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## CO homologation and isocyanide activation by a trisilyl alane radical anion

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**We report the divergent reactivities of a trisilyl-substituted alane and its radical anionic species towards isocyanides and carbon monoxide. While the neutral Al(III) species forms coordination complexes, the Al(II) radical promotes cyanide formation. Notably, the radical anion mediates CO homologation to yield a C<sub>3</sub> fragment, which provides new insight into main-group CO homologation.**

In recent decades, organoaluminium compounds have attracted considerable attention owing to their pronounced reactivity toward small molecules and their key roles in catalysis using earth-abundant elements.<sup>1–6</sup> Organoalanes containing an Al(III) center have been extensively studied in this research field. Previously, coordination products of several trialkyl- and triaryl-substituted organoalanes with isocyanides as well as the double insertion product of tri-*tert*-butyl isocyanide into an Al–C bond in AlCp'<sub>3</sub> (Cp' = C<sub>3</sub>Me<sub>4</sub>H) were isolated and characterized (A–J, Fig. 1a).<sup>7–9</sup> The carbon monoxide insertion of tri-*tert*-butylalane was also reported (K, Fig. 1a).<sup>10</sup> In comparison with trialkylalanes, trisilyl-alanes remain largely unexplored and have attracted considerable research interest due to the steric shielding and electron-donating capabilities of silyl substituents.<sup>11,12</sup> Since the first trisilyl-alane, Al(SiMe<sub>3</sub>)<sub>3</sub>, was synthesized in 1980, several alanes with bulkier silyl substituents have been reported.<sup>13–16</sup> Notably, *via* the reduction of Al(Si<sup>*t*</sup>Bu<sub>2</sub>Me)<sub>3</sub> (**1**) with elemental alkali metal, Sekiguchi's group isolated the mononuclear Al(II) radical anion [Al<sup>•</sup>(Si<sup>*t*</sup>Bu<sub>2</sub>Me)<sub>3</sub>]<sup>–</sup> [M]<sup>+</sup> (**2**[M], M = K, Na, Li, Fig. 1b).<sup>15</sup> To the best of our knowledge, no small molecule activation of trisilyl-alanes has been reported so far. Recent studies have shown that organoaluminium compounds can activate carbon monoxide towards C–O triple bond cleavage and C–C bond coupling.<sup>3,17–21</sup> This research domain has attracted great research interest as CO is both a key component of the Fischer-Tropsch process and an essential C<sub>1</sub> building block of many complex molecules.<sup>22,23</sup> CO homologation of transition metal

carbonyl compounds by Al(I) compounds has been reported.<sup>17,19</sup> Anionic aluminium imide complexes have been shown to be able to incorporate multiple CO molecules, forming C<sub>2</sub>, C<sub>4</sub> or C<sub>6</sub> chains (I and II, Fig. 1c).<sup>18,21</sup> In addition, reduction of CO to a C<sub>4</sub> chain by an alumanyl anion has been demonstrated (III, Fig. 1c).<sup>20</sup> More recently, our group reported CO homologation mediated by a neutral alumene (IV, Fig. 1c).<sup>3</sup> Herein, we report the reactivity of Al(Si<sup>*t*</sup>Bu<sub>2</sub>Me)<sub>3</sub> (**1**) and its radical anion **2**[K] toward CO and its isoelectronic analogues, isocyanides (Fig. 1d). Various isocyanide complexes (**3–6**) and a CO homologation product (**7**) were isolated and characterized.

The isocyanide trisilyl-alane complexes **3–5** were prepared by stirring the isocyanide with Al(Si<sup>*t*</sup>Bu<sub>2</sub>Me)<sub>3</sub> (**1**) at room temperature in a solution of toluene (Scheme 1). Colorless crystals of compounds **3–5** suitable for single crystal X-ray diffraction (scXRD) analysis were grown from the saturated pentane solution at –30 °C. Although the poor quality of the molecular structure data for **3** precluded detailed structural analysis, molecular connectivity could still be established (Fig. S22, SI). Comprehensive structures of **4** and **5** are shown in Scheme 1. The C1–Al1 coordination bonds in **4** and **5** (2.093(1) and 2.086(2) Å) are longer than those of isocyanide triarylalane complexes and shorter than those of isocyanide trialkyl complexes.<sup>7,8</sup> The N1–C1–Al1 skeleton in complex **5** is nearly linear with an angle of 177.3(2)°, while complex **4** shows a more bent structure (169.93(9)°).

We also explored the reactivity of radical anion **2**[K] with isocyanides. Interestingly, reactions of compound **2**[K] with different isocyanides afforded the same complex **6** along with the cleavage of the R–NC single bond (Scheme 2). The loss of <sup>*t*</sup>Bu as isobutylene, *m*-xylyl as *m*-xylene, and adamantyl as adamantane was corroborated by <sup>1</sup>H NMR spectroscopy (Fig. S14–S16, SI). Crystals of **6** were obtained by storing its pentane solution at –30 °C for several days. Due to the high symmetry of the structure, a full refinement was not achieved. Nevertheless, the bonding arrangement could still be determined (Fig. S25, SI). The C–N bond cleavage and CN<sup>–</sup> ion generation in the reactions of other organoaluminium compounds with <sup>*t*</sup>BuNC were observed in previous studies.<sup>24–26</sup> Similar reactivity has also been noted for other

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Moreover, CO homologation mediated by **2**[K] was demonstrated. Bicyclic compound **7** featuring a C<sub>3</sub> chain was fully characterized. Taken together, the silyl-substituted Al(III) species **1** and Al(II) species **2**[K] show promising potential in small molecule activation, and further studies on silyl-substituted aluminium compounds are ongoing in our research group.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included in the supplementary information (SI). Supplementary information: experimental procedures and spectra. See DOI: <https://doi.org/10.1039/d6cc02324j>.

CCDC 2543012 (**4**), 2543016 (**5**) and 2543019 for (**7**) contain the supplementary crystallographic data for this paper.<sup>31a-c</sup>

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