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## *In crystallo* homolytic cleavage of a terminal lanthanum(III)–methyl bond by Cu K $\alpha$ X-radiation forms a La(II) complex<sup>†</sup>

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A new method for generating La(II) complexes is described in which irradiation of single crystals of the La(III) terminal methyl complex La(SAr<sup>iPr6</sup>)<sub>2</sub>CH<sub>3</sub>, Ar<sup>iPr6</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>, with Cu K $\alpha$  X-rays (50 W, 8.04 keV/1.540 Å) during SCXRD experiments results in the homolytic cleavage of the La–C<sub>methyl</sub> bond and formation of the La(II) complex La(SAr<sup>iPr6</sup>)<sub>2</sub>.

The ability of single crystal X-ray diffractometry (SCXRD) to accurately determine the position and identity of every atom within a crystalline solid has rendered this technique the gold standard of structural determination in both small molecule and macromolecular chemistry<sup>1,2</sup> although the technique is not infallible.<sup>3,4</sup> The last several decades have seen major technological advances in X-ray generation and data acquisition, including cryogenic data collection and the use of large area CCD and CMOS detectors. These advances have allowed SCXRD, once a very time consuming and expensive technique, to become an analytical method of *first* resort in many laboratories.<sup>5</sup>

By collecting data at cryogenic temperatures and reducing the time that samples are exposed to X-rays, these same advances have also significantly lowered the degree to which crystalline samples are damaged by X-radiation. SCXRD is thus often assumed to be an essentially innocent probe of molecular structure when examining small molecule species, although X-ray damage is frequently observed in macromolecular SCXRD when high brilliance synchrotron X-ray sources are used.<sup>6,7</sup> However, a recent review<sup>8</sup> has summarized a growing body of research involving transformations in single crystals that can be induced by X-rays, which include crystalline phase transitions, redox isomerism,<sup>9</sup> transitions

between low-spin and high-spin electronic configurations in organometallic complexes,<sup>10</sup> and even racemization through cleavage and reformation of chemical bonds.<sup>11</sup> A more general review has also appeared which describes several additional means by which single-crystal-to-single-crystal transformations of molecular species may take place.<sup>12</sup> Thus, there is high potential for X-radiation to be more widely used not only as an analytical tool for crystalline materials, but also as a means to induce chemical changes in single crystals. However, more data are required in order to develop this into a practical technique that may be used in the laboratory.

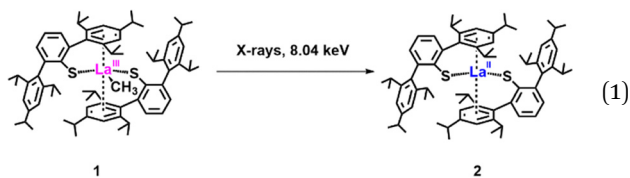
We report here the use of SCXRD to generate a highly reactive complex of La(II). This method of synthesis was discovered as part of a general effort to access rare-earth complexes in the +2 oxidation state beyond the traditional Ln(II) complexes of Eu, Yb, Sm, Tm, Dy, and Nd, which have 4f<sup>n+1</sup> electron configurations, to the other metals in the series that have Ln(II) ions with 4f<sup>n</sup>5d<sup>1</sup> configurations.<sup>13–17</sup> Specifically, we have been exploring the use of the terphenylthiolate ligand (SAr<sup>iPr6</sup>)<sup>1-</sup>, Ar<sup>iPr6</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>, that was originally developed by Power and coworkers to isolate stable low valent and low coordination number thiolate complexes of the main group and transition elements.<sup>18–20</sup> To this end, we have recently expanded upon Niemeyer's synthesis of the Ln(SAr<sup>iPr6</sup>)<sub>2</sub> complexes of Eu,<sup>21</sup> Yb<sup>21</sup> and Sm<sup>22</sup> to generate a complex of La(II) with sulfur donor atoms, namely, La(SAr<sup>iPr6</sup>)<sub>2</sub>.<sup>17</sup>

Parallel studies of the rare-earth metal chemistry of the (SAr<sup>iPr6</sup>)<sup>1-</sup> ligand have allowed the isolation of the rare terminal methyl complex, La<sup>III</sup>(SAr<sup>iPr6</sup>)<sub>2</sub>CH<sub>3</sub>, **1**.<sup>23</sup> During the course of this research, a SCXRD structural study of **1** revealed that it undergoes a transformation to form the La(II) complex La<sup>II</sup>(SAr<sup>iPr6</sup>)<sub>2</sub>, **2**, when the single crystals are exposed to Cu K $\alpha$  radiation, eq 1. In contrast, the molecular structure of **1** can be determined without inducing this transformation when Mo K $\alpha$  radiation is used. The details of this new Ln(II) synthesis are

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<sup>†</sup> The authors dedicate this work to the memory of Professor Marilyn M. Olmstead, an icon in structural chemistry.

reported here since it provides an option to generate new highly reactive oxidation states.



A routine attempt to collect structural data for the methyl complex **1** at a temperature of 100 K using Cu K $\alpha$  radiation (8.04 keV/1.540 Å,  $1.1 \times 10^{11}$  photon s $^{-1}$  mm $^{-2}$ ) from a recently obtained high intensity Bruker I $\mu$ S DIAMOND II source resulted in an observable color change of the single crystal sample from pale yellow before data acquisition to dark brown after a 5 h experiment, Fig. 1. Since most complexes of La(III) are pale in color and exposure of samples of **1** to air results in a material that is likewise pale in color, this transformation could not arise from oxidative or hydrolytic decomposition. Additionally, when a crystal of the methyl complex **1** was held for 12 h in the cold nitrogen stream of the diffractometer without exposure to X-radiation, no change to the crystal was observed. After this period, the data collected using Mo K $\alpha$  radiation showed that its structure remained unchanged which indicated that the change was apparently due to the Cu K $\alpha$  radiation.

The structural model obtained from the Cu K $\alpha$  data, Fig. 2, was at variance with the structure of **1** that had been determined previously using Mo K $\alpha$  radiation.<sup>23</sup> Specifically, when freely refined, the occupancy of the terminal methyl carbon bound to the lanthanum atom was determined to be only 87% of that expected. Additionally, the lanthanum atom was found to be disordered over two sites, with the minor component located further from the methyl carbon than the major component. These data, along with the color change that was observed after data collection, suggested that these structural discrepancies may not have been due to simple crystallographic disorder, but that **1** may have undergone a chemical change induced by Cu K $\alpha$  X-rays. To probe this, the 5 h data collection protocol was repeated three additional times (for a total of 20 h of irradiation over four experiments) in order to monitor any changes to the structure.

As shown in Table 1, the occupancy of the terminal methyl carbon became lower with each subsequent data collection, while that of the minor component of the disordered lanthanum atom increased. Additionally, severe disorder became

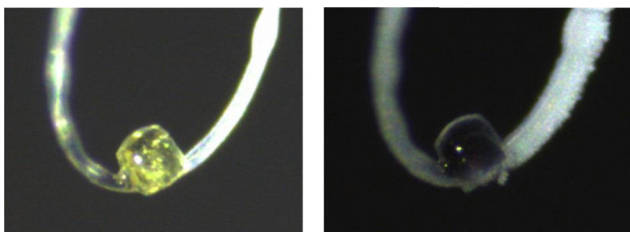


Fig. 1 Left: Image of a single crystal of La<sup>III</sup>(SAr<sup>iPr</sup>R<sup>6</sup>)<sub>2</sub>CH<sub>3</sub>, **1**, before data collection. Right: Image of the same crystal after a 5 h data collection using 50 W Cu K $\alpha$  X-rays.

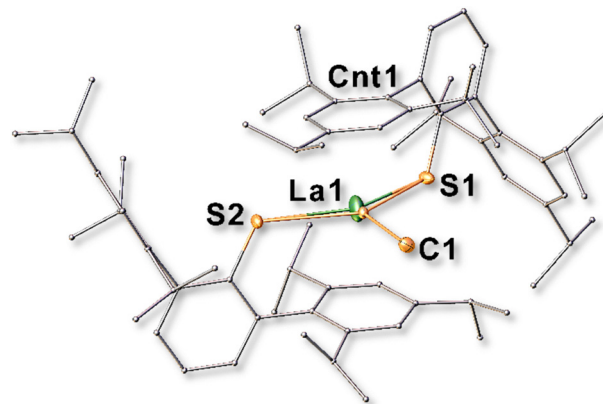


Fig. 2 Results of refinement on a crystal of La<sup>III</sup>(SAr<sup>iPr</sup>R<sup>6</sup>)<sub>2</sub>CH<sub>3</sub>, **1** (orange), after a 5 h data collection. The occupancy of the methyl carbon C1 and the La atom to which it is bound is 87%. The second La1 (green) has a site occupancy of 13%. Carbon atoms common to both species are colored in grey. Hydrogen atoms are not shown. Selected thermal ellipsoids are drawn at 30% probability. "Cnt1" denotes the centroid of the indicated flanking C<sub>6</sub> ring.

Table 1 Occupancies of the La and C<sub>methyl</sub> atoms in **1** compared with the occupancy of the La atom of **2** over 20 h of irradiation with Cu K $\alpha$  X-rays

Experiment	La/C <sub>methyl</sub> occupancy (1)	La occupancy (2)
1 (5 hours)	0.87	0.13
2 (10 hours)	0.78	0.22
3 (15 hours)	0.65	0.35
4 (20 hours)	0.53	0.47

apparent in one of the flanking arene rings of the ligand that is oriented toward the lanthanum atom as shown in Fig. 3. This is consistent with the structure of **2**,<sup>17,24</sup> wherein one flanking ring of a ligand is situated closer to the La atom and displays significant distortion from planarity as a result of a  $\delta$  bonding

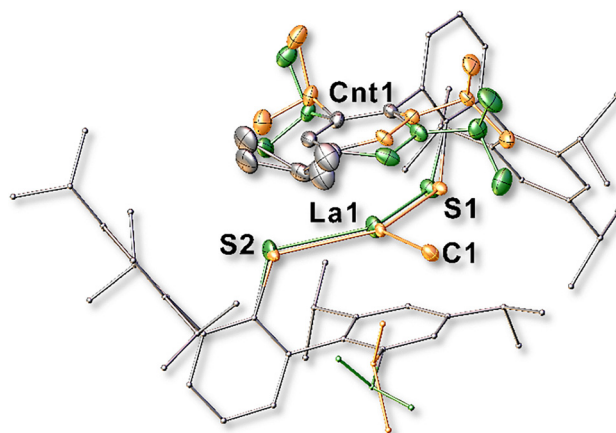


Fig. 3 Results of refinement on the same crystal of La<sup>III</sup>(SAr<sup>iPr</sup>R<sup>6</sup>)<sub>2</sub>CH<sub>3</sub>, **1** (orange), as in Fig. 2 after 20 h of irradiation showing La<sup>II</sup>(SAr<sup>iPr</sup>R<sup>6</sup>)<sub>2</sub>, **2** (green), which has formed. Selected thermal ellipsoids are drawn at 20% probability. Hydrogen atoms are not shown. Carbon atoms that are common to both species are colored in grey. The occupancy of the **1** component is 53%, while the occupancy of the **2** component is 47%. "Cnt1" denotes the centroid of the indicated flanking C<sub>6</sub> ring.

interaction between La and the C<sub>6</sub> ring. Similar annular distortions have been reported for the terphenylamide analogues of other f block elements.<sup>25,26</sup> In contrast, the La atom of **1** is located symmetrically between two flanking arene rings that each have a planar geometry.<sup>23</sup>

When **2** was synthesized from La<sup>III</sup>(SAr<sup>iPr6</sup>)<sub>2</sub>I by reduction with KC<sub>8</sub>, it crystallized in the space group *P* $\bar{1}$ .<sup>17</sup> However, when **2** is generated by X-irradiation in a crystal of **1** it retains the *C2/c* space group of **1** and only minor changes to the lattice constants were observed: after 5 h and 20 h of irradiation, the cell dimensions are, respectively, *a* = 21.1778(1) and 21.0895(8) Å, *b* = 18.236(1) and 18.2926(6) Å, *c* = 36.081(2) and 36.191(2) Å,  $\beta$  = 91.179(2) and 92.017(2).

Using the structural data from the crystal irradiated for 20 h, the structures of **1** and **2** reported here may be compared with the structures of the pure species reported previously.<sup>17,23</sup>

Selected structural metrics are listed in Table 2. Although two species are present in the crystal after irradiation and minor increases in the residuals of the structural model were observed after irradiation (5 h: *R*<sub>1</sub> = 0.0456, *wR*<sub>2</sub> = 0.1096, *R*<sub>int</sub> = 0.0602; 20 h: *R*<sub>1</sub> = 0.0699, *wR*<sub>2</sub> = 0.1638, *R*<sub>int</sub> = 0.0686), the structural metrics of the two sets of compounds are in good agreement. The La atom in **2** is situated asymmetrically between two flanking C<sub>6</sub> rings of the ligands due to the  $\delta$  bonding interaction between the metal and one flanking ring, and the variation of these distances between the two structures of **2** is probably a consequence of the incomplete occupancy of **2** in the structure reported here.

To demonstrate the reproducibility of this transformation and to attempt to effect complete conversion of **1** to **2** by radiolysis, additional experiments were performed on other crystals of **1**. In one case, the crystal used had been stored under an atmosphere of argon in the absence of solvent for approximately 7 months at a temperature of 238 K, which indicates that crystals of **1** are stable toward the formation of **2** over extended periods of time. The crystal structure was first determined using Mo K $\alpha$  radiation to establish the identity and quality of the crystalline material. These data were of good quality (*I*/ $\sigma$  = 18.1, *R*<sub>1</sub> = 0.0387, *wR*<sub>2</sub> = 0.0910) and the freely refined occupancy of the methyl carbon was found to be 0.995(7). No residual electron density was found in the difference map that indicated a second site occupied by La. Then, ten datasets using Cu K $\alpha$  X-rays were collected with an exposure time of 5 h and 12 min per dataset. The results of this set of experiments are summarized in Table 3. Ultimately, these data are consistent with the findings from the previous set of experiments shown in Table 2. We note that after *ca.* 40 h of

**Table 2** Selected bond distances (Å) in isolated samples of **1**<sup>23</sup> and **2**<sup>17</sup> compared with those determined from the crystal data obtained after irradiation of **1** with Cu K $\alpha$  for 20 h

	La-S	La-C <sub>methyl</sub>	La-C <sub>int</sub>
<b>1</b> , isolated	2.8488(7), 2.8545(7)	2.514(3)	2.802(1), 2.818(1)
<b>1</b> , 20 h Cu K $\alpha$	2.852(4), 2.853(8)	2.544(9)	2.767(3), 2.781(2)
<b>2</b> , isolated	2.805(3), 2.810(2)	—	2.524(4), 2.808(4)
<b>2</b> , 20 h Cu K $\alpha$	2.809(7), 2.82(1)	—	2.640(5), 2.745(3)

**Table 3** Occupancies of the La and C<sub>methyl</sub> atoms in a second crystal of **1** compared with the occupancy of the La atom of **2** over 41 h and 36 min of irradiation with Cu K $\alpha$  X-rays

Experiment	La/C <sub>methyl</sub> occupancy (1)	La occupancy (2)	<i>wR</i> <sub>2</sub>
1 (5 h 12 min)	0.93	0.07	0.0790
2 (10 h 24 min)	0.77	0.23	0.1095
3 (15 h 36 min)	0.65	0.35	0.1428
4 (20 h 48 min)	0.50	0.50	0.1491
5 (26 h)	0.43	0.57	0.1619
6 (31 h 12 min)	0.36	0.64	0.1915
7 (36 h 24 min)	0.31	0.69	0.2039
8 (41 h 36 min)*	0.25*	0.75*	0.2095

\* Note: the high-angle reflections of experiment 8 are of low intensity and many frames were excluded from the integration in order to generate a stable model. Two further experiments were run after experiment 8, but meaningful conclusions cannot be made from these due to the poor data quality.

irradiation with Cu K $\alpha$  X-rays, the quality of the diffraction data becomes quite poor. However, good quality data were obtained which showed about 75% conversion of **1** to the La(II) species **2** by radiolysis over 40 h. We also note that there was no apparent evidence of a phase transition in the data arising from these later experiments (see SI).

To the best of our knowledge, the reduction of the La(III) complex **1** with concomitant cleavage of a metal-alkyl bond to form the La(II) complex **2** appears to be a reaction without precedent, *in crystallo* or otherwise, among the rare-earth elements apart from the more easily reduced Ln(III) complexes of Sm, Eu, and Yb. For example, homolysis of the Yb-CH<sub>3</sub> bond in [Cp<sup>Me</sup><sub>2</sub>Yb<sup>III</sup>CH<sub>3</sub>]<sub>2</sub> occurs thermally and photolytically to form the polymeric Cp<sup>Me</sup><sub>2</sub>Yb<sup>II</sup> (Cp<sup>Me</sup> = C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>).<sup>27</sup> Eu(III) and Yb(III) amides have also been reported to undergo homolysis of a Ln-N  $\sigma$  bond to form Ln(II) complexes.<sup>28,29</sup> This is in contrast to the chemistry of the transition elements, where there are many examples of light- or thermally-induced homolysis of metal-alkyl bonds<sup>30</sup> including the conspicuous examples of methylcobalamin and its synthetic models.<sup>31-33</sup> We also note that recent work by Schelter and coworkers has described the *in crystallo* ring-opening isomerization of a cerium cyclopropenyl complex, the progress of which was monitored by SCXRD.<sup>34</sup> However, the authors do not attribute this transformation to radiolysis.

Thus, the finding reported here is particularly striking in view of the rarity of Ln(II) complexes beyond those of Sm, Eu, and Yb. While the structural data do not point to a particular mechanism for this reaction, homolysis of the La-C<sub>methyl</sub> bond in **1** is plausible when considering that damage to crystalline samples by X-irradiation is typically the result of the generation of radical species that form upon absorption of X-rays.<sup>7,8,35</sup> Indeed, perhaps the most comparable reactivity to that reported here is the X-ray induced racemization of a single crystal of a cobaloxime complex wherein the bond between cobalt and a chiral alkyl ligand is homolytically cleaved and then reformed with inversion of stereochemistry.<sup>11,36</sup> Oxidation of Co(II) to Co(III) with concomitant reduction of a ligand has also been observed in an organometallic complex.<sup>10</sup> We note that methane or ethane are the most plausible byproducts of the transformation of **1** to **2** by radiolysis. However, our

attempts to detect the generation of these byproducts *in situ* during experiments in solution and in the solid state in sealed vessels have to date been unsuccessful.

In summary, collection of SCXRD data with Cu K $\alpha$  radiation on La<sup>III</sup>(SAr<sup>iPr6</sup>)<sub>2</sub>CH<sub>3</sub>, **1**, has shown a new approach to the synthesis of Ln(II) complexes. Although this is not yet a viable synthetic method, since the Ln(II) product, La(SAr<sup>iPr6</sup>)<sub>2</sub>, **2**, is formed as a mixture with **1**, it does provide a new route that may be used to identify the new Ln(II) complexes that may be unstable in solution. This could be particularly useful for complexes of low stability, since the Ln(II) complex is not exposed to solvent and reactants by being trapped in the crystalline lattice of the host. Hence, extended data collection experiments on other Ln(III)-methyl complexes should be examined to determine if Ln(II) compounds can be generated and trapped in the crystal structure of the Ln(III) host. We are currently engaged in examining this possibility.

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## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cc04945h>.

CCDC 2481278 (5 h), 2481280 (10 h), 2481281 (15 h), and 2481282 (20 h) contain the supplementary crystallographic data for the first set of crystallographic experiments.<sup>37a-d</sup> CCDC 2495757 (Mo K $\alpha$ ), 2495762 (Cu K $\alpha$ , 5 h 12 min), 2495763 (Cu K $\alpha$ , 10 h 12 min), 2495764 (Cu K $\alpha$ , 15 h 36 min), 2495765 (Cu K $\alpha$ , 20 h, 48 min), 2495766 (Cu K $\alpha$ , 26 h), 2495767 (Cu K $\alpha$ , 31 h 12 min), 2495768 (Cu K $\alpha$ , 36 h 24 min), 2495769 (Cu K $\alpha$ , 41 h, 36 min) contain the supplementary crystallographic data for the second set of crystallographic experiments.<sup>38a-i</sup>

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