

**A STUDY OF THE INTERACTION OF POLYDENTATE BASES WITH
COMPLEXES OF ELECTROPOSITIVE METALS**

By

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LIST OF CHEMICAL ABBREVIATIONS

15-crown-5	1,4,7,10,13-pentaoxa-cyclopentadecane
Et ₂ O	diethyl ether, (C ₂ H ₅) ₂ O
terpy (tpy)	2,2':6',2''-terpyridine
(3- <i>t</i> -Bu)tpy	4, 4', 4''-tri(<i>tert</i>)butyl-2, 2': 2'', 6''-terpyridine
THF	tetrahydrofuran

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INTRODUCTION TO GROUP 2 METAL CHEMISTRY

The elements of Group 2 in the periodic table (Be-Ra) are known as the alkaline earth metals. They are divalent, almost exclusively exhibiting the +2 oxidation state in isolated compounds, although low oxidation state species can be obtained under gas phase or low temperature conditions. The bonding in Group 2 metal-ligand compounds is conventionally understood to be electrostatic in nature. Ligands are arranged around the metal so that the cation/anion contacts are maximized and intramolecular steric interactions are minimized. This analysis is generally applied to neighboring elements as well, i.e., the alkali metals, lanthanides and actinides, due to similarities in valence electron configuration, high electropositivity, and similar ionic radii.¹

Magnesium has been widely used in organometallic chemistry for over a century, but the chemistry of the heavier alkaline earth metals has been slower to emerge. Calcium, strontium, and barium form longer, weaker, and more ionic bonds to carbon than magnesium does. The result is that the organometallic compounds of these metals are much more reactive than organomagnesium compounds. They need to be handled under the exclusion of air and moisture and are less soluble in organic solvents. The use of sterically bulky ligands with these metals has been broadly helpful in shielding the reactive metal-carbon bonds and improving the solubility of the compounds.

Alkaline earth metals represent nontoxic and inexpensive alternatives to noble metals in catalysis. The Lewis acidity and steric effects in their compounds, rather than redox processes, contribute to their catalytic activity, and new frontiers in catalysis are currently being explored with these metals.²

CHAPTER 1

INTERACTION OF S-BLOCK DONOR CATIONS WITH A NON-INNOCENT *N*-DONOR LIGAND

1. Accessibility of the rare-earth (lanthanide) metals and the need to find functional equivalents

The ‘rare earth’ (lanthanide) elements are often found in the same ores or minerals and historically have been grouped together based on similar patterns of chemical reactivity. Scandium, yttrium and the lanthanides (Ln) make up this group of seventeen elements.³ Despite their moniker, the rare earths are fairly abundant in the Earth’s crust, but concentrated, commercially exploitable deposits of minerals containing these elements are indeed rare.⁴ China mines and produces 97% of the world’s supply of rare earth metals and oxides, even though the country only contains about half of the world’s reserves.⁵ Many manufacturers whose products heavily use rare earths have been forced to move their factories to China to avoid the steep prices of imported rare earths.⁶

As a major consumer, exporter, and importer of rare earth products, the United States is particularly concerned about the availability of these metals. Rare earths are employed in a large number of applications, including chemical catalysts, metallurgical applications and alloys, permanent magnets, and phosphors for computer monitors, lighting, radar, televisions, and x-ray-intensifying film.⁷ For example, lanthanum and cerium are critical in catalysts used to produce gasoline, neodymium and samarium make powerful magnets for wind turbines, and gallium, indium, and tellurium are heavily used in photovoltaic films in solar cells.⁵

The conceptually simplest solution to the supply issue would be to find abundant, inexpensive, nontoxic replacements and supplements for rare earth applications. For catalysis, the focus is on the size and Lewis acidity of possible metal replacements in order to replicate their catalytic activity. Lanthanide ions are large (0.86–1.03 Å for 6-coordinate centers), but since their most common oxidation state is +3 and above, they still have a high charge density. They are also hard Lewis acids that prefer to coordinate hard bases. Finally, the location of the buried 4f orbitals results in effectively empty valence shells, thus the complexes formed by lanthanides are largely held together by ionic (electrostatic) forces.⁴ The alkaline earth metals are also large, hard Lewis acids with empty valence shells as ions and thus emerge as contenders for rare earth substitutes.

If the properties of organo-alkaline earth metal complexes were better understood, suitable substitutes for rare earths in polymerization catalysts for monomers such as methyl methacrylate, caprolactone, and styrene could be rationally designed. For example, calcium and ytterbium have nearly identical ionic radii with a coordination number of 6 (Ca^{2+} 1.00 Å, Yb^{2+} 1.02 Å). Isostructural calcium and ytterbium compounds have isomorphous crystal structures and similar cell constants, nearly identical IR spectra, similar gas phase behavior, and analogous chemical reactivities.⁸ There are, however, some notable exceptions to the above similarities between calcium and ytterbium. This suggests that deeper analysis of the bonding in Ca^{2+} and Yb^{2+} compounds would reveal unique differences in electronic, structural, and molecular properties.

Some notable compounds in the literature reveal the subtleties involved when analyzing compounds of these metals. An exception to the prevailing similarity of isostructural calcium and ytterbium complexes is the divergence in catalytic activity of dibenzyl

polymerization catalysts bis(2-(dimethylamino)- α -(trimethylsilyl)benzyl-C,N)-bis(tetrahydrofuran)-calcium (**1**(Ca)) and -ytterbium (**1**(Yb)) as initiators for styrene polymerization. As noted by Harder, “Both structures are nearly identical and show very similar bond lengths and angles. Even the puckering in the THF rings, which usually shows strong disorder, is identical. In solution, **1**(Yb) and **1**(Ca) both exist as a pair of diastereomers and have close similarity in their ^1H NMR and IR spectra”⁸ (Figure 1).

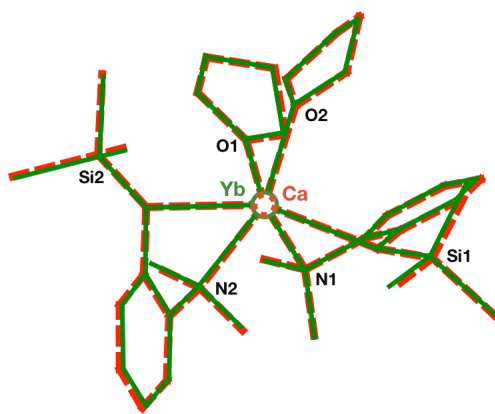


Figure 1. Superimposed solid-state structures of **1**(Ca) (*red*) and **1**(Yb) (*green*).⁸

However, the properties of these two compounds as catalytic initiators are remarkably different; **1**(Ca) yields largely atactic polystyrene, for example, while **1**(Yb) yields a polymer of high syndiotacticity. The authors proposed that Yb–L bonds may be weaker than analogous Ca–L bonds, even when of similar length, owing to repulsion from the filled f^{14} shell of Yb^{2+} . A much higher insertion rate for the ytterbium complex is suggested as a reason for the unexpectedly high stereoselectivity.

As another example, comparison of M–C bond lengths in isostructural calcium and ytterbium compounds $\text{M}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (M = Ca (Figure 2) or Yb) are provided in Table 1.⁹ It is notable that the ytterbium compound contains metal-carbon bonds

that are roughly 0.1 Å longer than its calcium counterpart. What could account for such a large difference in bond length when these two exceptionally similar metals are in the same bonding environment?

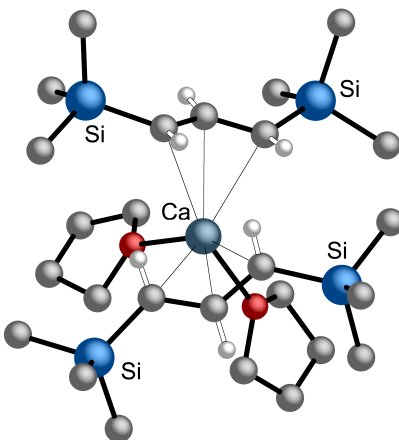


Figure 2. Solid-state structure of $\text{Ca}[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$.¹⁰

Table 1. Bond distances for monomeric divalent lanthanide and alkaline-earth allyl complexes. All bond distances and radii are in Å. $\text{A}' = [1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]$.

Complex	Radius	M–C	M–C (avg)	$R_{\text{M–C}}^a$
$\text{SrA}'_2(\text{thf})_2$	1.18 (CN 6)	2.797(3)–2.805(3)	2.801(5)	1.621
$\text{EuA}'_2(\text{thf})_2$	1.17 (CN 6)	2.762(14)–2.789(14)	2.77(2)	1.60
$\text{SmA}'_2(\text{thf})_2$	1.17 (CN 6)	2.765(6)–2.796(6)	2.78(1)	1.61
$[\text{SmA}'_2]^-$	1.17 (CN 6)	2.743(5)–2.895(5)	2.84(1)	1.67
$\text{YbA}'_2(\text{thf})_2$	1.02 (CN 6)	2.729(9)–2.754(9)	2.74(1)	1.72
$\text{CaA}'_2(\text{thf})_2$	1.00 (CN 6)	2.648(3)–2.662(3)	2.654(5)	1.654

^a $R_{\text{M–C}}$ is the allyl anion ‘radius’, defined by subtracting the metal radius from the average metal-carbon distance.

Differences in chemical reactivity are also noteworthy. The calcium compound is an active initiator for methyl methacrylate polymerization at 19,000 TOF/hr.¹¹ The ytterbium compound also initiates methyl methacrylate polymerization, but at only 89 TOF/hr.¹² Is there some property of the allyl anion that is contributing to the difference, or is it a property of one of the metals?

To answer some of these questions about the “same, but different” properties of calcium and ytterbium, the initial goal of the work described in this thesis involved attempts to study parallel complexes of the two metals; e.g., by preparing a calcium analogue of the compound $\text{Yb}(1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3)_2(\text{tpy})$ (tpy (terpy) = 2,2':6',2''-terpyridine) (Figure 3).¹² If a solid-state structure could be obtained, the bonding distances could be compared to see whether the calcium compound would mirror the 0.1 Å difference discussed above for the $\text{M}[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ complexes, exhibit isomorphous bonding, or display an entirely new bonding pattern.

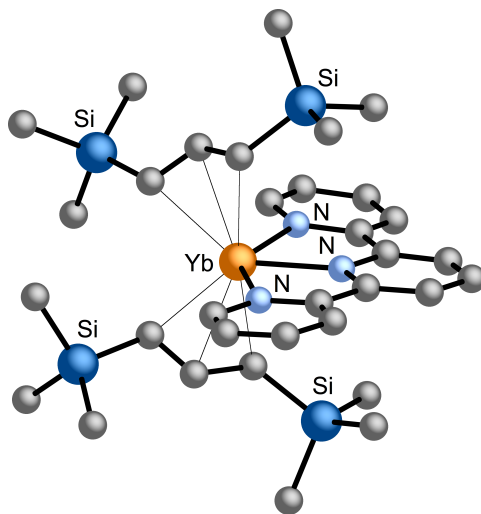


Figure 3. Structure of $\text{Yb}(1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3)_2(\text{tpy})$.¹²

Relatively few (currently ~25) terpyridine-containing crystal structures have been published containing the two metals of interest. The ytterbium compounds have a broad range of applications in the study of charge transfer, nonlinear optical properties, electronic and magnetic coupling, and luminescence.¹³⁻²⁴ Only two calcium compounds containing a terpyridine ligand have been crystallized: $[\text{Ca}(\text{tpy})_3]\text{I}_2$ from methanol, and $[(\text{Me}_2\text{NCHO})(\text{tpy})\text{ClCa}(\mu\text{-Cl})_2\text{CaCl}(\text{tpy})(\text{OCHNMe}_2)]$ from butanol.²⁵ By comparing magnetic data, Andersen, et al. have described an electron exchange model for spin coupling between Yb^{3+} with electron configuration $4f^{13}$, and the single unpaired electron in the bipyridyl radical anion.²⁶ Terpyridine is a “non-innocent” ligand, because it also can be partly reduced. Calcium does not possess any f electrons, so metal-to-ligand charge transfer is not expected in calcium-terpyridine compounds.

2. Experimental Section

General Considerations

All reactions and product manipulations were carried out under dry nitrogen using standard Schlenk and drybox techniques. Dry, oxygen-free solvents were employed throughout. ^1H NMR spectra were obtained at 300 MHz with a Bruker NR-300 spectrometer and were referenced to the residual proton resonances of C_6D_6 (δ 7.15). C_6D_6 was vacuum distilled from Na/K (22/78) alloy. Ethers and hydrocarbon solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. $\text{Ca}[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$,¹⁰ $\text{Ca}(\text{N}(\text{Si}(\text{CH}_3)_3)_2)_2$,²⁷ $\text{K}(1\text{-(SiMe}_3)\text{C}_3\text{H}_3)$,²⁸ and $\text{K}(1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3)$ ¹⁰ were prepared as previously described. The sodium salt of 1,2,3,4- $\text{Me}_4\text{C}_5\text{H}$ ($\text{Na}[\text{CpMe}^{4\text{Me}}]$) was prepared by treating the cyclopentadiene with NaH in hexane. Other commercially available reagents were used without further purification.

General Syntheses

The reactions followed a general protocol in which terpyridine or a similar heterocyclic amine was added to a solution of the Group 1 or 2 compounds in an organic solvent (typically ca. 20 mL). Removal of the solvent left sometimes highly colored diamagnetic products that could not be crystallized. Several reactions are described in more detail in the Results and Discussion section; others were performed more qualitatively, and a summary of the reagents used and outcomes is given in Table 2.

Table 2. Results of small-scale reactions.

Reaction No.	Metal Compound	Added Ligand	Solvent	Color Change Observed
1	Ca(N(Si(CH ₃) ₃) ₂) ₂ , 56 mg, 0.16 mmol	terpy, 34 mg, 0.15 mmol	toluene	yellow → green → blue over 2 hr
2	K(1,3-(SiMe ₃) ₂ C ₃ H ₃) ₂ , 49 mg, 0.22 mmol	terpy, 50 mg, 0.21 mmol	toluene	Immediately blue
3	KN(Si(CH ₃) ₃) ₂ , 46 mg, 0.23 mmol	terpy, 50 mg, 0.21 mmol	toluene	yellow → green → blue over 2 hr
4	KN(Si(CH ₃) ₃) ₂ , 123 mg, 0.62 mmol	(3- <i>t</i> -Bu)tpy, 215 mg, 0.54 mmol	toluene	Colorless to light blue over several hr
5	Ca[1,3-(SiMe ₃) ₂ C ₃ H ₃] ₂ (thf) ₂ , 49 mg, 0.88 mmol	(3- <i>t</i> -Bu)tpy, 361 mg, 0.90 mmol	toluene	Immediately blue
6	Li(1,3-(SiMe ₃) ₂ C ₃ H ₃)	terpyridine	toluene	Immediately blue
7	K(1-(SiMe ₃)C ₃ H ₃)	terpyridine	toluene	Immediately blue
8	CaI ₂	terpyridine	toluene	No change
9	KBr	terpyridine	toluene	No change
10	NaCp ^{4Me}	terpyridine	toluene	No change
11	KN(Si(CH ₃) ₃) ₂	2,2'-bipyridine	toluene	No change
12	KN(Si(CH ₃) ₃) ₂	terpyridine	THF	No change

3. Results and Discussion

Following the same procedure used to synthesize the dark green Yb(1,3-(SiMe₃)₂C₃H₃)₂(tpy),¹² one equiv of terpyridine (47 mg, 0.20 mmol) was added to Ca(1,3-(SiMe₃)₂C₃H₃)₂(thf) (114 mg, 0.21 mmol) in toluene (ca. 20 mL), resulting in a deep green solution that became dark blue after 12 h of stirring. This color change was unexpected, as the dark green color of the ytterbium compound stems from metal-to-ligand charge transfer involving f electrons, and calcium has no f electrons. Interestingly, when a light is passed through the concentrated dark blue solution, it appears red and when the solution is dilute, it appears purple. Efforts to crystallize the presumed complex (1,3-(SiMe₃)₂C₃H₃)₂Ca(tpy) ensued; the 14 different methods attempted included changes in temperature and concentration, all of which produced a solid powder or glass that appeared to be crystalline but was still amorphous.

In an attempt to understand whether the metal, the ligand, or both are responsible for the unique blue color, a series of small-scale reactions was conducted in toluene (Table 2).

Reactions 1–3. A compound tentatively identified as Ca(tpy)(N(Si(CH₃)₃)₂)₂ was synthesized as a green-black solid via the addition of terpyridine to Ca(N(Si(CH₃)₃)₂)₂ in toluene (no. 1). Similarly, what is presumably the complex K(tpy)(1,3-(SiMe₃)₂C₃H₃) was synthesized as a dark purple solid via the addition of terpyridine to K(1,3-(SiMe₃)₂C₃H₃) in toluene (no. 2). K(tpy)N(Si(CH₃)₃)₂ was likewise synthesized as a red-black solid via the addition of terpyridine (0.050 g) to KN(Si(CH₃)₃)₂ (0.046 g) in toluene (no. 3). The reaction mixture of all three of these compounds appeared dark blue during the transformation, but the products formed could not be crystallized, instead yielding finely divided colored powders.

$\text{Ca}(\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$, $\text{K}(\text{tpy})(1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3)$, and $\text{K}(\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$ were synthesized once more and dissolved in a mixture of methylcyclohexane and toluene for recrystallization. Only a dark solid residue was obtained and no crystals were present. $\text{K}(\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$ was synthesized for a third time, and the dark blue reaction mixture was reduced in volume and then partitioned among an NMR tube, a vial, and a flask for recrystallization purposes. Again, only amorphous solids were obtained.

Reactions 4,5. A substituted terpyridine ligand, 4, 4', 4''-tri(tert)butyl-2, 2': 2', 6-terpyridine ((3-*t*-Bu)tpy) (Figure 4), was used in place of terpyridine in an effort to promote crystallization. $\text{KN}(\text{Si}(\text{CH}_3)_3)_2$ was added to (3-*t*-Bu)tpy in toluene to produce $\text{K}((3\text{-}t\text{-Bu})\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$. The clear solution was allowed to stir for a few hours, until it turned light blue. Then the solution volume was reduced under vacuum, and the solution was placed in a freezer at $-35\text{ }^\circ\text{C}$. Large white clusters formed in the solution, and the liquid turned light yellow. Upon warming to room temperature, the white solid dissolved, and the solution turned blue again. This was found to be a completely reversible process and repeated several times.



Figure 4. Reversible progression of $\text{K}((3\text{-}t\text{-Bu})\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$ solution from deep blue at room temperature (far left) to light yellow solution with white clusters at $-35\text{ }^\circ\text{C}$ (far right).

$\text{Ca}(1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3)_2$ was added to $(3\text{-}t\text{-Bu})\text{tpy}$ in an attempt to make $\text{Ca}((3\text{-}t\text{-Bu})\text{tpy})(1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3)_2$. When dried, the product was a shiny blue film that cracks into small shiny pieces reminiscent of crystals, but no x-ray data could be obtained from them. A small amount (roughly 0.05 g) of the blue solid was placed into each of nine separate vials and dissolved in a variety of solvents in a glove box: THF, toluene, ether, methyl cyclohexane, benzene, 1,2-DME, heptane, pentane, and acetonitrile. The solid dissolved in all of the solvents, making a deep blue solution in each case, except for acetonitrile, which immediately made a very light blue-green solution and left a white insoluble solid. Upon evaporation of the solvent, either blue or white solid residues were left behind.

Attempts to make $\text{Ca}((3\text{-}t\text{-Bu})\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$ and $\text{K}((3\text{-}t\text{-Bu})\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$ in THF, generated yellow solutions, but no solid crystals of the products could be obtained. Some of the ligand crystallized out of the THF solution of the supposed $\text{K}((3\text{-}t\text{-Bu})\text{tpy})\text{N}(\text{Si}(\text{CH}_3)_3)_2$ as white needles, but no crystals of the actual product could be isolated.

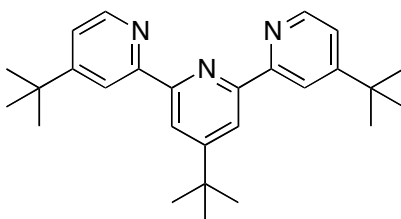


Figure 4. Structure of 4, 4', 4''-tri(*tert*)butyl-2, 2': 2'', 6'-terpyridine ((3-*t*-Bu)tpy)

Reactions 6–12. Reactions similar to the above were conducted in an attempt to identify the source of the color changes. A blue solution was immediately obtained on mixing

Li(1,3-(SiMe₃)₂C₃H₃) with terpyridine in toluene (no. 6), demonstrating that neither K⁺ or Ca²⁺ were specifically required for the color generation. Not surprisingly, the mono-substituted allylic species K(1-(SiMe₃)₂C₃H₄) also generated the blue color (no. 7), but it did not lead to a crystalline product. Several experiments with “null” results helped to narrow down the range of species that could be involved in the color generation. Neither CaI₂ (no. 8) nor KBr (no. 9) generated colored solutions, nor did NaCp^{4Me} and terpyridine (no. 10), or the smaller heterocyclic amine 2,2'-bipyridine and KN(Si(CH₃)₃)₂ (no. 11). Finally, no reaction was observed between KN(Si(CH₃)₃)₂ and terpyridine in THF (no. 12), suggesting that the use of a coordinating solvent blocks the interaction between K⁺ and the heterocyclic amine.

4. Conclusions

As part of a long-range project to develop inexpensive, earth-abundant alternatives to the use of rare-earth metals in catalysts, this research attempted to identify the source of a structural (and reactivity) anomaly between two allyl complexes containing Ca²⁺ and Yb²⁺, i.e., M[1,3-(SiMe₃)₂C₃H₃]₂(thf)₂. Specifically, the aim was to prepare a calcium analogue of the terpyridine-substituted complex Yb(1,3-(SiMe₃)₂C₃H₃)₂(tpy),¹² to determine whether the solid-state structures were indeed isomorphous. Although to date this goal has not been met, it was discovered that an unusual color is generated when solutions of Ca[1,3-(SiMe₃)₂C₃H₃]₂(thf)₂ and terpyridine are mixed in toluene. As the Ca²⁺ center lacks valence electrons, the deep blue coloration almost certainly arises from a ligand-to-metal charge transfer phenomenon. It was further determined that the color arises with Li⁺ and K⁺ centers in addition to Ca²⁺, and with the [1-(SiMe₃)C₃H₃]⁻ and [N(SiMe₃)₂]⁻ anions as well. The colors are not generated from halide salts of potassium

or calcium, nor in the presence of THF, nor with the smaller 2,2'-bipyridine ligand. The key requirements thus appear to be a Group 1 or 2 metal center, terpyridine, a noncoordinating solvent, and a ligand that contains delocalized π -electrons, such as the bulky amido or allyl ligands used here. The null result with $\text{NaCp}^{4\text{Me}}$ seems to be the only reaction that does not fit clearly within these parameters.

All available information indicates that the terpyridine compounds being synthesized exist in a dynamic equilibrium in solution, and the terpyridines are weakly bound to the metal. It may be difficult or impossible to obtain the terpyridine complexes as stable solids, although future success in the area would likely prove to be highly informative.

CHAPTER 2

COORDINATIVE FLEXIBILITY IN ALLYL COMPLEXES OF THE HEAVY GROUP 2 METALS

1. The allyl ligand in Group 2 complexes

Allyl ligands are inherently interesting as the smallest delocalized π -system that can adopt one of two fundamentally distinct modes of binding (σ or π) to metal centers. Being sensitive to the nature of the metal²⁹ and the steric demands of the coordination sphere, the flexible allyl ligand is useful when designing catalyst precursors. Homoleptic transition metal allyl complexes are notoriously unstable even at low temperature, however, exhibiting a common decomposition route involving reduction of the metal and oxidation of the allyl to produce radicals that couple to make hexadienes. The small size of the ligand leaves a large amount of unoccupied space on the metal. In order to block this decomposition route and provide improved solubility and thermal stability, trimethylsilyl groups have been added to the ends of the allyl; the addition of two trimethylsilyl groups increases the size of the ligand 4-fold (Figure 5).⁹

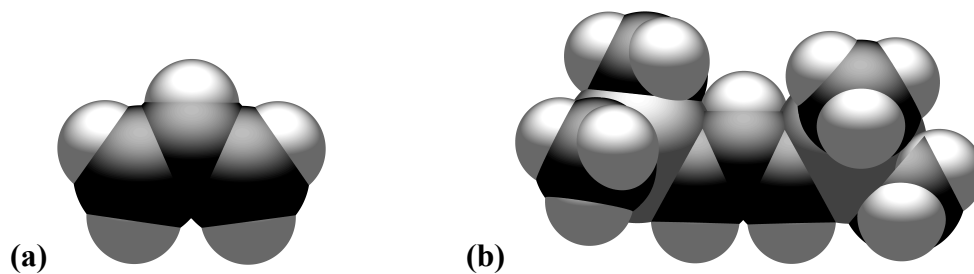


Figure 5. Space-filling models of the parent allyl ligand (a), and the *syn-syn*-form of the $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]^-$ substituted anion (b) indicate that the trimethylsilyl substitution on the allyl ligand increases its size by roughly a factor of 4.

Alkali and heavy alkaline earth metal (Ca, Sr, Ba) complexes with allyl ligands serve as initiators for methyl methacrylate polymerization, although their reactivity varies widely. The purely σ -bonded $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{Mg}(\text{thf})_2$ is inactive, for example, while the σ -cation- π μ -bonded $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{Mg}$ is weakly active at 300 TOF/hr.³⁰ This suggests that the mode of bonding employed by the allyl may have an effect on the catalytic activity of the compound, or that the presence of the co-ligand (THF) is suppressing the reactivity. It is also known that the purely π -bound $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{Ca}(\text{thf})_2$ is an active initiator at 19,000 TOF/hr.¹¹ How would the catalytic properties change if a calcium compound with σ -bonded allyls could be isolated?

Heavy alkaline earth metals (Ca-Ba) almost always form complexes with π -bound allyls owing to their highly electropositive nature and increased size (ca. 41% going from Mg^{2+} to Ca^{2+} for CN = 6).^{31,32} Until recently, Be and Mg were thought to form only σ -bound allyls; however, work in the Hanusa lab has shown that π -type bonding in magnesium allyl compounds is energetically feasible, but only in the absence of perturbing forces like coordinated solvent.³³ Therefore, if it is possible for an allyl ligand to switch from σ - to π -coordination when steric bulk and electron density are removed from a light alkaline earth metal center, is it possible to do the opposite with a heavy alkaline earth metal? Can a π -bound allyl be induced to switch to σ -coordination by adding steric bulk and electron density to a heavy alkaline earth metal center?

Evidence that this might be possible comes indirectly from solid-state structures of calcium and strontium that at first glance would not seem to be directly related to the allyl complexes under consideration here. The structures of both $\text{CaI}_2(\text{thf})_4$ and $\text{SmI}_2(\text{thf})_5$ are

shown in Figure 6. The ionic radius of Ca^{2+} is 1.00 Å while that of Sm^{3+} is 1.02 Å. The metal centers in each compound have practically identical radii and yet each binds a different number of THF molecules to fill its coordination sphere.^{34,35} Obviously, steric demand is not an issue, so perhaps the increased 3+ charge on the samarium is counterbalanced with the electron donation from an extra THF molecule. This example seems to validate the idea that increasing electron density at a metal center causes the metal to accept less electron donation from ligands, which is why the $\text{CaI}_2(\text{thf})_4$ is content with only four coordinated THF ligands when there is clearly space for more.

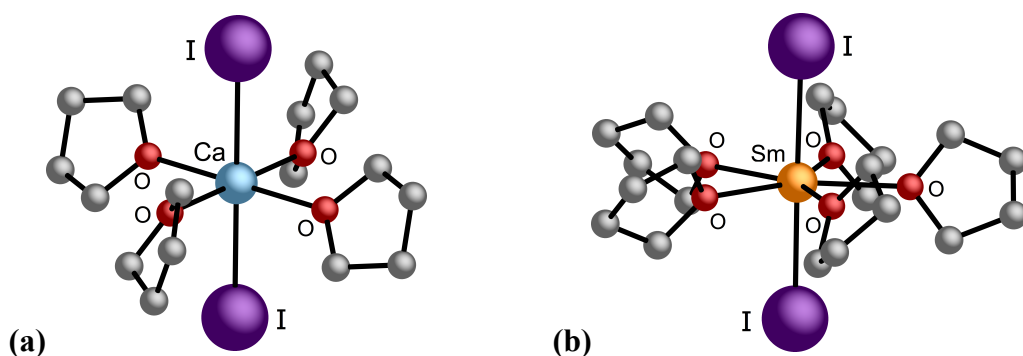


Figure 6. Structures of $\text{CaI}_2(\text{thf})_4$ **(a)** and $\text{SmI}_2(\text{thf})_5$ **(b)**.

In order to add extra electron density to a heavy alkaline earth metal center, it was proposed that if a crown ether were coordinated to a calcium center, the combination of the electron density from the crown ether oxygens and two π -bound allyl ligands would cause the metal center to become oversaturated with electron density. This overloading might then cause one or both of the allyl ligands to switch to a σ -bonding mode in order to relieve the accumulation of electron density on the positively charged metal center.

Ca^{2+} contains empty 3d-orbitals at a similar radial distance as its filled 3p orbitals, resulting in mixing that causes some of its bonding interactions to have a covalent compo-

ment. The bent molecular structure of calcium dihalides is an example of this kind of covalent d-orbital interaction in bonding.³⁶ An ionic environment generally favors π -bonding while a more covalent environment could favor σ -bonding, so it was expected that the addition of enough electron density to the positive metal center would provide a more covalent environment for σ -bonding.

Ca[1,3-(SiMe₃)₂C₃H₃]₂ and Yb[1,3-(SiMe₃)₂C₃H₃]₂ were prepared via a halide metathesis reaction ($\text{MI}_2 + 2\text{K}[1,3\text{-(SiMe}_3\text{)}_2\text{C}_3\text{H}_3] \rightarrow \text{M}[1,3\text{-(SiMe}_3\text{)}_2\text{C}_3\text{H}_3\text{]}_2(\text{thf})_2 + 2\text{KI}$) in THF. A series of reactions was then carried out on these starting materials in an attempt to isolate a calcium or ytterbium complex containing a crown ether and a η^3 -1,3-(SiMe₃)₂C₃H₃ ligand.

2. Experimental Section

General Considerations

All reactions and product manipulations were carried out under dry nitrogen using standard Schlenk and drybox techniques. Dry, oxygen-free solvents were employed throughout. ¹H NMR spectra were obtained at 300 MHz with a Bruker NR-300 spectrometer and were referenced to the residual proton resonances of C₆D₆ (δ 7.15). C₆D₆ was vacuum distilled from Na/K (22/78) alloy. Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. Ca[1,3-(SiMe₃)₂C₃H₃]₂(thf)₂¹⁰ and Yb[1,3-(SiMe₃)₂C₃H₃]₂(thf)₂⁹ were prepared as previously described. Other commercially available reagents were used without further purification.

Reaction of M[1,3-(SiMe₃)₂C₃H₃]₂(thf)₂ (M = Yb, Ca) with 15-crown-5. A slight excess of liquid 1,4,7,10,13-pentaoxa-cyclopentadecane (15-crown-5, 71 mg, 0.31 mmol)

was stirred with $\text{Yb}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (170 mg, 0.25 mmol) in 25 mL THF to produce an orange solid (0.31 g). 15-crown-5 (85 mg, 0.39 mmol) was also added to $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (150 mg, 0.27 mmol) in 25 mL toluene to produce a white solid (0.3 g). In both cases, impurities were present, but two distinctive singlets in the ^1H -NMR spectra near 0 ppm indicated the possible presence of a η^1 allyl ligand in both compounds. The distinctive peaks for coupled allyls (1,3,4,6-tetrakis(trimethylsilyl)-1,5-hexadiene, two diastereomers) were also observed in ^1H NMR spectra at δ 0.14 (s), 2.01 (mult), 5.47 (d), and 5.9 (mult).

Reaction of $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{Et}_2\text{O})_2$ with 15-crown-5. $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{Et}_2\text{O})_2$ (220 mg, 0.39 mmol) was prepared by stirring together CaI_2 (260 mg, 0.88 mol) and $\text{K}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$ (400 mg, 1.8 mmol) in 25 mL diethyl ether instead of THF to avoid the potential problem of THF ligands occupying coordination space around the metal; the more weakly basis Et_2O ligands are more easily displaceable than THF. 15-crown-5 (85 mg, 0.39 mmol) was added to $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{Et}_2\text{O})_2$ (150 mg, 0.27 mmol) in 25 mL toluene, which produced a dark brown oil. A variation of this reaction was also conducted with dibenzo-18-crown-6 (127 mg, 0.35 mmol); after it was added to $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{Et}_2\text{O})_2$ (0.14 g, 0.25 mmol) in toluene, an off-white solid (0.10 g) was obtained. ^1H -NMR spectra from the solids obtained with either crown ether indicated the possible presence of an η^1 allyl ligand, as well as coupled allyl ligands.

Reaction of $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ with 2,2'-bipyridine. Instead of a crown ether, the use of two bipyridine ligands was attempted as a substitute that would be able to fit around the calcium more snugly and still force η^1 - and η^3 -coordination of the allyl

ligands as well as help with crystallization attempts. Two equivalents of 2,2'-bipyridine (142 mg, 0.91 mmol) were added to $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (180 mg, 0.32 mmol) in 25 mL THF. The reaction mixture initially turned bright red, but a few hours later had turned black and all that could be isolated was a black solid. The $^1\text{H-NMR}$ spectra indicated the presence of a large amount of coupled allyls. The same reaction was attempted again at about 70% the previous reaction size in the same amount of solvent. The bipyridine (99 mg, 0.63 mmol) was added dropwise to a solution of $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (130 mg, 0.23 mmol) in THF, which remained a light tan color throughout the process. A light green solid was obtained which contained coupled allyls.

This reaction was also conducted at low temperature (0 °C) on a Schlenk line. The reaction mixture turned from red to orange to brown over the course of the addition of 2,2'-bipyridine (142 mg, 0.91 mmol) to $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (180 mg, 0.32 mmol) in 30 mL THF. The reaction mixture was placed in a freezer for two days and after that time it had turned light yellow. The $^1\text{H-NMR}$ spectra of the evaporated solid contained resonances appropriate for 2,2'-bipyridine that were shifted slightly downfield from those for the free ligand; i.e., doublets at 7.12 ppm, 7.66 ppm, 8.50 ppm, and 8.59 ppm. A very large crystal was grown from the reaction mixture, but it desolvated after isolation, turned opaque and would not diffract. Repeated crystallization attempts produced thin white crystals in solution above a yellow solid, indicating the probable decomposition of the compound.

Two more attempts were made to obtain a calcium crown ether compound with both a η^1 - and η^3 -1,3-(SiMe_3)₂C₃H₃ ligand. The 18-crown-6 ligand (163 mg, 0.62 mmol) was added to $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (250 mg, 0.45 mmol) in 25 mL THF at room tem-

perature, and a red oil was obtained. The 18-crown-6 ligand (156 mg, 0.59 mmol) was also added to $\text{Ca}[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_2(\text{thf})_2$ (240 mg, 0.43 mmol) in THF at $-30\text{ }^\circ\text{C}$ and again, a red oil was obtained. ^1H NMR spectroscopy in C_6D_6 confirmed the presence of coordinated 18-crown-6 ($\delta = 3.49\text{ ppm}$), but there was also evidence for vinyl-terminated alkoxy ligands (e.g., multiple resonances around $\delta 6.4$). Peaks were observed for the trimethylsilylated propene, $1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_4$, as a doublet of triplets at $\delta = 6.07\text{ ppm}$ and $\delta = 6.13\text{ ppm}$. Ether cleavage followed by oxidation and coupling of all the allyls was suspected as the likely decomposition route.

At the completion of this research, a paper appeared that featured the unsubstituted parent allyl in a calcium complex; it employed essentially the same approach as that described above to obtain $\text{Ca}(\eta^1\text{-C}_3\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(18\text{-crown-6})$ (Figure 7), “the first crystallographic evidence for a purely σ -bound allyl ligand in a mononuclear calcium complex.”³²

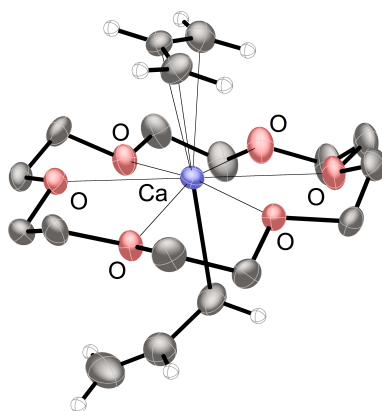
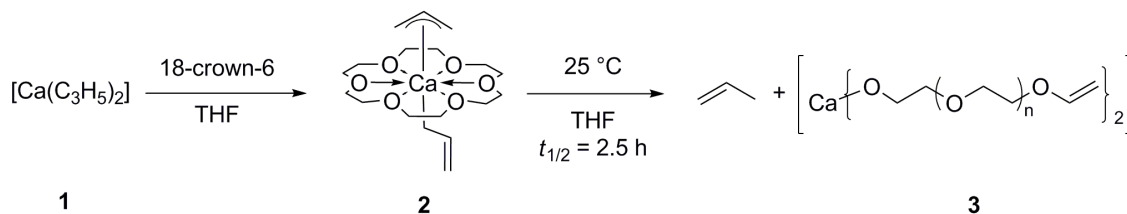


Figure 7. Structure of $[\text{Ca}(\eta^1\text{-C}_3\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(18\text{-crown-6})]$. For clarity, hydrogen atoms have been removed from the crown ether ligand.

The authors also explained the observed decomposition pathway, outlined in Equation 1. It was noted that the decomposition products formed a red oil. Miniscule amounts of the reactants were dissolved in THF and layered in a vial at $-35\text{ }^\circ\text{C}$ to allow the isolation of

the colorless crystals of $\text{Ca}(\text{C}_3\text{H}_5)_2(18\text{-crown-6})$. However, the authors were never able to obtain NMR spectra free of decomposition products, even at $-95\text{ }^\circ\text{C}$.



Equation 1. Decomposition of $\text{Ca}(\eta^1\text{-C}_3\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(18\text{-crown-6})$

In this case, the bulky substituents on the TMS-substituted allyl evidently served to destabilize the allyl crown ether complexes even at low temperatures. Even though the synthesis of a σ -bonded allyl on a heavy alkaline-earth metal was successful, the resulting complex was thermally unstable.

4. Conclusions

Isolation of $\text{Ca}(\eta^1\text{-C}_3\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(18\text{-crown-6})$ demonstrates that it is possible to manipulate the hapticity of a ligand on a Group 2 center by adjusting the electron density on the metal with a suitably strong donor ligand. A crown ether is a strong polydentate donor with a limited amount of steric bulk, providing enough room for the allyl ligands in the coordination sphere. The accumulation of electron density forces one of the allyl ligands to switch to a σ -bonding mode to relieve the buildup of negative charge on the positive metal center. This method for manipulating the hapticity of ligands could be applicable to a wide range of ligands and metal centers. Further use of this capability could lead to the development of more active catalysts based on earth-abundant Group 2 metals.

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