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## Reassessment of N<sub>2</sub> activation by low-valent Ti-amide complexes: a remarkable side-on bridged bis-N<sub>2</sub> adduct is actually an arene adduct†

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The complex  $\{(\text{TMEDA})_2\text{Li}\}\{\text{Ti}(\text{N}(\text{TMS})_2)_2(\mu\text{-}\eta^2\text{-N}_2)_2\}$  (**5-Li**) is the only transition metal N<sub>2</sub> complex ever reported with two side-on N<sub>2</sub> adducts. In this report, the similarity of **5-Li** to a new inverse sandwich toluene adduct  $\{(\text{PhMe})\text{K}\}\{\text{Ti}(\text{N}(\text{TMS})_2)_2(\mu\text{-PhMe})\}$  (**6-K**) necessitated a re-examination of the structure of **5-Li**. Through a reassessment of the original disordered crystal data of **5-Li** and new independent syntheses brought about through revisitation of the original reaction conditions, **5-Li** has been re-assigned as an inverse sandwich toluene adduct,  $\{(\text{TMEDA})_2\text{Li}\}\{\text{Ti}(\text{N}(\text{TMS})_2)_2(\mu\text{-PhMe})\}$  (**6-Li**). The original crystal data could be fitted almost equally well to structural solutions as either **5-Li** or **6-Li**, and this study highlights the importance of a holistic examination of modeled data and the need for secondary/complementary analytical methods in paramagnetic inorganic syntheses, especially when presenting unique and unexpected results. In addition, further examination of reduction reactions of  $\text{Ti}(\text{N}(\text{TMS})_2)_3$  and  $(\text{TMS})_2\text{N}_2\text{TiCl}(\text{THF})$  in the presence of  $\text{KC}_8$  revealed rich solvent- and counterion-dependent chemistry, including several degrees of N<sub>2</sub> activation (bridging nitride complexes, terminal bridging N<sub>2</sub> complexes) as well as ligand C–H activation.

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## Introduction

N<sub>2</sub> activation by reduced metal complexes is fundamentally important in understanding how to develop molecular alternatives to the Haber–Bosch process. Myriad N<sub>2</sub> complexes exist across the periodic table, and Ti is no exception:<sup>1</sup> there are examples of end-on and side-on bridging N<sub>2</sub> structures, including fully N–N cleaved nitrides from N<sub>2</sub>.<sup>2–7</sup> In some instances, Ti mediated N<sub>2</sub> reduction has also been used to incorporate nitrogen into organic molecules.<sup>8</sup> Recent examples of catalytic N<sub>2</sub> reduction with molecular Ti complexes<sup>2</sup> motivate our renewed interest in further developing the chemistry of low-valent Ti complexes in the context of small molecule activation.

Low-valent Ti complexes can also engender powerful reductive organic transformations,<sup>9–11</sup> such as C(sp<sup>3</sup>)–H and thiophene oxidative additions,<sup>12,13</sup> arene hydrogenation,<sup>14</sup> and diazene disproportionation.<sup>15</sup> Our group is interested in the synthesis and isolation of various low-valent Ti arene and (hetero)arene adducts, which have been invoked in the catalytic

synthesis of pyrroles<sup>15–17</sup> via nitrene transfer through a formal Ti<sup>II</sup>/Ti<sup>IV</sup> redox reaction.<sup>18</sup> To date, a variety of Ti<sup>II</sup> arene complexes have been isolated (Fig. 1A).<sup>19</sup> For example, Arnold reported a coordinated Ti–toluene complex **1** supported by a *N,N'*-bis(trimethylsilyl)benzamidinate ligand<sup>20</sup> while Ozerov reported a Ti–arene complex **2** supported by a *p*-*tert*-butyl calix[4]arene ligand.<sup>21</sup> Inverse-sandwich Ti complexes with bridging arenes have also been characterized, as demonstrated by a Cp\*Ti adduct **3** reported by Mach<sup>22</sup> and a tripyrrole Ti adduct **4** reported by Gambarotta and Budzelaar.<sup>23</sup> Multidentate intramolecularly bound arene examples have also been reported.<sup>12,24</sup>

Motivated by these examples, we investigated reduction reactions involving a well-known Ti-amido complex, Ti<sup>III</sup>[N(TMS)<sub>2</sub>]<sub>3</sub>,<sup>25</sup> envisioning that the electron-rich, sterically-encumbered (TMS)<sub>2</sub>N platform may readily bind free arenes. Herein, we report the synthesis of two inverse sandwich toluene adducts of low-valent Ti  $\{(\text{PhMe})\text{K}\}\{\text{Ti}(\text{N}(\text{TMS})_2)_2(\mu\text{-PhMe})\}$  (**6-K**) and  $\{(\text{TMEDA})_2\text{Li}\}\{\text{Ti}(\text{N}(\text{TMS})_2)_2(\mu\text{-PhMe})\}$  (**6-Li**) (Fig. 1B, right). The structures of **6-K** and **6-Li** are surprisingly similar to a previous report of a remarkable example of a doubly side-on bridged N<sub>2</sub> complex, **5-Li** (Fig. 1B, left).<sup>26</sup> **5-Li** was the landmark first report (30 years ago) of a side-on bridged Ti–N<sub>2</sub> complex and has been the only example of a transition metal complex with two side-on bound bridging N<sub>2</sub> ligands reported to date. Structural reassessment of **5-Li** has led us to conclude that this compound was originally mischaracterized as an N<sub>2</sub> adduct and is instead also an inverse sandwich adduct of

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**Fig. 1** A: Examples of monometallic (1–2) and bimetallic coordinated arenes (3–4). B: New examples of inverse sandwich toluene complexes (6-K and 6-Li) indicate that a reported Ti<sub>2</sub>–(N<sub>2</sub>)<sub>2</sub> complex 5-Li was originally mischaracterized.<sup>26</sup> Counteranions omitted for clarity.

toluene (**6-Li**). Further exploration of the reduction chemistry of Ti<sup>III</sup>[N(TMS)<sub>2</sub>]<sub>3</sub> and related low-valent Ti amides under an N<sub>2</sub> atmosphere demonstrate a suite of new N<sub>2</sub> reduction products, although no side-on N<sub>2</sub> adducts.

## Results and discussion

Ti<sup>III</sup>[N(TMS)<sub>2</sub>]<sub>3</sub> was reduced by KC<sub>8</sub> in toluene in an effort to isolate a reduced Ti–toluene complex (Fig. 2). When a concentrated toluene solution was passed through a KC<sub>8</sub> column,<sup>27</sup> the reaction mixture immediately turned near black yielding the mixed-valent inverse sandwich complex  $\{(\text{PhMe})\text{K}\}\{[\text{Ti}(\text{N}(\text{TMS})_2)_2]_2(\mu\text{-PhMe})\}$  **6-K** upon crystallization at –35 °C (40% isolated yield).

The X-ray crystal structure of **6-K** is shown in Fig. 2 along with relevant toluene C–C distances and angles. A comparison of **6-K** to Ti-arene complexes 1–4 is also shown in Table S15.† In the extreme electronic pictures, **6-K** could be described as a Ti<sup>II</sup>/Ti<sup>III</sup> complex bridged by a toluene dianion (Fig. 3, left), a Ti<sup>I</sup>/Ti<sup>II</sup> complex bridged by a neutral toluene (Fig. 3, right), or a Ti<sup>III</sup>/Ti<sup>IV</sup> complex bridged by a toluene tetraanion;<sup>28</sup> any of which could be consistent with the solution-state Evans method magnetic moment of **6-K** 1.67μ<sub>B</sub> (overall  $S = \frac{1}{2}$ ). The structural metrics indicated that **6-K** is best described as a toluene dianion: the C–C bond lengths of **6-K** are all remarkably elongated (1.436(4)–1.449(4) Å) and the toluene is significantly folded (dihedral angle = 20.0(2)°, indicating a loss of aromatic character, and ruling out the aromatic neutral or tetraanion toluene ligand descriptions. A picture of the formal oxidation states can also be distinguished by the Ti–N(TMS)<sub>2</sub> bond lengths. The Ti<sup>III</sup>–



**Fig. 2** Top: synthesis of **6-K** by KC<sub>8</sub> reduction of Ti<sup>III</sup>[N(TMS)<sub>2</sub>]<sub>3</sub> in toluene. Bottom: crystal structure of **6-K** with displacement ellipsoids drawn at the 50% probability level, including zoom-in of the bridging toluene showing the dihedral angle across the C<sub>5</sub>–C<sub>6</sub>–C<sub>1</sub>–C<sub>2</sub> and C<sub>2</sub>–C<sub>3</sub>–C<sub>4</sub>–C<sub>5</sub> planes. Hydrogen atoms and a disordered TMS group were omitted for clarity. Selected bond distance ranges (Å) and angles (°) are shown in Table S15.†

N(TMS)<sub>2</sub> moiety has Ti–N lengths of 2.028(2) and 2.030(2) Å which is consistent with Ti–N(TMS)<sub>2</sub> bond lengths in 18 other Ti<sup>III</sup> compounds (1.929(3) to 2.057(1) Å).<sup>25,26,29–37</sup> The Ti<sup>II</sup>–N(TMS)<sub>2</sub> bearing the (PhMe)K moiety has longer Ti–N(TMS)<sub>2</sub> bond lengths which range from 2.129(2) to 2.146(2) Å which is expected for an ion with a lower oxidation state. A similar difference in Ti–N lengths is been found in mixed-valent Ti<sup>II</sup>/Ti<sup>III</sup> inverse sandwich **4**.<sup>23</sup>

The synthesis of **6-K** caused us to re-investigate the very similar formally Ti<sup>II</sup>/Ti<sup>III</sup> complex, **5-Li**, which was reported to feature a bimetallic Ti–(μ-η<sup>2</sup>:η<sup>2</sup>-N<sub>2</sub>)<sub>2</sub>–Ti core containing two side-on bridging N<sub>2</sub> moieties (Fig. 4, left).<sup>26</sup> In the context of **6-K**, several features of **5-Li** are peculiar. First, the N–N bond lengths in **5-Li** (1.379(21) Å) are substantially longer than 37 of 39 reported Ti<sub>2</sub>–N<sub>2</sub> complexes (end-on range: 1.165(5)–1.315(3); side-on range: 1.216(5)–1.226(5)),<sup>1–8,26,33,38–49</sup> although there is one other example of a highly activated end-on Ti<sub>2</sub>–N<sub>2</sub> Tren<sup>TMS</sup>



**Fig. 3** Electronic representation of **6-K** as either Ti<sup>II</sup>/Ti<sup>III</sup> bridged by a toluene dianion (left) or Ti<sup>I</sup>/Ti<sup>II</sup> bridged by a neutral toluene (right).





Fig. 4 Reported examples of bimetallic Ti complexes bridged by a side-on  $\text{N}_2$  ligand. Left: double side-on  $\text{Ti}-(\text{N}_2)_2\text{-Ti}$ , **5-Li**, complex.<sup>26</sup> Right: single side-on  $\text{N}_2$  titanocene complexes.<sup>5,7</sup>



Fig. 5 Overlay of the crystal structures of **5-Li** (maroon) and **6-K** (teal). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms,  $\text{NTMS}_2$  disorder, and counterions were removed for clarity.

complex with an N-N distance of  $1.461(8) \text{ \AA}$ .<sup>2a</sup> Second, while there are 3 other side-on  $\text{Ti}_2\text{-N}_2$  complexes reported (Fig. 4, right),<sup>5,7</sup> **5** is the only reported doubly side-on complex, and in fact the only example of any transition metal containing 2 side-on bridging  $\text{N}_2$  ligands. These two  $\text{N}_2$  moieties were modelled as disordered over two crystallographically independent nitrogen-atom positions, with a further four positions being generated by symmetry. A close look at the six atomic sites found between the two Ti centers reveals an inverse sandwich motif that is strikingly reminiscent of the structure of **6-K**, and a direct overlay of the Ti coordination spheres of **5-Li** (maroon) and **6-K** (teal) reveal significant overlap (Fig. 5). These features indicate that **5-Li** may have been a mis-assigned arene adduct analogous to **6-K**; in fact, **5-Li** was synthesized in toluene.

Reinspection of the reflection intensities provided as ESI in the original publication led to the discovery of unassigned electron density surrounding the bridging  $\text{N}_2$  moieties (Fig. 6) corresponding to a largest difference peak of  $0.64 \text{ e}^- \text{ \AA}^{-3}$ . Remodeling of the original reflection intensities as a toluene adduct  $\{\text{Li}(\text{TMEDA})_2\}\{\text{Ti}(\text{NR}_2)_2\}_2(\mu\text{-PhMe})$  ( $\text{R} = \text{TMS}$ ) (**6-Li**) across 4 crystallographically-related toluene orientations resulted in slightly improved refinement metrics over the side-on  $\text{Ti}-(\text{N}_2)_2\text{-Ti}$  moiety **5-Li** (Fig. 7, top). Our model for **6-Li** gives unweighted and weighted  $R$ -factors of  $R_1 = 0.0601$ ,  $wR_2 = 0.172$ , and a largest difference peak of  $0.37 \text{ e}^- \text{ \AA}^{-3}$  versus  $R_1 = 0.0627$ ,  $wR_2 = 0.179$ , and  $0.64 \text{ e}^- \text{ \AA}^{-3}$  for **5-Li**. The relatively modest difference in model quality metrics for such different models ( $\text{C}_7\text{H}_8 = 50 \text{ e}^-$  vs.  $2 \times \text{N}_2 = 28 \text{ e}^-$ ) is no-doubt influenced by the



Fig. 6 Contour map of  $F_{\text{obs}}$  for **5-Li** showing the plane bisecting the  $\text{Ti-Ti}$  vector. Range:  $-0.60$  to  $3.80 \text{ e}^- \text{ \AA}^{-3}$  in steps of  $0.20$ . Negative contours are shown in red and positive in green. Residual electron density outside of the N ring indicates likely partial occupancy of another atom at those positions.

relatively poor  $I/\sigma$ , resolution and completeness of the original reflection data, which was not out of the norm for the era in which it was collected.

In order to definitively establish the true identity of **5-Li**, we turned our attention toward resynthesis of **5-Li** in an attempt to collect higher quality X-ray data (Fig. 8). The previous report



Fig. 7 Top: re-resolved SC-XRD of reported **5-Li** reflection data as either **5-Li** (left) or **6-Li** (right) as possible solutions, with displacement ellipsoids drawn at the 50% probability level. Bottom: XRD from new reflection data of re-synthesized **6-Li** following Reaction C from Fig. 8. Orange ellipsoids are disordered Me groups of the toluene dianion in 4 positions. Hydrogen atoms,  $\text{NTMS}_2$  disorder, and counterions were removed for clarity.





Fig. 8 Previously reported conditions for the synthesis of 5-Li and 7 (left) and the re-examined reactivity of (TMEDA)<sub>2</sub>TiCl<sub>2</sub> toward N<sub>2</sub> and in vacuum conditions for the synthesis of 6-Li and 7 (right).

described the synthesis of both side-on 5-Li and an end-on Ti-(μ-η<sup>1</sup>:η<sup>1</sup>-N<sub>2</sub>)-Ti complex 7 (Fig. 8, Reactions A and B). Attempts to synthesize 5-Li under the reported conditions were not successful, with only the end-on bridged 7 produced instead (Fig. 8, Reaction D). In the original synthesis of 5-Li, there is a discrepancy between the conditions reported in the experimental (under Ar) and in the reaction equation (under N<sub>2</sub>). When N<sub>2</sub> was rigorously excluded by performing the reaction on a Schlenk line under vacuum (Fig. 8, Reaction C) the toluene adduct 6-Li was isolated. This newly synthesized 6-Li has an identical unit cell to that reported for 5-Li with unweighted and weighted *R*-factors of *R*<sub>1</sub> = 0.0519 and *wR*<sub>2</sub> = 0.1320. Further, the previously published atomic coordinates for 5-Li can be refined directly against the reflection file obtained for the authentic sample of 6-Li. Modeling the new XRD data for 6-Li as 5-Li gives poorer metrics (*R*<sub>1</sub> = 0.0665 and *wR*<sub>2</sub> = 0.1874). Under this analysis, the largest peak in the difference map is again the unmodeled toluene methyl position which occurs at an identical position in the unit cell, being displaced by only 0.13 Å, a value well below the resolution of the experiment. Finally, hydrolysis of a crystalline sample of the newly-synthesized 6-Li yielded 57% of toluene by quantitative <sup>1</sup>H NMR analysis (ESI, Fig. S2†).

The Raman spectra of 6-K and 6-Li are also quite similar (Fig. S26 and S27†), and lack the expected N-N stretch in the 1700 cm<sup>-1</sup> region that is typical of bridging Ti-N<sub>2</sub> complexes (Table S16†).<sup>2a,6,7,50</sup> Further, attempts to calculate (m06 def2svp) optimized structures of [5]<sup>-</sup> from crystallographic coordinates of 5-Li result in either a single bridging side-on N<sub>2</sub> for a doublet electronic state, or an η<sup>2</sup>:η<sup>1</sup> side-on coordinated N<sub>2</sub> (ref. 51 and 52) and a terminal end-on N<sub>2</sub> for a quartet electronic state (ESI, Pages S26–S34†). The reorganization of the N<sub>2</sub> core in these structures provide evidence that a doubly bridging side-on dinitrogen complex like 5 may be unstable for this system. In contrast, geometry optimization of 6-Li is facile and accurately and precisely models the experimental structure.

Thus, through reassessment of the original data combined with new synthesis and DFT analysis, we can confidently assert that the species previously assigned as the Ti-(μ-η<sup>2</sup>:η<sup>2</sup>-N<sub>2</sub>)-Ti complex 5-Li is in fact the inverse sandwich complex Ti<sub>2</sub>-(PhMe)<sup>2-</sup> 6-Li. This result further highlights the importance of looking beyond residual factors when critically analyzing crystallography models, as it is possible to have multiple reasonable

solutions for the same data set. For example, Parkin and co-workers recently determined that the complex [Cd(CO)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>-Cl)]<sub>4</sub> with a reasonable *R*<sub>1</sub> = 0.068 was instead [Re(CO)<sub>3</sub>(C<sub>4</sub>N<sub>2</sub>-H<sub>3</sub>S)]<sub>4</sub> with an *R*<sub>1</sub> = 0.034.<sup>53</sup>

### Further reduction reactions with Ti amides

The formation of toluene dianion reaction products 6-Li and 6-K provided the incentive to examine the reduction of the pre-formed Ti amide complexes Ti[N(TMS)<sub>2</sub>]<sub>3</sub> (Fig. 9) and [(TMS)<sub>2</sub>-N]<sub>2</sub>TiCl(THF) (Fig. 10) under N<sub>2</sub> atmosphere.

Preliminary reactivity studies have revealed a suite of N<sub>2</sub> activation products, although in many cases the reaction products are inseparable. For example, reduction of Ti [N(TMS)<sub>2</sub>]<sub>3</sub> in hexanes generates a colorless Ti bridging nitride 8, the product of full N<sub>2</sub> cleavage, as an inseparable part of a larger mixture of unidentified products (Fig. 9). Analogous Ti-

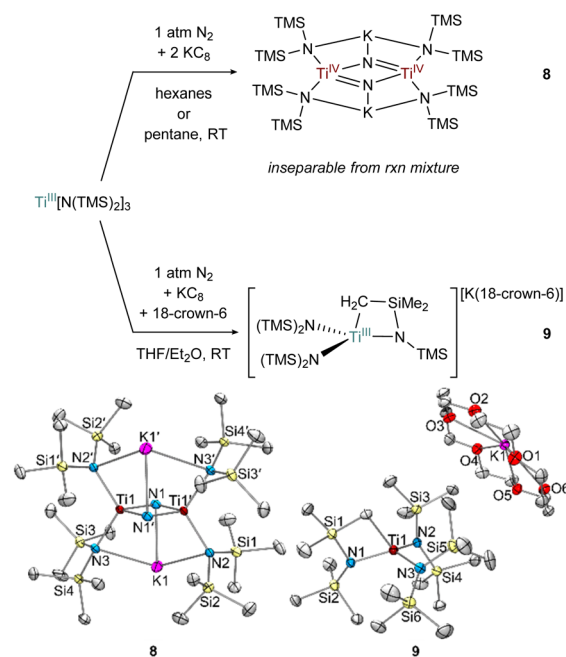


Fig. 9 Top: condition-dependent reduction of Ti[N(TMS)<sub>2</sub>]<sub>3</sub> forming 8 and 9 (top). Bottom: crystal structures of 8 and 9 (bottom) with displacement ellipsoids at the 50% probability level. Hydrogen atoms and were removed for clarity.



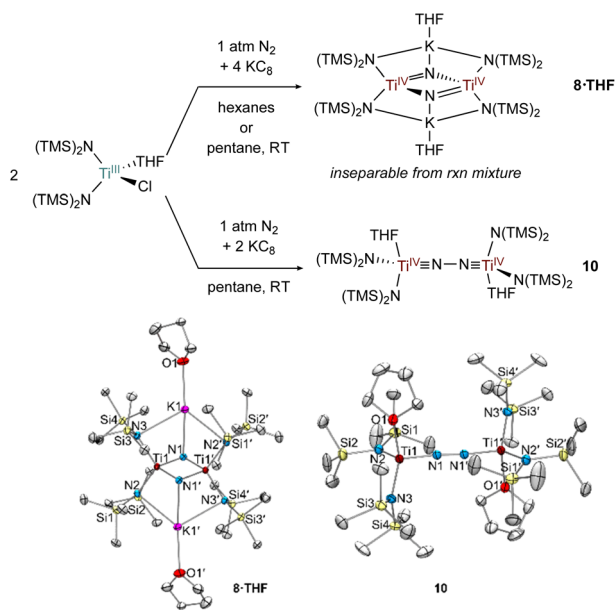


Fig. 10 1 : 2 reduction of  $[(\text{TMS})_2\text{N}]_2\text{TiCl}(\text{THF})$  using  $\text{KC}_8$  in the presence of  $\text{N}_2$  generates **8**·THF and a 1 : 1 reduction in pentane generates **10** (top). Crystal structures of **8**·THF and **10** (bottom) with displacement ellipsoids at the 50% probability level. Hydrogen atoms and disorder were removed for clarity.

nitride formation has also been reported by Liddle and co-workers using Mg as the reducing agent.<sup>2b</sup> Interestingly, reduction of  $\text{Ti}[\text{N}(\text{TMS})_2]_3$  in THF with 18-crown-6 instead generated the  $\text{Ti}^{\text{III}}$  C–H activated product  $\{[(\text{TMS})_2\text{N}]_2\text{Ti}[\text{N}(\text{TMS})\text{CH}_2\text{SiMe}_2]\}\{\text{K}(18\text{-crown-6})\}$ , **9** in 28% isolated yield. Similar examples of cyclometallation from  $\text{M}[\text{N}(\text{TMS})_2]_3$  ( $\text{M} = \text{Sc}, \text{Ti}, \text{Y}, \text{Er}, \text{Yb}, \text{Lu}$ ) complexes have been reported.<sup>54–58</sup> In this instance, an equivalent of  $\text{N}(\text{TMS})_2^-$  likely serves as a base to abstract a proton from the C–H bond, limiting the maximum reaction yield to 50%.

In the attempted reduction reactions with  $\text{Ti}[\text{N}(\text{TMS})_2]_3$  the co-product is the highly soluble  $\text{KN}(\text{TMS})_2$  which led to challenges in cleanly separating the Ti products. To circumvent this issue, reduction reactions of  $[(\text{TMS})_2\text{N}]_2\text{TiCl}(\text{THF})$  with  $\text{KC}_8$  were attempted, envisioning that the less soluble  $\text{KCl}$  co-product would be easier to separate (Fig. 10). Reduction of  $[(\text{TMS})_2\text{N}]_2\text{TiCl}(\text{THF})$  with 2 equiv.  $\text{KC}_8$  in hexanes or pentane yielded a THF adduct of a bridging nitride  $\{[(\text{TMS})_2\text{N}]_2\text{Ti}(\mu\text{-N})\}_2\{\text{K}(\text{THF})\}_2$  (**8**·THF), analogous to the reduction of  $\text{Ti}[\text{N}(\text{TMS})_2]_3$ . Unfortunately, the reaction mixture of **8**·THF was similarly intractable to that of **8**, and identification was only possible by picking single crystals from the mixture. However, reduction of  $[(\text{TMS})_2\text{N}]_2\text{TiCl}(\text{THF})$  with only 1 equiv. of  $\text{KC}_8$  in pentane yielded the end-on bridged  $\text{N}_2$  complex  $[(\text{TMS})_2\text{N}]_2\text{-Ti}(\text{THF})_2(\mu\text{-}\eta^1:\eta^1\text{-N}_2)$  (**10**). Interestingly, further reaction of **10** with excess  $\text{KC}_8$  did not result in significant formation of **8**·THF.

Selected bond distances from the solid-state structures of **8**, **8**·THF, **7** (ref. 26) and **10** are reported in Table 1. The  $\text{Ti}-\text{N}_{\text{nitride}}$  distances in **8** and **8**·THF have nearly identical bond metrical parameters despite containing an additional coordinated THF

Table 1 Selected bond distances (Å) the nitride complexes **8** and **8**·THF and the end-on  $\text{N}_2$  complexes **7** (ref. 26) and **10**

	Nitride complexes		$\text{N}_2$ complexes	
	<b>8</b>	<b>8</b> ·THF	<b>7</b> (ref. 26)	<b>10</b>
Ti1–N1	1.825(3)	1.824(1)	1.762(5)	1.763(1)
Ti1–N1'	1.836(3)	1.835(2)	—	—
Ti1–N2	2.073(3)	2.075(1)	2.023(5)	1.995(2)
Ti1–N3	2.092(3)	2.094(1)	—	2.011(1)
N1···N1'	2.505(4)	2.503(2)	—	—
N1–N1'	—	—	1.289(9)	1.276(2)

to each potassium cation in **8**·THF. The  $\text{N}\cdots\text{N}$  distances in **8** and **8**·THF are  $>2.5$  Å, consistent with complete N–N bond scission and the formation of bridging nitrides. Additionally, the  $\text{Ti}-\text{N}_{\text{nitride}}$  distances are symmetric, indicating resonance for the  $\text{Ti}=\text{N}$  double bonds. The N–N bond distances in **10**, (1.276(2) Å), and **7**,<sup>26</sup> (1.289(9) Å), are similar to many other reported  $\text{Ti}-\text{N}_2\text{-Ti}$  bridging complexes.<sup>2–7</sup> The short  $\text{Ti}-\text{N}_{\text{N}_2}$  bond distances in **7** and **10** are (1.76 Å) are indicative of  $\text{Ti}\equiv\text{N}$  triple bonds, suggesting that a  $\text{Ti}^{\text{IV}}\equiv\text{N}-\text{N}\equiv\text{Ti}^{\text{IV}}$  electronic structure is predominant in both cases. DFT analysis of **10** further corroborates the  $\text{Ti}\equiv\text{N}$  triple bond character, as both  $\text{Ti}-\text{N}$  p-bonds can be seen in the HOMO and HOMO – 1 (Fig. S20 and S21†). The  $\text{Ti}-\text{N}(\text{TMS})_2$  distances in **7** and **10** similar to those in the  $\text{Ti}^{\text{IV}}$  nitride compounds **8** and **8**·THF, further indicating  $\text{Ti}^{\text{IV}}\equiv\text{N}-\text{N}\equiv\text{Ti}^{\text{IV}}$  character in **7** and **10**. These electronic structures are consistent with a recent framework for classifying  $\text{N}_2$  complexes based on electron counting.<sup>59</sup>

## Conclusion

In summary, the bis- $\text{N}_2$  side-on complex, **5-Li** is in fact a bridging toluene complex, **6-Li**. This misassignment arises from the modeling of the disorder of the bridging atoms. Despite the reasonable difference in models ( $\text{C}_7\text{H}_8 = 50 e^-$  vs.  $2 \times \text{N}_2 = 28 e^-$ ) the poor  $I/\sigma$ , resolution and completeness of the original reflection data limited proper interpretation. New experimental and computational analysis of data confirmed the formation of the bridging toluene complex: synthesis under vacuum in toluene yields the same crystals as reported for the incorrectly-assigned  $\text{N}_2$  adduct, and NMR analysis of the hydrolyzed crystals reveals the presence of toluene. The reassignment of **5-Li** means that there are zero examples of a double-side-on bridging mode of  $\text{N}_2$  activation, and we posit that this particular bonding motif may not be possible.

## Experimental section

### General considerations

All syntheses and manipulations described below were conducted under nitrogen with exclusion of air using glovebox, Schlenk-line, and high-vacuum techniques.  $\text{Ti}[\text{N}(\text{TMS})_2]_3$ ,<sup>25</sup>  $(\text{TMEDA})_2\text{TiCl}_2$ ,<sup>60</sup> and  $\text{KC}_8$  (ref. 61) were prepared using previously published procedures. TMEDA was vacuum transferred, passed through activated alumina, stored over 4 Å molecular



sieves in the glovebox prior to use. 18-Crown-6 was sublimed prior to use. NMR solvent  $C_6D_6$  was dried over  $Na^0/Ph_2CO$  and vacuum transferred before passing through activated alumina in the glovebox. Pentane, hexanes, and toluene were dried on a Pure Process Technology solvent purification system, passed through activated alumina, and stored over activated 4 Å molecular sieves prior to use.  $^1H$  NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer at 298 K. Elemental analysis was shipped to and performed by Midwest Microlab. Attempts to collect elemental analysis on samples of the newly-reported **6-K**, **6-Li**, **9**, and **10** were unsuccessful as these sensitive complexes decomposed during shipment. SC-XRD data of **6-K**, **7**, **8·THF**, **9** and **10** were collected on a Bruker-AXS Venture Photon-III using a Mo source, **6-Li** on a Bruker-AXS Venture Photon-III using a Cu source, and **8** was collected on a Bruker-AXS Smart Apex-II using a Mo source. Crystal and refinement data are available in ESI.† UV-visible absorption spectra were recorded on a HP8453A diode array spectrometer from Unisoku, Scientific Instruments (Osaka, Japan). Raman spectra were obtained at room temperature with excitation at 457 nm (500 mW at source, Cobolt Lasers) through the sample in a J. Young NMR tube using a  $135^\circ$  backscattering arrangement. The collimated Raman scattering was collected using two plano convex lenses ( $f = 12$  cm, placed at an appropriate distance) through appropriate long pass edge filters (Semrock) into an Acton AM-506M3 monochromator equipped with a Princeton Instruments ACTON PyLON LN/CCD-1340  $\times$  400 detector. The detector was cooled to  $-120^\circ C$  prior to the experiments. Spectral calibration was performed using the Raman spectrum of acetonitrile/toluene 50 : 50 (v/v).<sup>62</sup> Each spectrum was acquired 60 times with 1 s acquisition time, resulting in a total acquisition time of 1 min per spectrum. The collected data was processed using Spectragryph<sup>63</sup> and a multi-point baseline correction was performed for all spectra.

#### Synthesis of $\{(PhMe)K\}\{[Ti(N(TMS)_2)_2]_2(\mu-PhMe)\}$ **6-K**

In an  $N_2$ -filled glovebox, a blue toluene (1.5 mL) solution of  $Ti[N(TMS)_2]_3$  (196 mg, 0.37 mmol) was passed through a  $KC_8$  filled 7 mm diameter pipette column (5 cm of  $KC_8$ ) yielding a darkly coloured eluent. An additional 1.5 mL of PhMe was used to wash the  $KC_8$  column. The resulting near black solution was dried *in vacuo* to yield an oil. This oil was extracted with  $-78^\circ C$  pentane ( $3 \times 1.5$  mL) and the pentane solution was filtered through glass wool. The resulting pentane solution was then dried *in vacuo* to yield a dark navy-blue powder with colorless crystals (identified as  $KN(TMS)_2$  *via* SC-XRD). The powder was then extracted and filtered two additional times with  $-78^\circ C$  pentane ( $3 \times 1.5$  mL) until colorless solids were no longer observed. Upon final drying, near black microcrystalline solids of  $\{(PhMe)K\}\{[Ti(N(TMS)_2)_2]_2(\mu-PhMe)\}$  formed (71 mg, 40%). Single crystal X-ray quality crystals were obtained from a concentrated PhMe solution at  $-35^\circ C$ . Evans method:  $1.67\mu_B$ .

#### Synthesis of $\{(TMEDA)_2Li\}\{[Ti(N(TMS)_2)_2]_2(\mu-PhMe)\}$ , **6-Li**

In an  $N_2$ -filled glovebox, purple  $(TMEDA)_2TiCl_2$  (300 mg, 0.84 mmol) and colorless  $LiN(TMS)_2$  (422 mg, 2.52 mmol) were

added to a Teflon screw cap 100 mL flask. To another 100 mL Teflon screw cap flask, toluene (10 mL) and TMEDA (0.5 mL) were added. Both flasks were sealed, removed from the glovebox, and placed on a high-vac line. The flask containing the solid  $(TMEDA)_2TiCl_2$  and  $LiN(TMS)_2$  were placed under vacuum ( $10^{-4}$  torr) for 3 h. The PhMe/TMEDA solution was degassed *via* three 1 h freeze-pump-thaw cycles. The PhMe/TMEDA solution was vacuum transferred to the flask containing solids using a  $-78^\circ C$  bath. The flask was then sealed and the purple mixture was stirred and warmed to room temperature. After 30 min of stirring, the purple mixture turned brown. After 1 d, degassed  $Et_2O$  (*via* three 1 h, freeze-pump-thaw cycles) was vacuum transferred to the frozen brown mixture. Upon thawing, an  $Et_2O$  layer on the brown solution formed. The sealed flask was stored in a  $-30^\circ C$  freezer. After 1 d, both colorless and brown crystals formed. The colorless crystals were identified as  $[Li(TMEDA)_2]\{[(TMS)_2N]_2TiCl_2\}$  *via* unit-cell analysis (CSD Refcode: JOHBAJ). A full dataset of the brown crystals were collected and identified as  $\{(TMEDA)_2Li\}\{[Ti(N(TMS)_2)_2]_2(\mu-PhMe)\}$ , **6-Li**.

#### Synthesis of $[(TMEDA)Ti(N(TMS)_2)Cl]_2(\mu-N_2)$ , **7**

In an  $N_2$ -filled glovebox, purple  $(TMEDA)_2TiCl_2$  (300 mg, 0.84 mmol) and colorless  $LiN(TMS)_2$  (421 mg, 2.52 mmol) were added to a 100 mL flask and chilled to  $-78^\circ C$ . To this flask,  $-78^\circ C$  toluene (10 mL) and TMEDA (0.5 mL) were added. The purple mixture was stirred and warmed to room temperature. The purple mixture turned brown within minutes. After 1 d, the brown solution was layered with  $Et_2O$  and placed in a  $-30^\circ C$  freezer. After 1 d, colorless and brown crystals formed. The colorless crystals were identified as  $[Li(TMEDA)_2]\{[(TMS)_2N]_2TiCl_2\}$  *via* unit-cell analysis (CSD Refcode: JOHBAJ). A full dataset of the brown crystals were collected and identified as  $[(TMEDA)Ti(N(TMS)_2)Cl]_2(\mu-N_2)$ , **7**.

#### Synthesis of reaction mixture containing **8**

In an  $N_2$ -filled glovebox, a blue  $Ti[N(TMS)_2]_3$  (100 mg, 0.19 mmol) solution in hexanes (5 mL) was added to  $KC_8$  (54 mg, 0.38 mmol) forming a darkly coloured mixture. After stirring for 3 d, the near black mixture was filtered through Celite to remove graphite. The resulting near black solution was placed in a  $-30^\circ C$  freezer. After 1 d, colourless crystals covered in tar formed from the near black solution and were identified as the bridging nitride complex **8**. Crystals of  $K[N(TMS)_2]$  were also identified in the mixture by matching the unit-cell (CSD Refcode: VETFOP).

#### Synthesis of reaction mixture containing **8·THF**

In an  $N_2$ -filled glovebox, a light blue  $[(TMS)_2N]_2TiCl(THF)$  (100 mg, 0.21 mmol) solution in hexanes (5 mL) was added to  $KC_8$  (57 mg, 0.42 mmol) forming a darkly coloured mixture. After stirring for 3 d, the black mixture was filtered through Celite to remove graphite. The resulting solution was placed in a  $-30^\circ C$  freezer. After 1 d, colorless crystals covered in tar formed from the near black solution and were identified as the bridging nitride complex **8·THF**.



### Synthesis of $[\text{K}(18\text{-crown-6})]\{[(\text{TMS})_2\text{N}]_2\text{Ti}[\text{N}(\text{TMS})(\text{SiMe}_2\text{CH}_2)]\}$ , **9**

In an  $\text{N}_2$ -filled glovebox, a blue 3 : 1  $\text{Et}_2\text{O} : \text{THF}$  (4 mL) solution of  $\text{Ti}[\text{N}(\text{TMS})_2]_3$  (100 mg, 0.19 mmol) was added dropwise to a dark blue 3 : 1  $\text{Et}_2\text{O} : \text{THF}$  (10 mL) mixture of 18-crown-6 (52 mg, 0.19 mmol) and  $\text{KC}_8$  (27 mg, 0.19 mmol) forming a darkly coloured mixture. After 4 d of stirring, the dark green mixture was filtered through Celite to remove graphite and the dark green solution was placed under vacuum. The resulting green oil was redissolved in  $\text{Et}_2\text{O}$  (1 mL) and layered into pentane (10 mL) and placed in a  $-30\text{ }^\circ\text{C}$  freezer. After 1 d, green single-crystals formed and were identified as  $[\text{K}(18\text{-crown-6})]\{[(\text{TMS})_2\text{N}]_2\text{Ti}[\text{N}(\text{TMS})(\text{SiMe}_2\text{CH}_2)]\}$ , **9**, via SC-XRD (44 mg, 28%).

### Modified synthesis of $[(\text{TMS})_2\text{N}]_2\text{TiCl}(\text{THF})$ <sup>36</sup>

In an  $\text{N}_2$ -filled glovebox,  $\text{TiCl}_3(\text{THF})_3$  (1006 mg, 2.7 mmol) and  $\text{LiN}(\text{TMS})_2$  (918 mg, 5.4 mmol) were stirred in pentane (50 mL) for 1 h. The resulting light blue mixture was filtered through Celite twice to remove  $\text{LiCl}$ . The clear blue solution was placed in a  $-30\text{ }^\circ\text{C}$  freezer. After 1 d, light blue crystals formed in a dark green solution. The green solution was decanted away and the light blue crystals were washed with  $-78\text{ }^\circ\text{C}$  pentane ( $3 \times 2\text{ mL}$ ) and isolated (983 mg, 76%).

### Synthesis of $[(\text{TMS})_2\text{N}_2\text{Ti}(\text{THF})]_2(\mu\text{-N}_2)$ , **10**

In an  $\text{N}_2$ -filled glovebox, light blue pentane (5 mL) solution of  $[(\text{TMS})_2\text{N}]_2\text{TiCl}(\text{THF})$  (200 mg, 0.42 mmol) was added to  $\text{KC}_8$  (57 mg, 0.42 mmol) forming a darkly coloured mixture. After stirring for 1 d, the mixture was filtered through Celite to remove graphite and  $\text{KCl}$ . The resulting brown solution was concentrated to  $\sim 0.5\text{ mL}$  of pentane and placed in a  $-30\text{ }^\circ\text{C}$  freezer. After 1 d, brown single-crystals formed and were identified as  $[(\text{TMS})_2\text{N}_2\text{Ti}(\text{THF})]_2(\mu\text{-N}_2)$ , **10**. The crystals were washed with  $-78\text{ }^\circ\text{C}$  pentane and isolated (34 mg, 18%). Crystalline yields are low due to the high solubility of this compound.  $^1\text{H}$  (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^\circ\text{C}$ ,  $\delta$ , ppm) 4.17 (s, 8H, THF) 1.46 (m, 8H, THF), 0.43 (s, 72H,  $\text{SiMe}_3$ ).

## Data availability

All experimental and computational data is available as a part of the ESI.†

## Author contributions

Daniel N. Huh: conceptualization, investigation, formal analysis, writing – original draft, writing – review & editing, funding acquisition. Ross F. Koby: investigation, formal analysis, writing – original draft, writing – review & editing. Zoe E. Stuart: investigation. Rachel J. Dunscomb: investigation. Nathan D. Schley: investigation, formal analysis, writing – original draft, writing – review & editing. Ian A. Tonks: conceptualization, writing – review & editing, supervision, funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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