

**Reductive Activation of N₂ using a Calcium/Potassium Bimetallic System
Supported by an Extremely Bulky Diamide Ligand**

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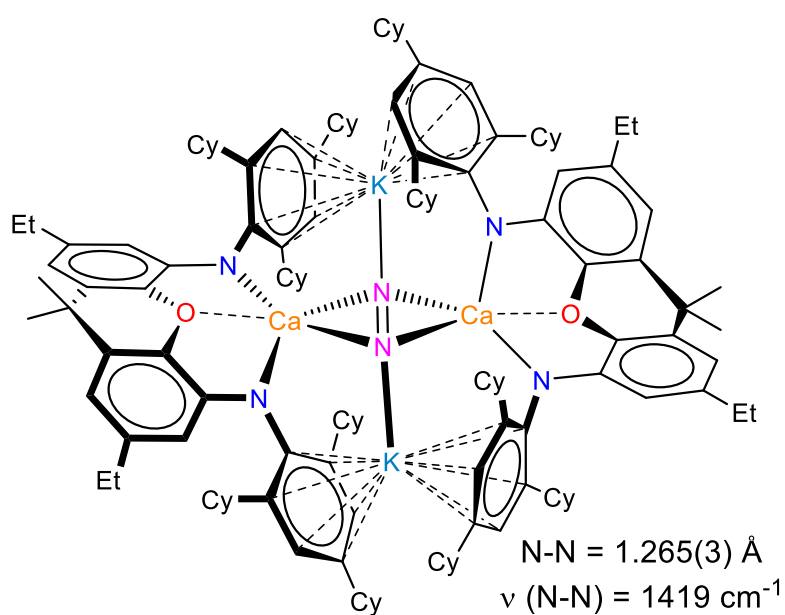
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Summary for contents page:

Reductive Activation of N₂ using a Calcium/Potassium Bimetallic System Supported by an Extremely Bulky Diamide Ligand

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Potassium reduction of a bulky diamido-calcium complex under an N₂ atmosphere afforded the first well-defined, anionic s-block complex of activated dinitrogen (see picture).

Keywords: calcium, N₂ activation, potassium, reduction, DFT calculations.

Abstract:

An extremely bulky xanthene bridged diamide ligand (${}^{\text{TCHP}}\text{NON} = 4,5\text{-bis}(2,4,6\text{-tricyclohexylanilido})\text{-}2,7\text{-diethyl-}9,9\text{-dimethyl-xanthene}$) has been developed and used to prepare two monomeric diamido-calcium complexes [${}^{\text{TCHP}}\text{NONCa}(\text{D})_n$] ($\text{D} = \text{THF}$, $n = 2$, **3**; $\text{D} = \text{toluene}$, $n = 1$, **4**). Reduction of **4** with 5% w/w K/KI under an N_2 atmosphere gave the first well-defined, anionic s-block complex of activated dinitrogen, [$\{\text{K}({}^{\text{TCHP}}\text{NON})\text{Ca}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$] **5**, presumably *via* a transient calcium(I) intermediate.

Dinitrogen (N_2) is the most abundant gas in Earth's atmosphere, and is inert under most conditions. This lack of reactivity arises from the extremely strong triple bond of the non-polar molecule (bond dissociation energy = 944 kJ mol^{-1}), and its large HOMO-LUMO energy gap (10.82 eV).¹ Despite this, nature has found a number of ways to transform N_2 to bio-available molecules; for example the conversion of N_2 to NH_3 by nitrogenase.² Moreover, the artificial production of more than 200 million tonnes/annum of ammonia from N_2 and H_2 is achieved using heterogeneous d-block metal catalysts in the Harber-Bosch process. This ammonia is used as a feed stock for the production of nitrogenous fertilizers and other N-chemicals that are essential to sustaining the global population. Notwithstanding this, the Harber-Bosch process consumes 1-2% of the world's energy, and produces approximately 500 million tonnes of CO_2 per annum.³ As a result, a considerable amount of research is currently directed towards the more sustainable activation of N_2 under mild conditions.

Towards this end, the coordination and activation of N_2 by d-block metal organometallic and coordination complexes under ambient homogeneous reaction conditions has been well developed since the 1960's.⁴ Such activations typically involve energetically accessible, occupied d-orbitals of the transition metal donating electron density to a π^* -orbital of N_2 , thereby weakening its bond. Although less reactive towards N_2 , a variety of low-valent f-block metal complexes have

also been shown to reductively activate the diatomic molecule in solution.⁵ Given the perceived inaccessibility, or absence, of occupied main group metal d-orbitals, it is not surprising that the first ambient temperature activation of N₂ in solution using a p-block element (*viz.* boron) compound, was not reported until 2018, by Braunschweig and co-workers.^{1,6} Similarly, and although elemental lithium is well known to react with N₂ to give Li₃N under ambient conditions,⁷ the only solely s-block metal complex to effect coordination and activation of N₂ in solution was described by Harder and co-workers in 2021.^{8,9} This was achieved by reducing a solution of an extremely bulky β -diketiminato calcium iodide complex, under an N₂ atmosphere, with 5% w/w K/KI,¹⁰ yielding complexes **1**, after treatment with cyclic ether donors (Figure 1). It is likely that **1** are formed *via* a short-lived Ca^I intermediate which reduces N₂ to the N₂²⁻ dianion, prior to ether coordination. The complexes are extremely reactive, and act as masked sources of calcium(I), for example in the reduction of H₂ and inert arenes.

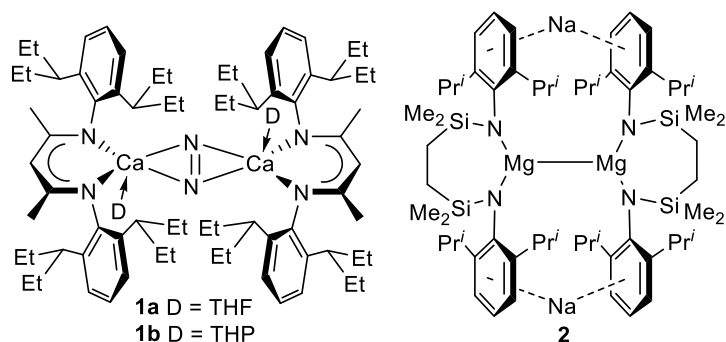
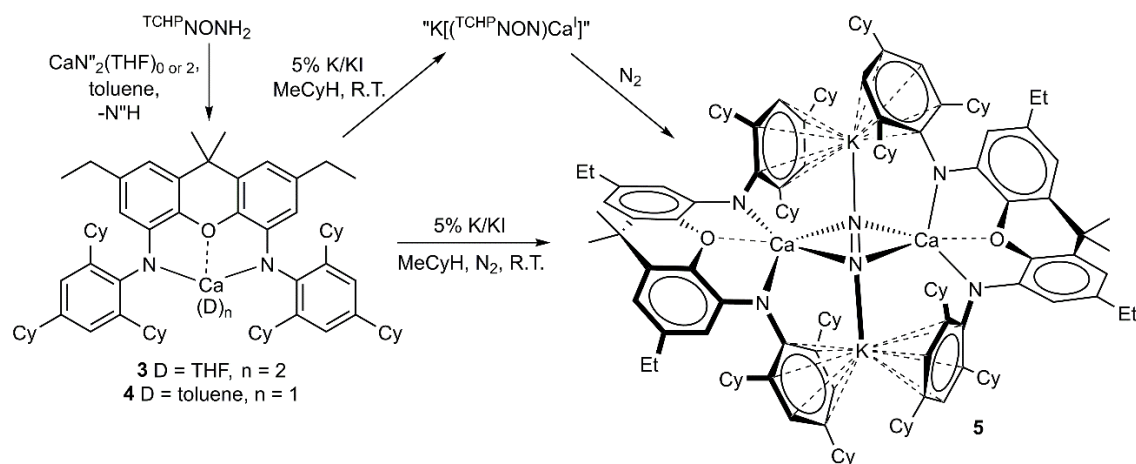


Figure 1. Harder's Ca-activated N₂ complexes **1**, and Hill's dianionic magnesium(I) complex **2** (THP = tetrahydropyran).

It is noteworthy that Harder's preparation of **1** was serendipitous, and his original target was a dicalcium(I) complex, LCa–CaL (L = β -diketiminato). Given our background in related dimagnesium(I) chemistry,¹¹ we believed that a Ca–Ca bonded species might be accessible with a different, but still very bulky ligand system. In this context, Hill and co-workers recently reduced a bulky cyclic diamido magnesium(II) complex with sodium to give the dianionic magnesium(I) complex, **2**.¹² It seemed to us that a bulkier, more rigid diamide ligand system might allow access

to a related calcium(I) complex, or a reduced Ca-N₂ complex, *cf.* **1**. Here we describe the development of a new, extremely bulky, xanthene based diamide ligand, and its use for the stabilisation of the first anionic calcium complex of reductively activated N₂.

Xanthene based diamide ligands have been widely used for the preparation of complexes of metals from across the periodic table for more than 15 years. More recently, bulky examples have proved their worth for the stabilisation of low oxidation state p-block metal complexes, which have shown remarkable reactivity.¹³ While there is one recent report of xanthene based diamido-complexes of magnesium(II) and calcium(II),¹⁴ reduced examples are unknown. In efforts to kinetically stabilise such a complex, we developed a synthetic route to a xanthene bridged diamide pro-ligand, 4,5-bis(2,4,6-tricyclohexylaniline)-2,7-diethyl-9,9-dimethyl-xanthene, ^{TCHP}NONH₂, of unprecedented steric bulk (see ESI for full details). This incorporates 2,4,6-tricyclohexylphenyl (TCHP) N-substituents, which we have recently shown¹⁵ to be more sterically shielding than widely used 2,6-diisopropylphenyl (Dip) groups (e.g. as in **2**), and of a comparable bulk to the 2,6-di-3-pentylphenyl (DIPeP) N-substituents in **1**. Deprotonation of ^{TCHP}NONH₂ with toluene solutions of either [Ca{N(SiMe₃)₂}] or [Ca{N(SiMe₃)₂}(THF)₂] afforded good yields of the calcium(II) diamides, **3** and **4**, respectively (Scheme 1).



Scheme 1. Synthesis of compounds **3-5** (MeCyH = methylcyclohexane, N'' = N(SiMe₃)₂).

Both **3** and **4** are thermally very stable and were spectroscopically characterised (see ESI for details). The X-ray crystal structure of **3** (Figure 2) shows it to be monomeric with a square based pyramidal calcium coordination geometry, with one THF ligand in the apical position. This situation is similar to that found for the related complex, $[(^{\text{Dip}}\text{NON})\text{Ca}(\text{OEt}_2)_2]$ ($^{\text{Dip}}\text{NON}$ = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene).¹⁴ Although **4** could not be crystallographically characterised, it seems likely that the arene ring of the toluene molecule is coordinated to its calcium centre, similar to the two Ca-coordinated benzene molecules in $[(^{\text{Dip}}\text{NON})\text{Ca}(\text{C}_6\text{H}_6)_2]$.¹⁴

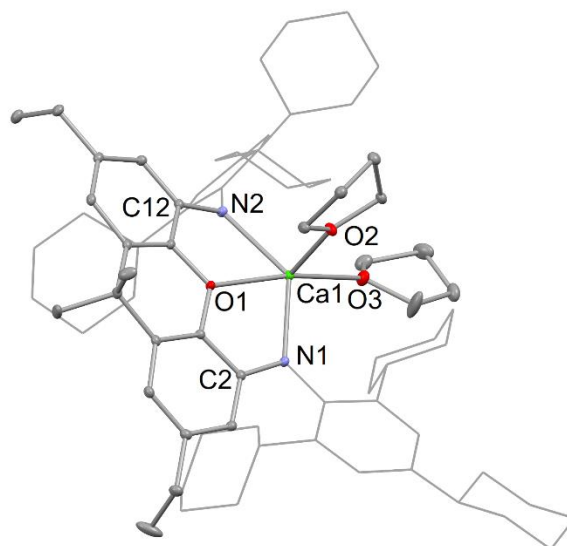


Figure 2. The molecular structure of **3** (20% ellipsoids; TCHP substituents shown as wire frame for clarity; hydrogen atoms omitted).

With **3** and **4** in hand, their reductions with 5% w/w K/KI¹⁰ were investigated under a number of conditions. Reduction of benzene, toluene or methylcyclohexane solutions of **3** under atmospheres of either argon or N₂, in all cases led to intractable mixtures of products. This may occur due to the generation of transient, highly reactive calcium(I) species, e.g. “K[(^{TCHP}NON)Ca]”, which, in preference to forming a Ca–Ca bonded product, undergo intramolecular C–H activation processes, or react with the reaction solvent, both of which have

been reported for **1**.⁸ Similarly, reduction of benzene solutions of THF free **4** under argon or N₂ atmospheres gave complicated product mixtures, from which, in one case, a few crystals of the dipotassium salt of the ligand, K₂[^{TCHP}NON], were obtained. This presumably occurs due to over-reduction of **4**. Interestingly, the crystal structure of the compound (see ESI) shows it to be polymeric, with K₂[^{TCHP}NON] units being alternately bridged by K-coordinated biphenyl and benzene units. This provides good evidence that calcium(I) reaction intermediates induce C-H activation of the benzene solvent, ultimately giving rise to phenyl coupling processes. In this context, it is worth mentioning that we have previously observed biphenyl formation resulting from C-F activation reactions involving photochemically generated magnesium(I) radicals and fluorobenzene.^{15(a)}

In order to circumvent both arene solvent and intramolecular C-H activation pathways, the reduction of **4** was carried out in a methylcyclohexane solution, under an N₂ atmosphere. Upon work-up, a low, but reproducible yield (15%) of the calcium-N₂ complex, **5**, was obtained, as a deep red crystalline solid (Scheme 1). Following the reaction by ¹H NMR spectroscopy revealed a number of species in the reaction solution, none of which could be confidently identified. Compound **5** is thermally stable at room temperature, though is extremely air sensitive in the solid state. Once crystallised, it has negligible solubility in aliphatic solvents. Attempts to dissolve it in benzene, toluene or THF lead to immediate reactions, and formation of complex product mixtures predominated by ^{TCHP}NONH₂. Similarly, compounds **1** react with arenes or THF, though those reactions give well defined THF or arene activation products.⁸ Reactions of slurries of **5** in methylcyclohexane with H₂, H⁺, CO, or PhI all proceeded rapidly at room temperature, but again gave intractable product mixtures.

It seems reasonable that, as potassium alone does not react with N₂, the mechanism of formation of **5** involves potassium reduction of **4** to give a transient calcium(I) radical salt, “K[(^{TCHP}NON)Ca·]”, two units of which reduce N₂, in preference to undergoing an intramolecular reaction. Given the insolubility or reactivity of **5** in common organic solvents, no solution state

spectroscopic data could be obtained for the compound. In the solid state its Raman spectrum displays an N-N stretching band at $\nu = 1419 \text{ cm}^{-1}$. This is at higher wavenumber than the corresponding bands observed for **1a** (1375 cm^{-1}) and **1b** (1376 cm^{-1}),⁸ indicating a lower degree of N₂ activation in **5**. With that said the value for **5** is at the lower end of the range ($1406\text{-}1473 \text{ cm}^{-1}$) typically seen for related neutral $\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2$ bridged dilanthanide complexes,^{5(b)} in which the dinitrogen unit is viewed as an N₂²⁻ dianion.

Like Harder's complexes **1**, the solid-state structure of **5** (Figure 3) shows it to be dinuclear, with an N₂ unit bridging two Ca centres in a side-on fashion. However, unlike **1**, compound **5** is dianionic with the N₂ unit additionally coordinated "end-on" to arene sandwiched potassium ions, with N-K separations (2.690 \AA mean) that imply weak dative bonding interactions. The N-N distance in **5** ($1.265(3) \text{ \AA}$) is close to those in **1a** and **1b** (1.263 \AA mean, and $1.268(2) \text{ \AA}$, respectively), but markedly longer than the bond in N₂ (1.098 \AA).¹⁶ This indicates considerable reduction of the N₂ unit, which should be considered as an N₂²⁻ dianion, while the calcium centres are formally in the +2 oxidation state. The Ca-N₂ bond lengths (2.350 \AA mean) are almost equivalent to the Ca-N_{NON} distances (2.346 \AA mean), while the O-Ca separations (2.409 \AA mean) are comparable to that in [^{Dip}NON)Ca(C₆H₆)₂] (2.378 \AA mean).¹⁴

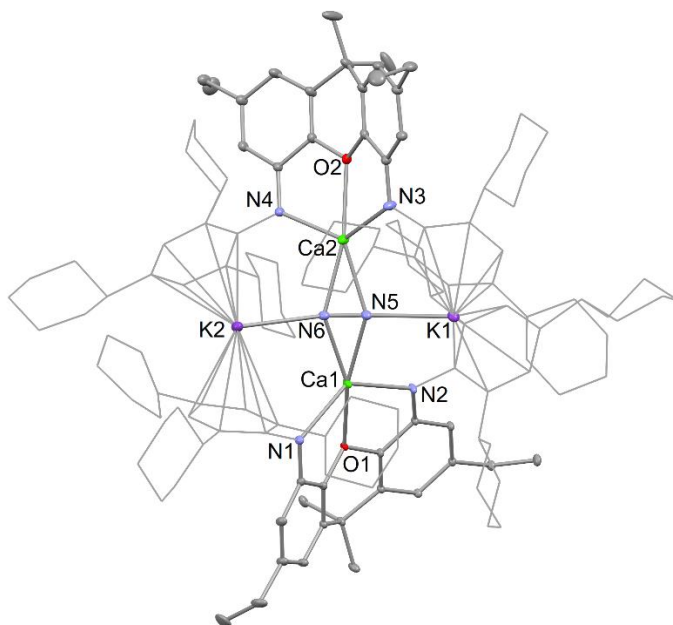


Figure 3. The molecular structure of **5** (20% ellipsoids; TCHP substituents shown as wire frame for clarity; hydrogen atoms omitted).

In order to examine the electronic structure of **5**, DFT calculations (B3PW91) were carried out on the full molecule in the gas phase. The geometry of the molecule optimised to be close to the solid-state structure. As was the case with **1** the dinitrogen unit is essentially doubly reduced to N_2^{2-} (natural charge = -1.43) with both the HOMO and the LUMO being of very high $N_2-\pi^*$ character (energy gap = 2.4 eV, Figure 4). This is reflected in the N-N Wiberg bond index (WBI) of 1.997. Although the bonding between the central N_2^{2-} unit and the Ca and K centres (natural charges = 1.46 and 0.66 respectively) has high ionic character, as shown by the relatively low N-Ca and N-K WBIs (averages of 0.15 and 0.06 respectively), there is a degree of covalency to those interactions. Bond critical points exist between the dinitrogen unit and both Ca and K cations. Moreover, each N_2Ca fragment exhibits a ring critical point (see ESI for further details). The non-trivial involvement of bonding calcium d-orbitals in complexes of that metal has recently been discussed,¹⁷ and has been invoked for **1**. In **5**, however, the contribution of Ca d-orbitals to the HOMO is small (5% according the CMO analysis in NBO06).

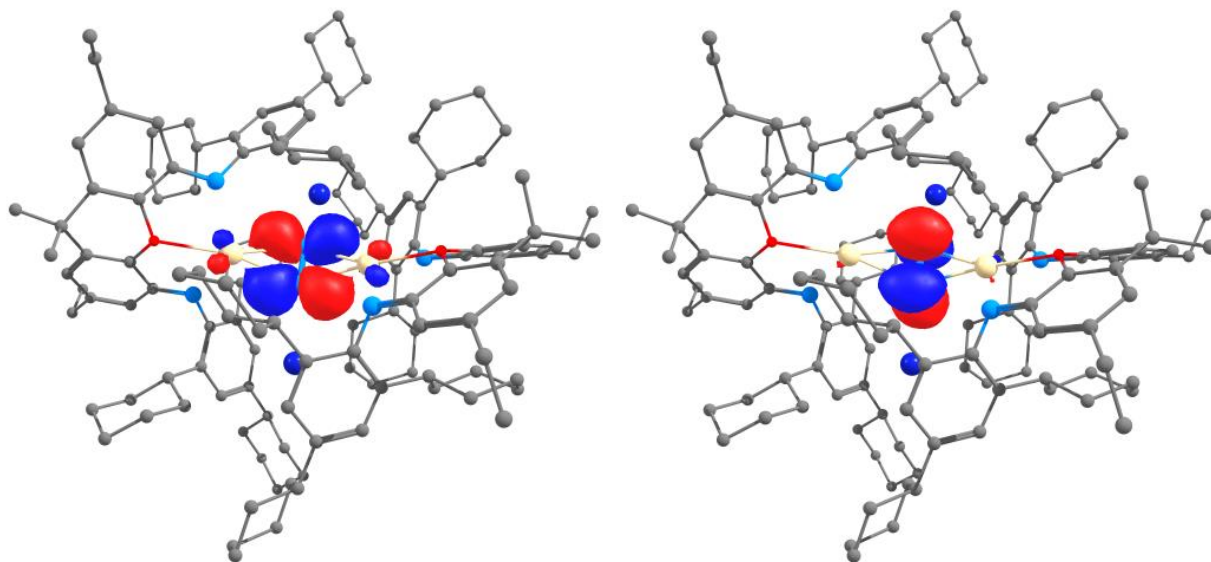


Figure 4. Calculated (B3PW91) HOMO (left) and LUMO (right) of **5**.

In summary, an extremely bulky diamide ligand has been developed, and used to form two monomeric diamido-calcium complexes. Potassium reduction of one of these under an N_2 atmosphere has given the first well-defined, anionic s-block complex of activated dinitrogen; a reaction which likely proceeds *via* a transient calcium(I) intermediate. Raman spectroscopy, X-ray crystallography and computational studies indicate that the complex contains an N_2^{2-} anion, which has a high degree of ionic character to its bonding with the Ca^{2+} and K^+ cations. We continue to pursue the kinetic stabilisation of heavier group 2 metal(I) complexes using bulky diamide ligands, and their use for the activation of dinitrogen.

Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for all new compounds. Full details of computational studies. Crystal data, details of data collections and refinements. CCDC numbers: 2204507-2204511. For ESI and crystallographic data in CIF format see DOI: 10.xxxxxxx

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgement

CJ is grateful to the Australian Research Council and the US Air Force Asian Office of Aerospace Research and Development (grant FA2386-21-1-4048) for funding this work. LM is a senior member of the Institut Universitaire de France and thanks the Humboldt Foundation. CalMip is acknowledged for a generous grant of computing time.

References

1. See, for example: T.-T. Liu, D.-D. Zhai, B.-T. Guan, Z.-J. Shi, *Chem. Soc. Rev.*, 2022, **51**, 3846-3861.
2. See, for example: (a) C. Van Stappen, L. Decamps, G. E. Cutsail, R. Bjornsson, J. T. Henthorn, J. A. Birrell, S. DeBeer, *Chem. Rev.*, 2020, **120**, 5005–5081; (b) B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean, L. C. Seefeldt, *Chem. Rev.*, 2014, **114**, 4041–4062.
3. See, for example: (a) A. J. Martin, T. Shinagawa, J. Perez-Ramirez, *Chem*, 2019, **5**, 263-283; (b) Z.-J. Lv, J. Wei, W.-X. Zhang, P. Chen, D. Deng, Z. J. Shi, Z. Xi, *Nat. Sci. Rev.*, 2020, **7**, 1564-1583; (c) R. Schlögl, *Ammonia Synthesis*, in *Handbook of Homogeneous Catalysis*, G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Eds., Wiley-VCH, 2008.
4. See, for example: (a) M. J. Chalkley, M. W. Drover, J. C. Peters, *Chem. Rev.*, 2020, **120**, 5582-5636; (b) S. Kim, F. Loose, P. J. Chirik, *Chem. Rev.*, 2020, **120**, 5637-5681; (c) D. Singh, W. R. Buratto, J. F. Torres, L. J. Murray, *Chem. Rev.*, 2020, **120**, 5517-5581.
5. See, for example: (a) A. J. Ryan, S. G. Balasubramani, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.*, 2020, **142**, 9302-9313; (b) M. E. Fieser, D. H. Woen, J. F. Corbey, T. J. Mueller, J. W. Ziller, W. J. Evans, *Dalton Trans.*, 2016, **45**, 14634-14644.
6. (a) M.-A. Legare, G. Belanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels, H. Braunschweig, *Science*, 2018, **359**, 896-900; (b) M.-A. Legare, M. Rang, G. Belanger-Chabot, J. I. Schweizer, I. Krummenacher, R. Bertermann, M. Arrowsmith, M.

- C. Holthausen, H. Braunschweig, *Science*, 2019, **363**, 1329-1332; (c) M.-A. Legare, G. Belanger-Chabot, M. Rang, R. D. Dewhurst, I. Krummenacher, R. Bertermann, H. Braunschweig, *Nat. Chem.*, 2020, **12**, 1076–1080.
7. G. J. Moody, J. D. R. Thomas, *J. Chem. Educ.*, 1966, **43**, 205–206.
8. R. Bösch, T. X. Gentner, J. Langer, C. Fäber, J. Eysel, L. Zhao, C. Ding, G. Frenking, S. Harder, *Science*, 2021, **371**, 1125-1128.
9. N.B. s-Block/d-block bimetallic systems are known to cooperatively activate N₂. See, for example: K. Yuvaraj, A. Paparo, A. J. R. Matthews, C. Jones, *Eur. J. Inorg. Chem.*, 2021, **2021**, 4998-5003.
10. J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics*, 2018, **37**, 4810-4813.
11. (a) C. Jones, *Nat. Rev. Chem.*, 2017, **1**, 0059; (b) C. Jones, *Commun. Chem.*, 2020, **3**, 159.
12. H.-T. Liu, R. J. Schwamm, S. E. Neale, M. S. Hill, C. L. McMullin, M. F. Mahon, *J. Am. Chem. Soc.*, 2021, **143**, 17851-17856.
13. See, for example: (a) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Angew. Chem. Int. Ed.*, 2021, **60**, 1702-1713; (b) L. F. Lim, M. Judd, P. Vasko, M. G. Gardiner, D. A. Pantazis, N. Cox, J. Hicks, *Angew. Chem. Int. Ed.*, 2022, **61**, e202201248; (c) F. Kramer, M. S. Luff, U. Radius, F. Weigend, F. Breher, *Eur. J. Inorg. Chem.*, 2021, **2021**, 3591-3600; (d) J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, *Nature*, 2018, **557**, 92-95.
14. J. S. McMullen, A. J. Edwards, J. Hicks, *Dalton Trans.*, 2021, **50**, 8685-8689.
15. (a) D. D. L. Jones, I. Douair, L. Maron, C. Jones, *Angew. Chem. Int. Ed.*, 2021, **60**, 7087-7092; (b) K. Yuvaraj, I. Douair, D. D. L. Jones, L. Maron, C. Jones, *Chem. Sci.*, 2020, **11**, 3516-3522; (c) D. D. L. Jones, S. Watts, C. Jones, *Inorganics*, 2021, **9**, 72.
16. “*Tables of Interatomic Distances and Configurations in Molecules and Ions*”, *Chemical Society Special Publications*, ed. L. E. Sutton, The Chemical Society, London, 1958, vol. 11.

17. See, for example: (a) X. Wu, L. Zhao, J. Jin, W. Lei, X. Jin, G. Wang, M. Zhou, G. Frenking, *Science*, 2018, **361**, 912-916; (b) C. R. Landis, R. P. Hughes, F. Weinhold, *Science*, 2019, **365**, aay2335.