl_3 with 3 or 4 equiv of **6**, according to the ^1H NMR spectra of the crude reaction mixtures, although a handful of minor unidentified species are present in these reaction mixtures, as well.

The ^1H NMR spectrum of **7** in $\text{THF-}d_8$ features 14 broad and paramagnetically-shifted resonances. Assuming a C_{2v} -symmetric structure, as is observed in the solid-state (see below), we would expect to observe 30 unique proton environments. The observation of fewer resonances, however, suggests that **7** undergoes fluxional behavior in solution. To rationalize this discrepancy, we hypothesize that its coordinated Li cation can exchange between ketimide donors, giving the complex

higher effective symmetry. Finally, the $^7\text{Li}\{^1\text{H}\}$ NMR spectrum of **7** features a single broad resonance, as anticipated, centered at -5.74 ppm (Figure S17).



Scheme 3. Synthesis of $[\text{Li}][\text{Cr}_2(\text{N}=\text{C}_{10}\text{H}_{14})_7]$ (**7**).

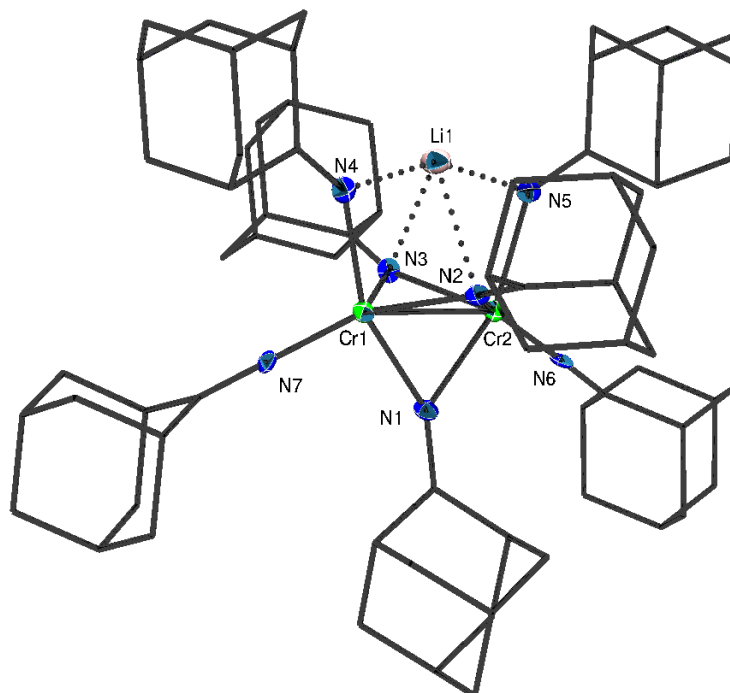


Figure 3. Solid state molecular structure of $[\text{Li}][\text{Cr}_2(\text{N}=\text{C}_{10}\text{H}_{14})_7]\cdot\text{C}_6\text{H}_6$ (**7**· C_6H_6), with 50% probability ellipsoids shown for non-carbon atoms. Hydrogen atoms and benzene solvate have been removed for clarity. Selected bond lengths (Å) and angles (°): Cr1–Cr2 = 2.653(2), Cr1–N1 = 2.065(7), Cr1–N2 = 1.997(8), Cr1–N3 = 1.965(7), Cr1–N7 = 1.844(8), Cr2–N1 = 2.070(8), Cr2–N2 = 2.014(8), Cr2–N3 = 1.977(7), Cr2–N6 = 1.839(8), N4–Li1 = 1.94(2), N5–Li1 = 1.94(2), N2–Li1 = 2.47(2), N3–Li1 = 2.32(2), C51–N6–Cr2 = 177.9(7), C61–N7–Cr1 = 171.0(8).

Complex **7** crystallizes in the orthorhombic space group $\text{Pna}2_1$ as the benzene solvate, **7**· C_6H_6 (Figure 3). Its Li^+ cation coordinates to four of the nitrogen atoms of the ketimide ligands and features two short and two long Li–N distances (N4–Li1 = 1.94(2), N5–Li1 = 1.94(2), N2–Li1 = 2.47(2), N3–Li1 = 2.32(2) Å). As a result of the Li^+ coordination, complex **7** features three μ_2 -ketimide ligands, two μ_3 -ketimide ligands, and two terminal ketimide ligands. As anticipated, the two terminal ketimide ligands feature the shortest Cr–N distances (1.844(8) and 1.839(8) Å) and linear Cr–N–C angles (171.0(7) and 177.9(8)°). The Cr–N distances of the bridging ketimide ligands are longer, but span a narrow range (1.965(7) to 2.070(8) Å), and are in line with previously reported values for μ -($\text{N}=\text{CR}_2$) interactions.^{2, 32}

The Cr–Cr distance in **7** (2.653(2) Å; formal shortness ratio = 1.13) is not particularly short in the grand scheme of Cr–Cr distances,^{93–95} but it is among the shortest distances observed for $[\text{Cr}_2]^{6+}$ -containing complexes, such as $[\text{Cp}^*\text{Cr}(\text{Me})]_2(\mu\text{-Me})_2$ (Cr–Cr = 2.606 Å),⁹⁶ $[\{(\text{Me}_3\text{tacn})\text{Cr}\}_2(\mu\text{-OH})_3][\text{I}]_3\cdot\text{H}_2\text{O}$ (Cr–Cr

= 2.642(2) Å),⁹⁷ [Cr₂(μ-NH₂)₃(NH₃)₆][I]₃ (Cr-Cr = 2.649(2) Å),⁹⁸ and [CpCr]₂(μ-SPh)₂(μ-S) (Cr-Cr = 2.676(1) Å),⁹⁹ and may be evidence of a weak interaction. In contrast, most [Cr₂]⁶⁺-containing complexes feature longer Cr-Cr distances, such as [Cp*Cr(Cl)]₂(μ-Cl)₂ (Cr-Cr = 3.287(1) Å),¹⁰⁰ [Cr₂(dpa)₄][PF₆]₂ (dpa = 2,2'-dipyridylamido) (Cr-Cr = 3.197(3) Å),¹⁰¹ [Cs]₃[Cr₂Cl₉] (Cr-Cr = 3.12 Å).¹⁰²

To further probe the nature of the Cr-Cr interaction in **7**, we measured its magnetic susceptibility via SQUID magnetometry. Complex **7** exhibits an observed χ_{MT} value of 0.86 cm³·mol⁻¹·K at 295 K, which drops to 0.087 cm³·mol⁻¹·K at 2 K (Figure 4). The low room temperature moment, coupled with the shape of the curve, suggests the presence of strong antiferromagnetic coupling between the two $S = 3/2$ Cr³⁺ centers. The magnetic susceptibility could be fit with the exchange Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ using $S_1 = S_2 = 3/2$, giving fit parameters of $J = -200$ cm⁻¹, $g_1 = g_2 = 1.933$, and TIP = 1.659×10^{-3} cm³ mol⁻¹, with 4.4% of an $S = 3/2$ paramagnetic impurity,¹⁰³ and confirming our hypothesis. Several other ketimide-bridge dimers feature similarly large antiferromagnetic coupling constants. For example, the magnetic susceptibility of [Fe₂(N=C^tBu₂)₅] was modeled with $J = -235$ cm⁻¹, whereas the magnetic susceptibility of [Mn₂(N=C^tBu₂)₅]⁻ was modeled $J = -78$ cm⁻¹. In these cases, magnetic coupling was thought to be mediated via super-exchange,³² which is also likely the case for **7**. The value of J observed for **7** is also substantially larger than those measured for other [Cr₂]⁶⁺ complexes, including those with bridging oxo ligands. For example, the magnetic susceptibility of [{(Me₃tacn)Cr}₂(μ-OH)₃][I]₃ was modeled with $J = -66$ cm⁻¹,¹⁰⁴ whereas the magnetic susceptibility of

[{(Me₃tacn)Cr}₂(μ-O)(μ-OH)₂][ClO₄]₂ was modeled with $J = -125 \text{ cm}^{-1}$.¹⁰⁴ Overall, these comparisons suggest that 2-adamantyl ketimide can mediate stronger magnetic communication than either the hydroxo or oxo ligands. Accordingly, we suggest that **6** could be broadly useful for the generation of new materials with novel magnetic properties.^{32, 35} Its narrow steric profile, relative to other ketimide ligands, should also contribute to its utility for this purpose.

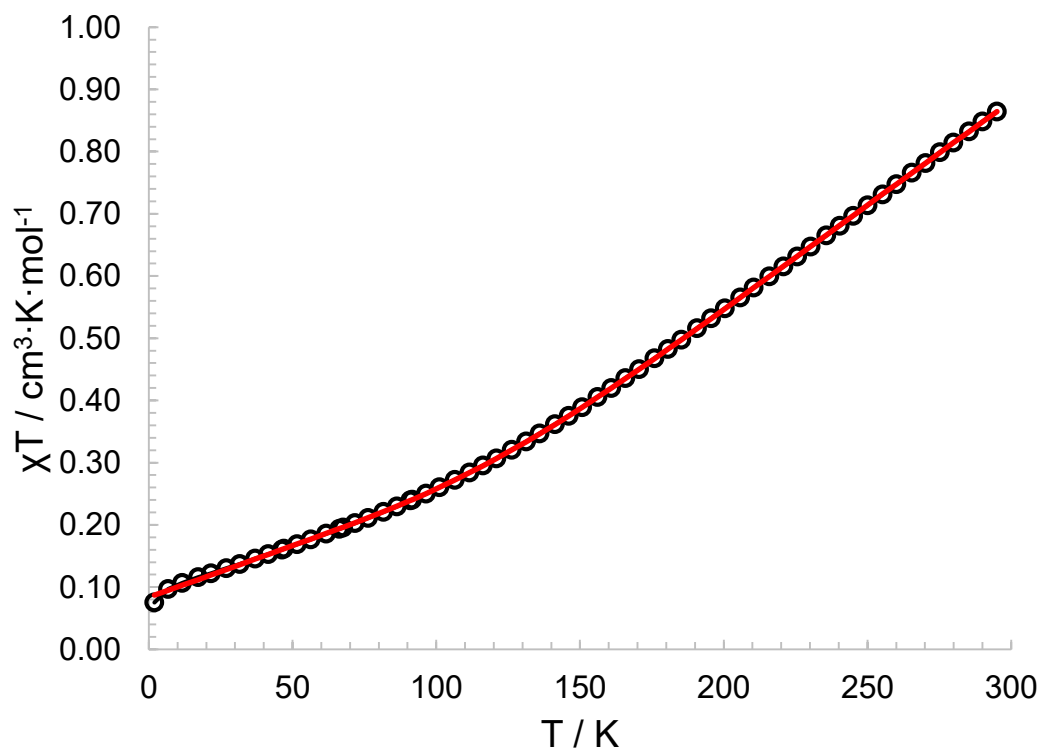


Figure 4. Solid-state magnetic susceptibility data ($\chi_M T$ vs. T) for complex **7** ($\circ$). The red line is the fit (See text for details).

Summary

In summary, we have developed high-yielding, anhydrous synthetic protocols for the lithium salts of 9-fluorenone imine and 2-adamantanone imine. Our three-step synthetic sequence provides a general, efficient route to convert non-enolizable ketones into ketimide ligands with a wide array of electronic and steric profiles. Additionally, we explored the reaction of lithium 2-adamantyl ketimide with CrCl_3 which resulted in isolation of the ketimide-bridged $[\text{Cr}_2]^{6+}$ dimer, $[\text{Li}][\text{Cr}_2(\text{N}=\text{C}_{10}\text{H}_{14})_7]$. This complex features strong antiferromagnetic coupling between the two Cr^{3+} centers, confirming the ability of 2-adamantyl ketimide to mediate magnetic communication between metal centers. Moving forward, we plan to use these two lithium ketimides to explore the development of new single-molecule magnets.³⁵

ASSOCIATED CONTENT

Supporting Information. Experimental details, spectral data, CIF files, and additional figures and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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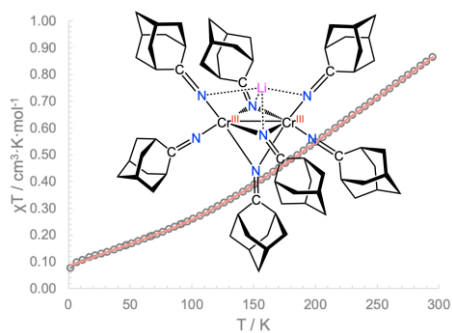
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TOC Graphic



Reaction of CrCl_3 with 3.5 equiv of lithium 2-adamantyl ketimide results in formation of $[\text{Li}][\text{Cr}_2(\text{N}=\text{C}_{10}\text{H}_{14})_7]$, which features strong antiferromagnetic coupling between its two Cr^{3+} centers.