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Synthesis and Crystal Structures of Magnesium and Calcium Triazenide Complexes

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Recent interest in the chemistry of group 2 metal complexes has been inspired, in part, by the demand for development of alkaline-earth compounds suitable for chemical vapor deposition (CVD)[1,2] and sol−gel processes.[3] An example of the application of these complexes is the fabrication of magnesium-doped group 13 nitrides, which are important in the production of high-luminosity blue and green photonic devices.[4−6] The synthesis of monomeric, well-behaved candidates for such applications is challenging due to the ionic nature of group 2 metals and their large radii. Nonetheless, a variety of monomeric compounds with anionic metal−carbon[2,7] and metal−heteroatom based ligands have been described.[8−12]

We are interested in the use of triazenide-based complexes[13,14] (Figure 1) to prepare compounds which exhibit greater electrophilicity at the metal center.[15] Deprotonation of the triazene[16−18] gives the triazenide which readily binds to main group and transition metals. A ligand which is related to the triazenide is the amidinate (Figure 1).[19−21] Both ligands have been shown to bind in monodentate, bidentate and bridging fashions by X-ray crystallographic methods.[13,19−22] The ligands differ, however, in the amount of electron density that they donate to the metal center. Carbonyl stretching frequencies are higher in isoelectronic carbonyl containing triazenide complexes than their amidinate counterparts, consistent with greater electrophilicity of the metal in triazenide-based systems.[23]

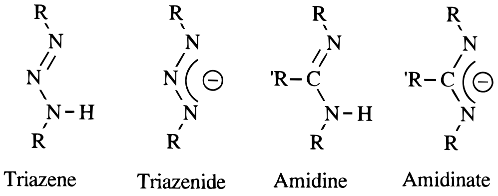

Figure 1.

The differences in donating properties of these ligands arises from the electronegativity of the central element. The inner nitrogen of the triazene significantly increases the acidity of the N−H over the N−H of the amidine. The greater acidity of the triazene allows more flexibility in the choice of bases used to generate the triazenide.[15]

In this report, we present the synthesis and structure of the magnesium and calcium triazenide complexes, $[(\mathrm{Tol})\mathrm{NNN}(\mathrm{Tol})]_2\mathrm{M}(\mathrm{sol})_2$ (**1**, M = Mg, sol = THF; **2**, M = Ca, sol = DME). Both compounds are monomeric in the solid state. The triazenides share some features with the group 2 amidinates $[\mathrm{PhC}(\mathrm{NSiMe}_3)_2]_2\mathrm{M}(\mathrm{sol})_n$;[8,9,24] however, there are also notable differences in their bonding.

Experimental Section

General. Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres drybox with attached MO-40 Dritrain, or by using standard Schlenk or vacuum line techniques. Melting points were performed in flame-sealed capillaries and were uncorrected.

^{1}H NMR spectra were obtained on either a Varian Gemini 2000-BB 200 MHz Fourier transform spectrometer or a Varian Unity 500 MHz Fourier transform spectrometer at the San Diego State University NMR facility. ^{1}H NMR spectra were recorded relative to residual protiated solvent. ^{13}C{^{1}H} NMR spectra were obtained at either 50 or 125 MHz on the 200 or 500 MHz instruments, respectively, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane and all coupling constants are reported in Hz. IR spectra were obtained on a Perkin−Elmer 1600 series spectrometer.

Unless otherwise specified, all reagents were purchased from Aldrich Chemical Co. and used without further purification. Calcium diiodide was purchased from Strem Chemicals, Inc. 1,3-Ditolyltriazene was prepared by the literature method.[18]

Diethyl ether, THF, and dimethoxyethane (DME) were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was dried by refluxing over calcium hydride followed by distillation. Chloroform-d_1 (purchased form Cambridge Isotopes) was dried over calcium hydride and vacuum transferred.

X-ray Crystallographic Procedures. Crystals were isolated from the mother liquor and immediately immersed in paratone under a

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Table 1. Crystal Data and Structure Refinement Parameters for **1** and **2**

compound	**1**	**2**
empirical formula	$C_{36}H_{44}MgN_6O_2$	$C_{36}H_{48}CaN_6O_4$
fw	617.08	668.88
a (Å)	20.30(2)	27.62(2)
b (Å)	11.038(9)	7.681(5)
c (Å)	15.11(2)	22.30(2)
α (deg)		
β (deg)		127.74
γ (deg)		
V (Å^3)	3386(6)	3742(4)
Z	4	4
space group	*Pccn*	*C*2/*c*
T (°C)	−87	−86
radiation, λ (Å)	Mo Kα, 0.710 373	Mo Kα, 0.710 373
ρ(calcd) (g/cm^3)	1.210	1.187
μ (mm$^{-1)}$	0.093	0.212
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0629	R1 = 0.0423
	wR2 = 0.1625	wR2 = 0.1078
R indices (all data)	R1 = 0.0898	R1 = 0.0544
	wR2 = 0.1934	wR2 = 0.1179

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$.

nitrogen atmosphere in a drybox. A crystal was selected for the X-ray diffraction study and mounted in paratone on a quartz fiber and rapidly placed in a nitrogen gas cold stream of the cryostat of the Seimans P3/PC defractometer. The crystal was indexed, and data were collected at low temperature. Corrections for the effects of absorption anisotropy were made. Structure solutions were performed by direct methods, and structure refinement was done with the programs SHELXS and SHELXL.[25] Crystallographic parameters are given in Table 1, and selected bond distances and angles are provided in the figure captions.

Synthesis and Characterization of 1. Under a nitrogen atmosphere 1,3-ditolyltriazene (261 mg, 1.16 × 10^{-3} mol, 1.8 equiv) was stirred in 2 mL of THF at 23 °C. To this solution was added $MgBu_2$ (1.0 M in heptane, 0.64 mL, 0.64 × 10^{-3} mol, 1.1 equiv) dropwise over 5 m. On addition of the $MgBu_2$, the solution went from the gold color of the triazene to clear brown. After stirring for 1 h, the solvent was removed under reduced pressure. The resulting solid was dissolved in dichloromethane, and diethyl ether was diffused in at −25 °C. After 3 days, amber crystals formed which were isolated in 82% yield (293 mg, 9.52 × 10^{-4} mol, 82% based on triazene). Data for **1**: mp 165−169 °C (decomposition); ^1H NMR (200 MHz, −70 °C, $CDCl_3$) δ 7.34 (d, J = 8.2 Hz, 8H), 7.08 (d, J = 8.2 Hz, 8H), 3.84 (m, 8H), 2.17 (s, 12H), 1.78 (m, 8H) ppm; $^{13}C\{^1H\}$NMR (30 °C, $CDCl_3$) δ 150.0, 131.9, 129.7, 118.2, 69.2, 25.1, 20.7 ppm; IR ($CHCl_2$) 2923, 1607, 1505, 1474, 1458, 1341, 1298 (s), 1166, 1108, 1032, 827 cm^{-1}. Anal. Calcd for $C_{36}H_{44}MgN_6O_2$: C, 70.07; H, 7.19; N, 13.63. Found: C, 69.71; H, 7.28; N, 13.72.

Synthesis and Characterization of 2. Procedure 1: Under a nitrogen atmosphere the triazene (260 mg, 1.15 × 10^{-3} mol, 2 equiv) was dissolved in 3 mL of DME and stirred. To this golden colored solution was added solid KO-*t*-Bu (129.4 mg, 1.15 × 10^{-3} mol, 2 equiv) resulting in formation of a yellow precipitate. Solid CaI_2 (170 mg, 5,78 × 10^{-4} mol, 1 equiv) was added and the solution stirred for 2 days at 23 °C. Dichloromethane was added until most of the solids had dissolved, and the solution was filtered. Over a period of 1 week, large orange crystals of **2** grew which were suitable for an X-ray structural determination. The crystals were isolated by decanting the solvent and washing with DME (251 mg, 3.76 × 10^{-4} mol, 65%).

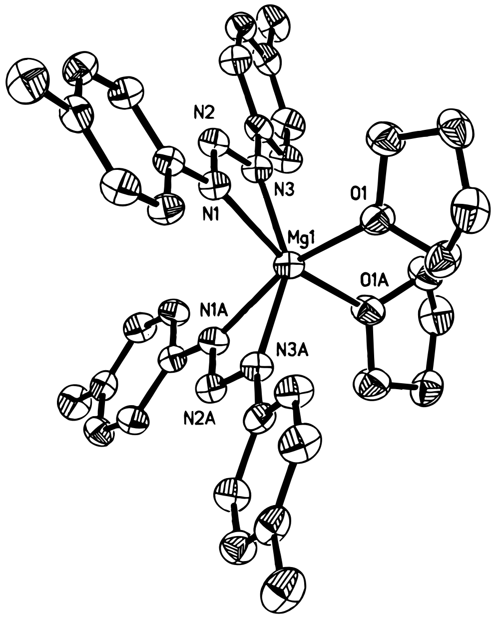
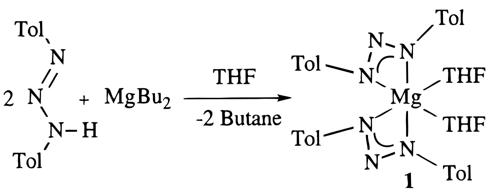


Figure 2. Molecular structure of **1** showing 50% probability ellipsoids. Important distances (Å) and angles (deg): Mg(1)−N(1) = 2.148(3), Mg(1)−N(2) = 2.663(3), Mg(1)−N(3) = 2.217(2), Mg(1)−O(1) = 2.091(2), N(1)−N(2) = 1.312(3), N(2)−N(3) = 1.318(3), N(1)−N(2)−N(3) = 109.2(2), N(1)−Mg(1)−N(3) = 58.78(9), N(1)A−Mg(1)−N(1) = 98.03(14), N(3)A−Mg(1)−N(3) = 148.31(13), O(1)A−Mg(1)−O(1) = 85.35(13), N(1)A−Mg(1)−O(1) = 161.13(8).

Procedure 2: Under a nitrogen atmosphere $LiN(SiMe_3)_2$ (210 mg, 1.26 × 10^{-3} mol, 2 equiv) was dissolved in 2 mL of DME and stirred at 23 °C. To this solution was added CaI_2 (184 mg, 6.27 × 10^{-4} mol, 1 equiv) as a solid. As the CaI_2 reacted, it dissolved. After stirring for 30 min all the CaI_2 had dissolved generating the calcium bis(amide) $Ca[N(SiMe_3)_2]_2(DME)_x$. Addition of 2 equiv of 1,3-ditolyltriazene (283 mg, 1.26 × 10^{-3} mol, 2 equiv) to the calcium bis(amide) resulted in the formation of an orange-brown solution. The reaction mixture was stirred for 30 min, during which time a precipitate formed. The solvent was removed under reduced pressure, and the resulting solid dissolved in dichloromethane and filtered. The solution was recrystallized by diffusing diethyl ether into the dichloromethane at −25 °C. The orange crystals which grew under these conditions were isolated in 91% (382 mg, 1.04 × 10^{-3} mol). Data for **2**: mp discoloration 125−145 °C; ^1H NMR (500 MHz, 30 °C, $CDCl_3$) δ 7.31 (d, J = 8.3 Hz, 8H), 7.02 (d, J = 8.3 Hz, 8H), 3.53 (s, 8H), 3.35 (s, 12H), 2.27 (s, 12H) ppm; ^{13}C-$\{^1H\}$NMR (125 MHz, 30 °C, $CDCl_3$) δ 150.5, 130.5, 129.3, 118.1, 71.2, 60.4, 20.8 ppm; IR ($CHCl_2$) 2923, 2833, 1604, 1502, 1296 (s), 1222, 1162, 1119, 1107, 1072, 1028, 865, 828 cm^{-1}. Anal. Calcd for $C_{36}H_{48}CaN_6O_4$: C, 65.88; H, 7.37; N, 12.80. Found: C, 64.49; H, 7.45; N, 12.47.

Results and Discussion

The magnesium bis(triazenide) complex (**1**) was prepared by the dropwise addition of $MgBu_2$ to a solution containing 2 equiv of the triazene in THF under a nitrogen atmosphere (eq 1). After 1 h, the resulting brown solution was evaporated to dryness under reduced pressure and was crystallized from dichloromethane/diethyl ether by vapor diffusion. Large orange crystals of **1** formed under these conditions and were isolated by decanting the solvent in 82% yield. Data for the structure determination were collected at −87 °C, and the structure was solved using standard techniques. An ORTEP diagram is shown in Figure 2 along with important bond distances and angles.



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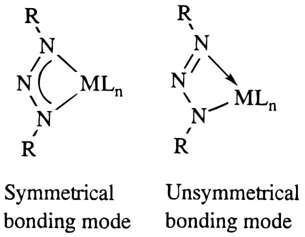


Figure 3.

The structure of **1** consists of two η^2-triazenide ligands and two molecules of THF bound to the magnesium. The geometry about the magnesium center is that of a distorted octahedron. The Mg(1)−N(1) distances is 2.148(3) Å while the Mg(1)−N(3) is significantly longer at 2.217(2) Å. It is not clear whether the cause of these differences is electronic or steric in origin. The N(1)−N(2) and the N(2)−N(3) distances are 1.312(3) and 1.318(3) Å, respectively. The differences in the N−N distances are not statistically significant since they are within 2 esd's of each other. The Mg−N and N−N distances indicate that the bonding might be best described as lying between the symmetrical and unsymmetrical bonding modes (Figure 3). The THF is bonded to the magnesium with a Mg(1)−O(1) distance of 2.091(2) Å.

The Mg−N distances of **1** can be compared with those of related compounds. The Mg−N distances of the bis(trimethylsilyl)amide complex Mg[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ are significantly shorter at 2.015(5) and 2.027(5) Å, while the Mg−O distances are at 2.086(5) and 2.101(5) Å.[24] The amidinate complex, [Ph(NSiMe$_3$)$_2$]$_2$Mg(NC−Ph) has also been structurally characterized. The Mg−N distances in the amidinate ligand were found to be 2.138(3) and 2.109(3) Å.[10] In both of these structures the amidinate ligand binds in a more symmetrical fashion to the metal center.

In contrast to the solid-state structure of **1**, which contains two types of tolyl groups, the ^{1}H and ^{13}C{^{1}H} NMR spectra at room temperature indicated that the tolyl groups are equivalent. Cooling the sample to −70 °C resulted in no change in the ^{1}H NMR spectrum. Several possible pathways for interconversion of the tolyl groups can be envisioned. Associative routes are unlikely since there is no excess THF in solution. A dissociative pathway involving formation of a five-coordinate intermediate which undergoes pseudorotation, however, seems reasonable. To examine this possibility, a solution of **1** containing two equivalents of THF was cooled to −70 °C. At this temperature, all of the peaks were sharp and only one set of resonances for the THF was observed. This indicates that bound and free THF are exchanging readily at this temperature.

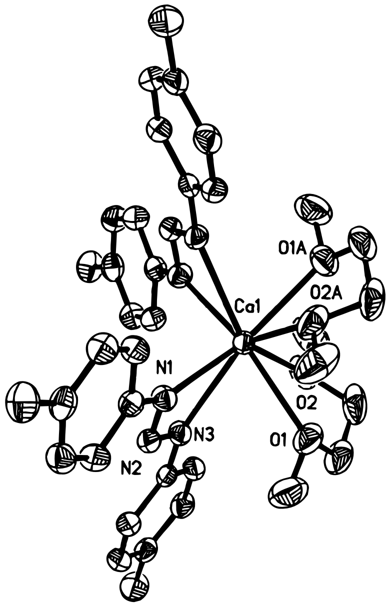
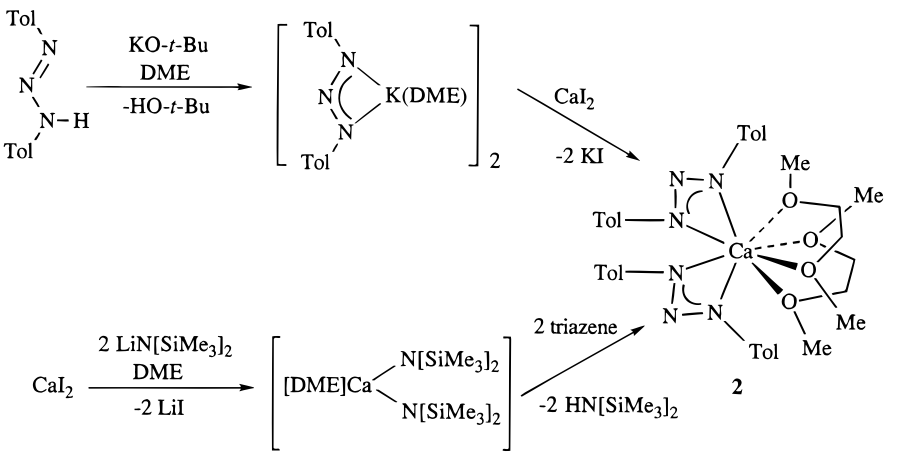


Figure 4. Molecular structure of **2** showing 30% probability ellipsoids. Important distances (Å) and angles (deg): Ca(1)−N(1) = 2.446(2), Ca(1)−N(2) = 3.028(2), Ca(1)−N(3) = 2.602(2), Ca(1)−O(1) = 2.561(2), Ca(1)−O(2) = 2.488(2), N(1)−N(2) = 1.318(2), N(2)−N(3) = 1.305(2), N(1)−N(2)−N(3) = 110.6(2), N(1)−Ca(1)−N(3) = 50.46(6), O(1)−Ca(1)−O(2) = 66.3(7).

The calcium triazenide complex [(Tol)NNN(Tol)]$_2$Ca(DME)$_2$ (**2**) was prepared by two methods (Scheme 1). The first involved metathesis with the potassium triazenide. The potassium triazenide can be readily prepared by deprotonation of the triazene with KO-*t*-Bu.[15] Reaction of this material with CaI$_2$ resulted in formation of the triazenide complex **2**. Crystallization of **2** from CH$_2$Cl$_2$ and ether provided orange crystals of **2** in 65% yield. The second route to **2** entailed the generation of the calcium bis(trimethylsilylamide). Rapid proton exchange between the silylamide and the triazene gave **2** in 91% yield.

X-ray-quality crystals were grown from CH$_2$Cl$_2$ at 23 °C and data was collected at −86 °C. An ORTEP drawing of **2** is shown in Figure 4. The structure is of eight-coordinate calcium with two η^2-triazenide ligands and two chelating DME solvent molecules. The triazenide ligands are bonded to the calcium in a very unsymmetrical fashion. The Ca(1)−N(1) and Ca(1)−N(3) distances are 2.446(2) and 2.602(2) Å, respectively. As found in **1**, the N−N distances of **2** are similar, but the

Scheme 1



difference is more pronounced in **2**. The N(1)−N(2) distance is 1.318(2) while the N(2)−N(3) distance is markedly shorter at 1.305(2) Å. The Ca−N and N−N distances indicate that the binding of the ligand to calcium also lies between the symmetrical delocalized structure and the unsymmetrical localized bonding mode (Figure 3). The DME ligands, which are crystallographically related, are bonded with distances of Ca(1)−O(1) and Ca(1)−O(2) of 2.561(2) and 2.488(2) Å, respectively. The Ca−N distances are longer than the Ca−N distances found in $Ca[N(SiMe_3)_2]_2(DME)$ (2.271(3) Å).[8] In the amidinate $[Ph(NSiMe_3)_2]_2Ca(THF)_2$, which has trans amidinate ligands,[11] the Ca−N distances are very similar at 2.424(4) and 2.438(2) Å while the Ca−O distances to the bound THF ligands are 2.388(3) and 2.370(3) Å, respectively.

In conclusion, we have developed a facile synthesis of triazenide complexes of magnesium and calcium and characterized them structurally. Both compounds have $[(Tol)NNN(Tol)]_2M(sol)_2]$ structures. In these complexes, the triazenide ligand binds to the metal in a less symmetrical manner than the related amidinate complexes. We are currently exploring the use of these compounds in metathesis reactions with transition metal halide complexes. Future work comparing metal triazenide complexes to the related amidinate complexes is in progress.

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Supporting Information Available: The characterization and X-ray crystal structure data for **1** and **2**, including tables of final atomic coordinates for the non-hydrogen atoms, anisotropic thermal parameters, complete list of bond distances and angles, and complete crystallographic data for the X-ray structures (17 pages). Ordering information is given on any current masthead page.

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