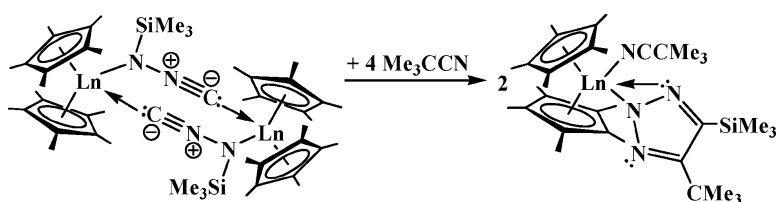


## Organolanthanide-Based Synthesis of 1,2,3-Triazoles from Nitriles and Diazo Compounds

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## Organolanthanide-Based Synthesis of 1,2,3-Triazoles from Nitriles and Diazo Compounds

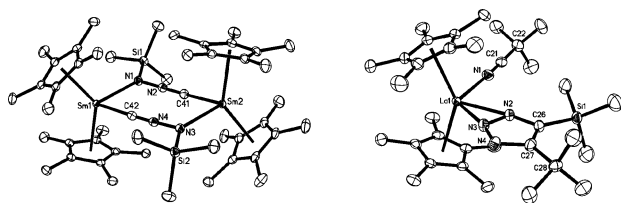
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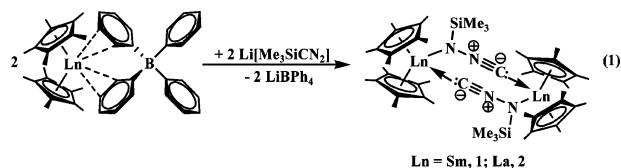
In contrast to the well documented reactivity studies of transition metals with diazoalkanes,  $RR'CN_2$ ,<sup>1–5</sup> the chemical reactivity of these substrates with lanthanides has not been extensively explored. A single paper in the literature describes spectroscopic data supporting the synthesis of  $(C_5Me_5)_2M[C(SiMe_3)N_2](THF)$  from  $Li[Me_3SiCN_2]$  and “ $(C_5Me_5)_2MCl$ ” ( $M = Y, Yb, Lu$ ) prepared in situ, but definitive crystallographic characterization and satisfactory elemental analysis of these complexes were not obtained.<sup>6</sup>

We report here our efforts to expand diazoalkane chemistry taking advantage of the special reactivity of the cationic metallocene complexes of the tetraphenylborate anion,  $[(C_5Me_5)_2Ln][(\mu-Ph)_2BPh_2]^-$ .<sup>7–11</sup> These complexes were chosen as precursors since the loosely ligated  $(BPh_4)^-$  anion is easily displaced by alkali metal reagents,  $MX$ , to make  $MBPh_4$  and unsolvated  $(C_5Me_5)_2MX$  moieties ( $X = \text{alkyl, azide}$ ).<sup>7–11</sup> With diazoalkanes, this has led to a new class of lanthanide metallocenes that react with nitriles to make 1,2,3-triazoles, ring systems that have pharmaceutical, industrial, and agrochemical applications.<sup>12</sup>

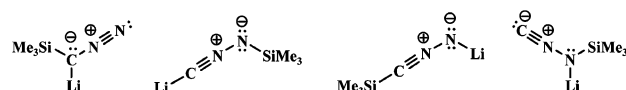


**Figure 1.** Thermal ellipsoid plots of (a)  $\{(C_5Me_5)_2Sm[\mu-N(SiMe_3)NC]\}_2$ , **1**, and (b)  $(C_5Me_5)_2La(NCCMe_3)[NNC(SiMe_3)C(CMe_3)N]$ , **4**, drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity.

The complexes  $[(C_5Me_5)_2Ln][(\mu-Ph)_2BPh_2]^-$  ( $Ln = Sm, La$ ) react with the salt obtained from  $tBuLi$  and  $Me_3SiCHN_2$  in hexane to form products formulated as isomorphous bimetallic isocyanotrimethylsilyl amide complexes,  $\{(C_5Me_5)_2Ln[\mu-N(SiMe_3)NC]\}_2$  ( $Ln = Sm, 1$ ;  $La, 2$ ), eq 1, on the basis of structural (Figure 1a) and reactivity data. This requires a 1,3-silyl migration from carbon to

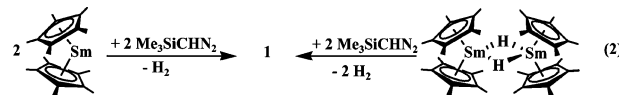


nitrogen if the lithium salt has a carbon-bound silyl group. Theoretical and experimental studies of these lithium salts show that several isomers are possible, Figure 2.<sup>13–15</sup> An N-bound silyl product,  $[(MeC_5H_4)TiCl(\mu-NSiMe_3)]_2$ , has been previously observed in the reaction of  $Li[Me_3SiCN_2]$  with  $(MeC_5H_4)TiCl_3$ .<sup>16</sup>



**Figure 2.** Possible isomers of the lithium salt of (trimethylsilyl)diazomethane,  $Li[Me_3SiCN_2]$ .

Since the 1,3-silyl migration could have occurred in the  $tBuLi/Me_3SiCHN_2$  reaction, direct routes to **1** from  $Me_3SiCHN_2$  were examined.  $Me_3SiCHN_2$  is reduced by divalent  $(C_5Me_5)_2Sm^{II}$  in benzene to form **1** and trivalent  $[(C_5Me_5)_2Sm(\mu-H)]_2^{III}$  also reacts with  $Me_3SiCHN_2$  to form **1**, eq 2.  $H_2$  is a byproduct in both reactions and the products of each reaction were fully characterized by X-ray crystallography. Again, silyl migration is required in eq 2.



Crystallographic studies on two different samples of both **1** and **2** indicated the N-bound structure shown rather than a C-bound structure,  $(C_5Me_5)_2Ln-C(SiMe_3)N_2$ , was present. This assignment was supported in all four structures by the Si–N bond length data. The 1.761(2)–1.7545(15) Å Si–N bond lengths in **1** and **2** are in the Si–N range<sup>19–22</sup> not in the 1.81–1.84 Å Si–C range.<sup>23–26</sup>

However, the bond lengths in **1** and **2** suggest that the resonance structure shown in eq 1 is not the only contributor to these complexes: a resonance form in which N(1) and N(3) have neutral donor character and C(41) and C(42) are anionic may also be involved, that is, formally  $Ln^+-N(SiMe_3)=N=C$ . For example, the 1.329(2) Å N(1)–N(2) and 1.327(2) Å N(3)–N(4) bond lengths in **1** are shorter than expected for a single bond (1.41–1.45 Å),<sup>22</sup> and the 2.498(2) and 2.475(2) Å Sm(1)–N(1) and Sm(2)–N(3) bond lengths are long compared to the 2.301(3) Å Sm–N bond length in  $(C_5Me_5)_2Sm[N(SiMe_3)_2]$ .<sup>20</sup> However, the 1.170(3) Å N(2)–C(41) and 1.168(3) Å N(4)–C(42) bond lengths are comparable to the corresponding average distances in bridged cyanide lanthanide metallocenes, 1.17(2) and 1.161(4) Å in  $[(C_5Me_5)_2Sm-(CNC_6H_{11})(\mu-CN)]_2^{27}$  and  $[(C_5Me_5)_2Sm(CNCMe_3)(\mu-CN)]_3^{28}$  respectively, and the 2.524(2) and 2.536(2) Å Sm(1)–C(42) and Sm(2)–C(41) bond lengths are within the broad 2.49(2)–2.64(2) Å range observed for Sm–(CN)/Sm–(NC) connections in the latter two compounds.<sup>29,30</sup>

The bond lengths observed in **1** and **2** could also arise if the crystals contained some amount of a  $Ln-C(SiMe_3)=N=N-Ln$  isomer.<sup>31</sup> In support of this possibility, a fifth crystallographically analyzed sample of **1** showed 1.823(2) and 1.837(2) Å  $Me_3Si$ -element bond lengths and refined slightly better with the trimethylsilyl group bound to carbon. Disordered models did not improve the refinements for the five samples. Interestingly, the IR spectra of both **1** and **2** had two absorptions in the multiple bond region. The most prominent absorptions for **1** and **2** are at 1974

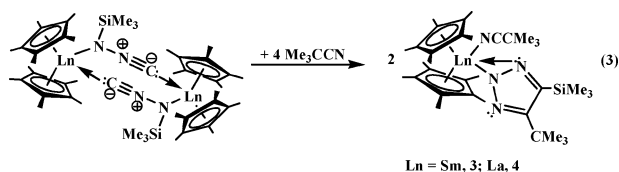
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and 1970  $\text{cm}^{-1}$ , respectively, but substantial bands at 2057 and 2063  $\text{cm}^{-1}$  are also observed. However, neither variable temperature NMR studies nor an 800 MHz  $^1\text{H}$  NMR spectrum showed evidence of two  $(\text{C}_5\text{Me}_5)^{-}$  resonances.

To obtain additional derivatives of **1** and **2** for structural characterization, recrystallization in the presence of coordinating solvents was attempted. Surprisingly, **1** and **2** also crystallize from THF, that is, the bridging arrangement shown in Figure 1 is preferred over formation of a monomeric THF adduct. However, examination of nitriles as coordinating solvents gave a very different result with these complexes.

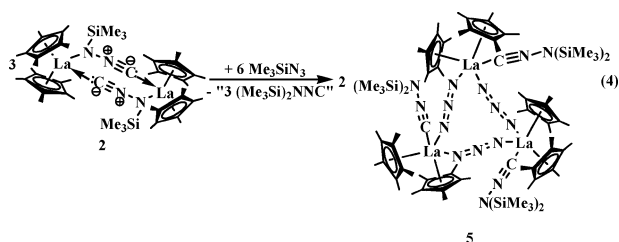
Complexes **1** and **2** react with nitriles to make products containing triazole rings. Reactivity is observed with acetonitrile, but crystal quality precluded definitive identification of the products. However,  $\text{Me}_3\text{CCN}$  reacts with **1** and **2** to form isomorphous 1,2,3-triazolato complexes  $(\text{C}_5\text{Me}_5)_2\text{Ln}(\text{NCCMe}_3)$  [ $\text{NNC}(\text{SiMe}_3)\text{C}(\text{CMe}_3)\text{N}$ ] ( $\text{Ln} = \text{Sm}$ , **3**;  $\text{La}$ , **4**), eq 3, that could be fully characterized by X-ray crystallography, Figure 1b. The data clearly show the heterocycle as a 1,2,3-triazole, a result that once again requires silyl migration if **1** and **2** have silyl groups bound to N and not C.



Details of the mechanism of the formation of the triazolato complexes **3** and **4** from  $\{(\text{C}_5\text{Me}_5)_2\text{Ln}[\mu\text{-N}(\text{SiMe}_3)\text{NC}]\}_2$  are unknown, but the overall reaction likely involves a 1,3-dipolar cycloaddition.<sup>32</sup> Alkali metal salts of diazoalkanes are known to form heterocycles through unusual mechanisms.<sup>13,33</sup> Bond lengths in the 1,2,3-triazolato ligands in **3** and **4** are consistent with delocalization of the double bonds shown in the resonance structure in eq 3.

The 1,2,3-triazolato ligands have their closest attachment to the  $\text{Ln}^{3+}$  ions through N(3), 2.368(5) Å in **3** and 2.472(2) Å in **4**, a difference consistent with the larger radius of  $\text{La}^{3+}$ .<sup>30</sup> The  $\text{Ln}-\text{N}(2)$  bond lengths are longer, which is consistent with more donor bond character, and the  $\text{Ln}-\text{N}(1)$  bond lengths, 2.518(6) in **3** and 2.645(2) Å in **4**, are the longest for this purely neutral donor nitrile. The 1.859(7) and 1.862(2) Å  $\text{C}(26)-\text{Si}(1)$  bond lengths in **3** and **4**, respectively, match the range expected for  $\text{C}-\text{Si}$  bonds.<sup>22</sup>

To probe this system further, the reaction of  $\text{Me}_3\text{SiN}_3$  with **2** was examined. A trimeric azide product was obtained,  $\{(\text{C}_5\text{Me}_5)_2\text{La}[\text{CNN}(\text{SiMe}_3)_2](\mu\text{-N}_3)\}_3$ , **5**, eq 4, as an adduct of an isocyanide  $(\text{Me}_3\text{Si})_2\text{NNC}$  generated in the course of the reaction. The isolation of  $(\text{Me}_3\text{Si})_2\text{NNC}$  rather than  $(\text{Me}_3\text{Si})_2\text{CN}_2$  supports the assignment of N-bound  $\text{Me}_3\text{Si}$  in **2**.



In summary, diazoalkanes are viable reagents not only for the transition metals, but also for the f elements. As expected, the

special nature of the f elements will lead to different reactivity patterns, which is one of the important reasons to study these metals.

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**Supporting Information Available:** Synthetic, spectroscopic, and X-ray diffraction details (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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