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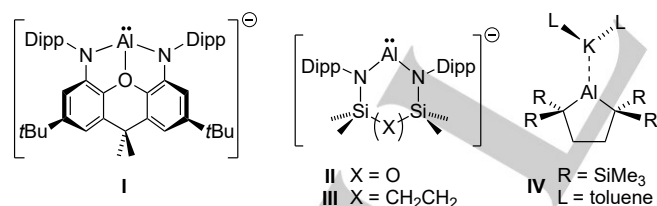
# New Carbon-Carbon Bond Forming Reactions Promoted by Alumanyl and Alumoxane Anions: Introducing the Ethenetetraolate Ligand

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**Abstract:**  $[K\{Al(NON^{Dipp})\}]_2$  ( $NON^{Dipp} = [O(SiMe_2NDipp)_2]^{2-}$ ,  $Dipp = 2,6\text{-}iPr_2C_6H_3$ ) reacts with  $CS_2$  to afford the trithiocarbonate species  $[K(OEt_2)[Al(NON^{Dipp})(CS_3)]$  **1** or the ethenetetrathiolate complex,  $[K\{Al(NON^{Dipp})(S_2C)\}]_2$  **3**. The dimeric alumoxane  $[K\{Al(NON^{Dipp})(O)\}]_2$  reacts with carbon monoxide to afford the oxygen analogue of **3**,  $[K\{Al(NON^{Dipp})(O_2C)\}]_2$  **4** containing the hitherto unknown ethenetetraolate ligand,  $[C_2O_4]^{4-}$ .

The elaboration of  $C_1$  sources (e.g. CO,  $CO_2$ ,  $CS_2$ ) into more complex molecular species is of fundamental interest to the scientific community.<sup>[1]</sup> Coupled with the advantage of upgrading the economic value of these reactants, the requirement for innovative solutions that mitigate the consequences of releasing such volatile compounds into the environment requires urgent attention. The development of new carbon-carbon bond forming reactions that efficiently functionalize these feedstocks is essential. However, this is challenging as stable carbon-heteroatom bonds must be activated, a role that has traditionally fallen to d- and f-block elements. A more beneficial approach is to use terrestrially abundant, less environmentally impactful main group elements. Towards this goal, the chemistry of the p-block metals has been advanced such that their chemical behaviour can mimic certain characteristics typically associated with the transition metals.<sup>[2]</sup>

A new class of alumanyl anion that shows a rich chemistry for the activation of small molecules has recently been discovered (**I**)



**Figure 1.** The current family of anionic alumanyl species

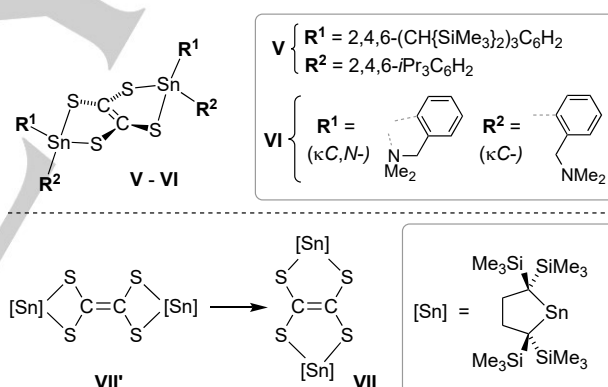
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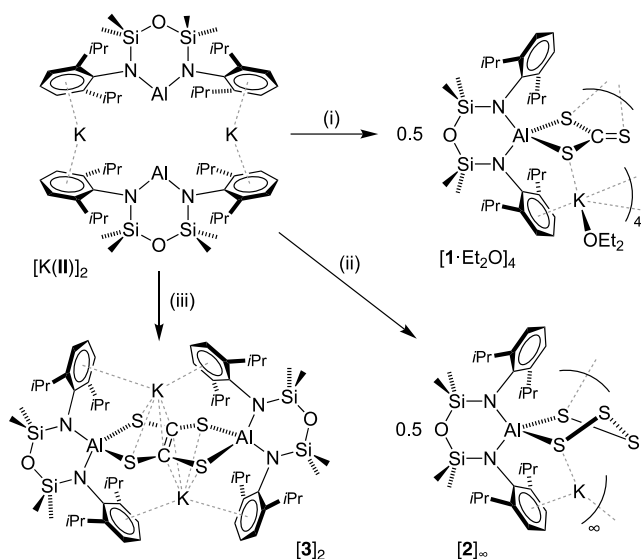
– **IV**, Fig. 1).<sup>[3]</sup> Examples of reactivity include the rupture of aromatic C-H,<sup>[3a,3c,4]</sup> and C-C<sup>[4]</sup> bonds, heterolytic cleavage of  $H_2$ ,<sup>[3a]</sup> extrusion of CO from  $CO_2$  and  $N_2$  from  $N_2O$ ,<sup>[5]</sup> and C-X bond activation ( $X = Cl, F$ ).<sup>[3c]</sup> However, the potential of these compounds to use small molecules as building blocks to construct more complex systems by forming new bonds is relatively under developed.

In this contribution we show that  $K[Al(NON^{Dipp})]$  (**K[III]**) promotes reductive coupling of organic fragments to form new carbon-carbon (double) bonds. We first discovered this using carbon disulfide, producing a complex containing the ethenetetrathiolate anion,  $[C_2S_4]^{4-}$ . This transformation has been observed using low oxidation state transition-metal complexes,<sup>[6]</sup> and more recently with uranium.<sup>[7]</sup> The only p-block element active for this transformation is tin, affording dimeric 3,7-distanna-2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-enes **V – VII** (Fig. 2).<sup>[8]</sup>

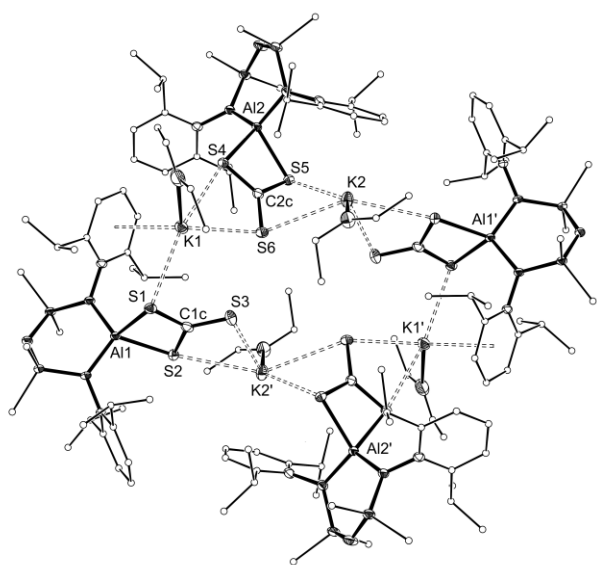


**Figure 2.** Products of the reductive coupling of  $CS_2$  initiated by tin. Coordination mode of the ethene-1,1,2,2-tetrathiolate ligand: **VII'** =  $\mu\text{-}(1\kappa S^1, 1\kappa S^1:2\kappa S^2, 1\kappa S^2)$ ; **V – VII** =  $\mu\text{-}(1\kappa S^1, 1\kappa S^2:2\kappa S^1, 1\kappa S^2)$ .

Addition of two equivalents of  $CS_2$  to a hexane solution of **K[III]** at room temperature afforded yellow crystals of the trithiocarbonate,  $K[Al(NON^{Dipp})(CS_3)]$  (**1**, Scheme 1). The NMR resonance for the quaternary  $[CS_3]^{2-}$  carbon atom was not observed (Fig. S2), likely due to its proximity to the quadrupolar  $^{27}Al$  ( $I = 5/2$ ) and  $^{33}S$  ( $I = 3/2$ ) nuclei. Compound **1** crystallized from diethylether as  $[K(OEt_2)[Al(NON^{Dipp})(CS_3)]$  (**1**· $Et_2O$ ), and consists of two symmetry related dimers linked through  $K\cdots S$  and  $K\cdots\pi\text{-arene}$  interactions (Fig. 3). The trithiocarbonate ligand is bidentate at aluminium, with localized bonding evidenced by longer C–S bonds involving the ligated sulfur atoms (range 1.739(2) Å – 1.744(2) Å) relative to the 'terminal' C=S bond (1.661(2) Å and 1.668(2) Å). Each sulfur atom is involved in  $K\cdots S$  interactions, with distances 3.2311(8) Å – 3.4148(6) Å (Fig. S3b).

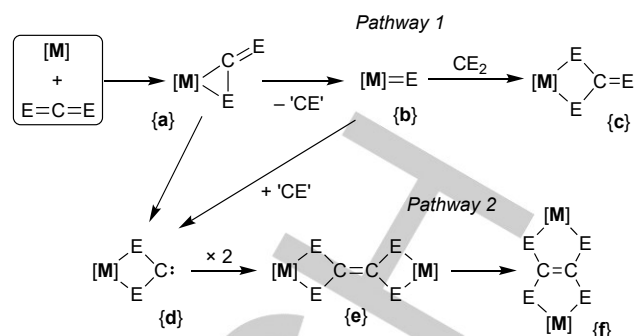


**Scheme 1.** Synthesis of  $[K(OEt_2)]\{Al(NON^{Dipp})(CS_3)\}$  ( $1 \cdot Et_2O$ ),  $K[Al(NON^{Dipp})(S_4)]$  (**2**) and  $[K\{Al(NON^{Dipp})(S_2C)\}]_2$  (**[3]<sub>2</sub>**). (i)  $CS_2$  (2 equiv., hexane, 298 K); (ii) 0.5  $CS_2$ ; (iii)  $CS_2$  (4 equiv., toluene, 195 K).



**Figure 3.** Thermal displacement plot (30% probability, C-atoms reduced for clarity, H-atom omitted) of  $[K(OEt_2)]\{Al(NON^{Dipp})(CS_3)\}_4$  ( $1 \cdot Et_2O$ )<sub>4</sub>,  $^i = 1-x, -y, -z$ . Selected bond lengths (Å) and angles (°): Al1-S1 2.3171(7), Al1-S2 2.3077(7), Al2-S4 2.3076(7), Al2-S5 2.3201(7), C1c-S1 1.744(2), C1c-S2 1.742(2), C1c-S3 1.661(2), C2c-S4 1.739(2), C2c-S5 1.739(2), C2c-S6 1.668(2); S1-Al1-S2 78.11(2), S4-Al2-S5 78.03(2), S1-C1c-S2 113.45(12), S1-C1c-S3 122.59(13), S2-C1c-S3 123.95(14), S4-C2c-S5 113.80(11), S4-C2c-S6 123.16(12), S5-C2c-S6 123.03(12).

The formation of **1** suggests that the aluminyl anion cleaves a C=S double bond to form the intermediate sulfido compound  $K[Al(NON^{Dipp})(S)]$  (**{b}**; E = S, Scheme 2). This mechanism implies loss of 'CS', which although unstable, has been trapped in other systems during the disproportionation of  $CS_2$ .<sup>[9]</sup> We propose that the postulated sulfide is highly reactive and undergoes [2+2]-cycloaddition with a second equivalent of  $CS_2$  to afford **1** (**{c}**; E = S) *via* Pathway 1 (Scheme 2). Such reductive disproportionation of  $CS_2$  *in situ* is unusual in main group chemistry,<sup>[10]</sup> although the



**Scheme 2.** General scheme describing the mechanism leading to the formation of compounds identified during this study.  $[M] = K[Al(NON^{Dipp})]$ ; E = S or O. Note: for simplicity the scheme is shown for the monomeric species (*vide infra*).

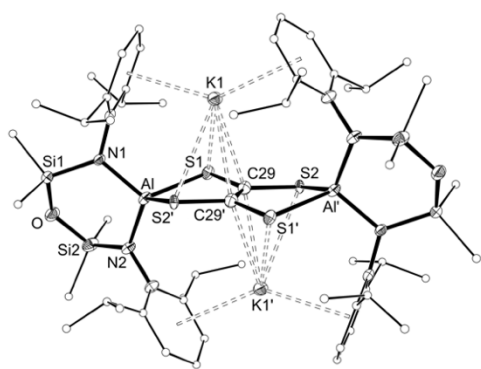
[2+2]-cycloaddition of  $CS_2$  to terminal  $Ge=S$ ,<sup>[11]</sup> bridging  $M(\mu-S)_2M$  ( $M = Sb, Bi$ ),<sup>[12]</sup> and *in situ* generated  $Sn=S$ <sup>[13]</sup> bonds has produced a family of p-block trithiocarbonate compounds, equivalent to step **{b}** → **{c}**.

Attempts to access the proposed sulfido intermediate  $K[Al(NON^{Dipp})(S)]$  from the direct combination of  $K[III]$  with sulfur (analogous to the formation  $K[Al(NON^{Dipp})(Se)]$ <sup>[14]</sup>) were unsuccessful. X-ray crystallography shows the product as the 1,2,3,4,5-tetrathiaaluminyl anion  $K[Al(NON^{Dipp})(S_4)]$  (**2**, Scheme 1, Fig. S6), analogous to previous main group examples from groups 13<sup>[15]</sup> and 14.<sup>[16]</sup>

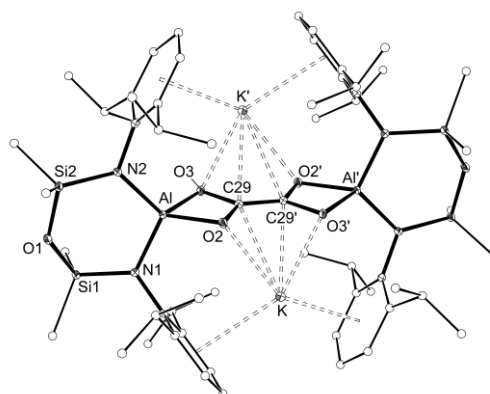
The reaction between  $CS_2$  (4 equiv.) and  $K[III]$  in toluene at  $-78^\circ C$  initially generated a red solution, which turned deep green as it warmed to room temperature. Colourless crystals of  $[K\{Al(NON^{Dipp})(S_2C)\}]_2$  (**[3]<sub>2</sub>**) were isolated from the reaction. NMR spectroscopy was uninformative and no resonance observed for the ' $CS_2$ ' carbon atom (*vide supra* for compound **1**). X-ray diffraction showed a dimeric structure with a  $\mu$ -[C<sub>2</sub>S<sub>4</sub>] ligand located on an inversion centre (Fig. 4). The 3,7-dialuminylnyl-2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-ene unit consists of two planar AlSCCS-rings, with the aluminium displaced by 0.597(4) Å from the mean square plane defined by the C<sub>2</sub>S<sub>4</sub>-group (fold angle =  $22.0^\circ$ ).

The C-C bond length is used as a measure of the charge in  $[C_2S_4]^{n-}$  ligands. Values for the tetrathiooxalate ligand ( $n = 2$ ) are  $\sim 1.46$  Å, whereas the ethenetetrathiolate ligand ( $n = 4$ ) has values closer to the C=C double bond,  $\sim 1.35$  Å.<sup>[17]</sup> The C29–C29' distance in **[3]<sub>2</sub>** is 1.355(5) Å, confirming formation of the ethenetetrathiolate ligand predicted for the oxidation of Al(I) to Al(III).

A proposed mechanism for the formation of **[3]<sub>2</sub>** involves rearrangement of an initial  $CS_2$  adduct to generate an intermediate carbene (**{d}**; E = S, Scheme 2). This species dimerizes to form the bimetallic  $\mu$ -( $1\kappa S^1, 1\kappa S^1: 2\kappa S^2, 1\kappa S^2$ ) compound **{e}** (equivalent to **VII'**), which rearranges to the  $\mu$ -( $1\kappa S^1, 1\kappa S^2: 2\kappa S^1, 1\kappa S^2$ ) product, **{f}** (Pathway 2).<sup>[8a]</sup> We have been unable to isolate any proposed intermediates in the sequence **{a}** → **{d}** → **{e}** → **{f}** during the synthesis of **[3]<sub>2</sub>**. We therefore investigated the corresponding oxygen-containing system, in which we reasoned that the increased strength of the Al–O bonds (bond dissociation energy BDE (diatomic) = 501 kJ mol<sup>-1</sup>),<sup>[18]</sup> relative to Al–S (BDE = 332 kJ mol<sup>-1</sup>) would facilitate the isolation of intermediates.



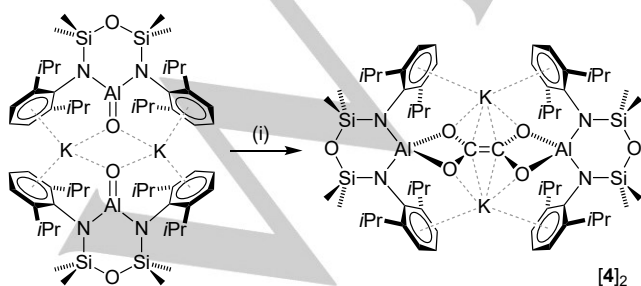
**Figure 4.** Thermal displacement plot (30% probability, C-atoms reduced for clarity, H-atoms omitted) of  $[K\{Al(NON^{Dipp})(S_2C)\}]_2$  (**3**)<sub>2</sub>, '1-x, -y, 1-z'. Selected bond lengths (Å) and angles (°): C29-C29' 1.355(5), C29-S1 1.779(3), C29-S2 1.774(5), Al-S1 2.2785(10), Al-S2' 2.293(4); N1-Al-N2 108.87(10), S1-Al-S2' 91.21(11), S1-C29-S2 114.92(19), S1-C29-C29' 122.8(3), S2-C29-C29' 122.3(3).



**Figure 5.** Thermal displacement plot (30% probability, C-atoms reduced for clarity, H-atoms omitted) of  $[K\{Al(NON^{Dipp})(O_2C)\}]_2$  (**4**)<sub>2</sub>, '1-x, -y, -z'. Selected bond lengths (Å) and angles (°): C29-C29' 1.338(2), C29-O2 1.3842(15), C29-O3 1.3841(15), Al-O2 1.8217(9), Al-O3 1.8171(9); N1-Al-N2 108.81(5), O2-Al-O3 76.08(4), O2-C29-O3 108.18(10), O2-C29-C29' 126.26(15), O3-C29-C29' 125.54(15).

An alternative approach to compounds **{d}** – **{f}** is required when  $E = O$ , as the reaction of  $K[III]$  with  $CO_2$  exclusively forms the carbonate  $K[Al(NON^{Dipp})(CO_3)]$  (**{c}**:  $E = O$ ).<sup>[5b]</sup> We therefore reacted the isolated alumoxane anion ' $K[Al(NON^{Dipp})(O)]$ ' (**{b}**:  $E = O$ ) with carbon monoxide, which we postulated would proceed *via* a [2+2]-cycloaddition to afford carbene **{d}** (Scheme 2). Similar reactions of neutral,<sup>[19]</sup> and anionic<sup>[20]</sup> aluminium imides with CO have been reported.

A toluene solution of  $[K\{Al(NON^{Dipp})(O)\}]_2$  was exposed to 1 atmosphere of CO at room temperature, affording colourless crystals corresponding to  $[K\{Al(NON^{Dipp})(O_2C)\}]_2$  (**4**)<sub>2</sub>, Scheme 3). As for the sulfur compounds **1** and **3**, NMR spectroscopy failed to locate the resonance for the quaternary ' $O_2C$ ' carbon atom. The molecular structure of **4**<sub>2</sub> (Fig. 5) is dimeric in the solid state with the  $\mu$ -[C<sub>2</sub>O<sub>4</sub>]<sup>2-</sup> ligand located on an inversion centre. The C29-C29' distance of 1.338(2) Å indicates a double bond and therefore adopting the same criteria for defining the charge as noted for [C<sub>2</sub>S<sub>4</sub>]<sup>2-</sup>, the ligand is present as the ethenetetraolate ligand [C<sub>2</sub>O<sub>4</sub>]<sup>4-</sup> and not the much more commonly observed oxalate dianion. The C–O bond lengths in **4**<sub>2</sub> (1.3842(15) Å and 1.3841(15) Å) are also longer than the delocalized bonds observed in the oxalate ligand, consistent with C–O single bonds. The aluminium centre in **4**<sub>2</sub> forms four-membered AlO<sub>2</sub>C-rings corresponding to a  $\mu$ -(1 $\kappa$ O<sup>1</sup>, 1 $\kappa$ O<sup>1</sup>:2 $\kappa$ O<sup>2</sup>, 1 $\kappa$ O<sup>2</sup>) bonding mode (**e**:  $E = O$ ), suggesting the stronger Al–O bonds may prevent the isomerization of **{e}** → **{f}**.

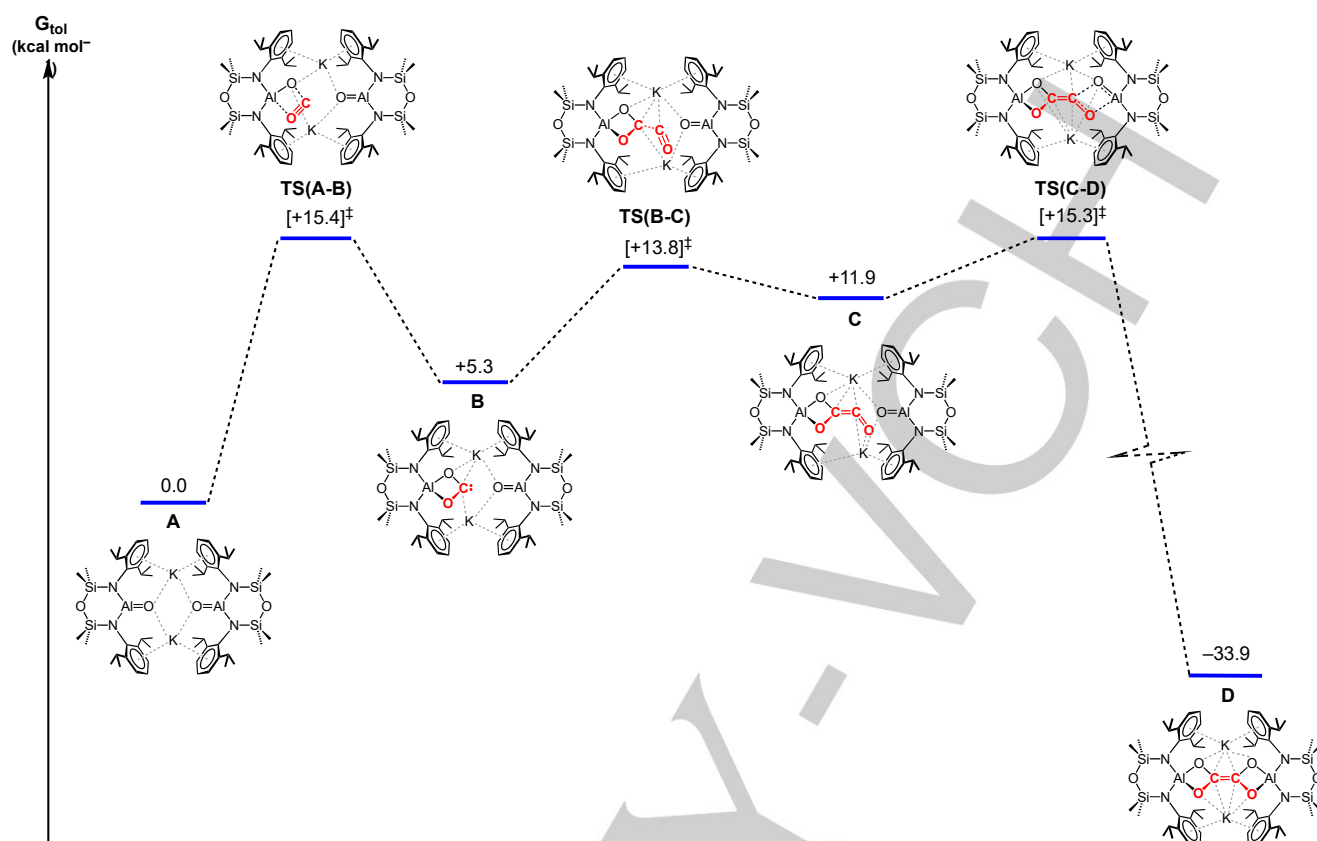


**Scheme 3.** Synthesis of  $[K\{Al(NON^{Dipp})(O_2C)\}]_2$  (**4**)<sub>2</sub>. (i) CO (1 atmosphere).

Although several crystallographic reports of 'ethenetetraolate' ligands with isolated C=C and C–O bonds have been deposited in the CCDC (Table S1),<sup>[21]</sup> examination of the C–C (range: 1.504(1) Å – 1.601(9) Å) and C–O (range: 1.207(8) Å – 1.302(5) Å) bond lengths indicate that each structure is better represented as the oxalate ligand. Therefore, to the best of our knowledge compound **4**<sub>2</sub> contains the first structural example of the ethenetetraolate ligand, [C<sub>2</sub>O<sub>4</sub>]<sup>4-</sup>.

We have examined the mechanism leading to **4**<sub>2</sub> by DFT calculations, performed at the (BP86-D3(BJ)-toluene/DS2//BP86/DS1) level of theory. Initial work focused on a reaction profile involving a monomeric alumoxane, with either aggregation of two aluminium carbene species (**{d}**:  $E = O$ ), Scheme 2) or the formation of a monomeric aluminium ketene intermediate before reaction with a second monomeric aluminium oxide group to give the final product (Pathways III and IV, Fig. S16-17). Whilst both of these pathways were calculated to be accessible at room temperature and consistent with experimentally observed synthesis of **4**<sub>2</sub>, we have previously demonstrated that rupturing the  $[K\{Al(NON^{Dipp})(O)\}]_2$  dimer results in facile ligand C–H activation across the Al=O bond.<sup>[5b]</sup> Therefore calculations were performed using the dimeric alumoxane (**A**) as the starting point (Fig. 6).

Coordination of the first CO molecule to one of the Al=O bonds proceeds *via* the rate limiting transition state **TS(A-B)** with an activation barrier of 15.4 kcal mol<sup>-1</sup>, generating the aluminium carbene species **B** (Pathway I, Fig. 6). Reaction with the second equivalent of CO can occur either symmetrically to the remaining Al=O group (Pathway II, Fig. S15) or asymmetrically to the carbeneic carbon of **B**. The asymmetric attack is calculated to be 4.7 kcal mol<sup>-1</sup> more favourable, with the CO coordinating *via* transition state **TS(B-C)**, forming a bent aluminium ketene complex **C** ( $G_{tot} = +11.9$  kcal mol<sup>-1</sup>). The terminal oxygen of the bent ketene moiety then coordinates to the second Al=O bond in the dimer *via* transition state **TS(C-D)** before the extremely favourable exergonic formation of **4**<sub>2</sub> ( $G_{tot} = -33.9$  kcal mol<sup>-1</sup>). Throughout this pathway, multiple interactions between the potassium cations and the carbon, oxygen and Dipp-aromatic groups stabilize the intermediates and transition-states,



**Figure 6** DFT-calculated free energy profile (BP86-D3(BJ)-toluene/DS2/BP86/DS1), in kcal mol<sup>-1</sup>, for the reaction of **A** with CO (Pathway I).

suggesting an important role for the K<sup>+</sup> in the formation of **[4]**<sub>2</sub>. It is noteworthy, that the BP86 optimised geometry of **[4]**<sub>2</sub> gives a C=C bond length of 1.36 Å and C-O bond lengths of 1.39 Å, which is fully consistent with formation of the first ethenetetraolate ligand, [C<sub>2</sub>O<sub>4</sub>]<sup>4-</sup>.

In summary, we have utilized CS<sub>2</sub> and CO to form new carbon-carbon bonds promoted by alumanyl and alumoxane anions. The isolation of the trithiocarbonate or ethenetetrathiolate complexes from [Al(NON<sup>Dipp</sup>)]<sup>-</sup> and CS<sub>2</sub> can be controlled using different reaction conditions. We also report the first example of the ethenetetraolate ligand [C<sub>2</sub>O<sub>4</sub>]<sup>4-</sup> from the reductive coupling of two CO molecules by a dimeric alumoxane. A computational investigation found that the formation of the ethenetetraolate complex is highly favourable at room temperature, with retention of a bimetallic species thought out the reaction.

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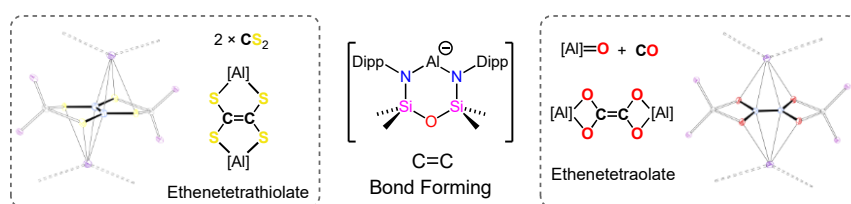
**Keywords:** C-C bond formation • alumanyl anion • carbon disulfide • ethylenetetrathiolate • ethenetetraolate

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- [21] Several examples of the [C<sub>2</sub>O<sub>4</sub>]-ligand have been registered with C=C double bonds and C-O single bonds. These bond lengths are better described as C-C single bonds and delocalized C-O bonds. See Table S1.

## Entry for the Table of Contents



$K[Al(NON^{Dipp})]$  has been used to construct new C=C double bonds. The reaction with  $CS_2$  generates the ethenetetrathiolate  $[C_2S_4]^{4-}$  containing product through a reductive coupling strategy. To obtain similar carbon-oxygen products, the alumoxane  $[K\{Al(NON^{Dipp})(O)\}]_2$  was reacted with CO, affording a hitherto unknown ethenetetraolate  $[C_2O_4]^{4-}$  ligand. DFT analysis indicates retention of a bimetallic species throughout the reaction with CO.