



Cite this: DOI: 10.1039/d5cc06477e

Received 14th November 2025,
Accepted 4th December 2025

DOI: 10.1039/d5cc06477e

rsc.li/chemcomm

Fluorenyl-tethered N-heterocyclic carbene complexes of the heavy alkali metals

Stuart Burnett,^a Alan R. Kennedy,^a Stephen M. Mansell^{*b} and Catherine E. Weetman^{†a}

The coordination chemistry of N-heterocyclic carbenes (NHCs) with Group 1 metals remains comparatively underdeveloped relative to their extensive application across the periodic table. Herein, we describe the synthesis of rubidium and caesium complexes incorporating a fluorenyl-tethered NHC ligand. Additionally, the first heterobimetallic Cs/Li NHC complex was obtained via treatment with a combination of alkali metal amide bases.

Since the first discovery of a stable N-heterocyclic carbene (NHC), this ligand class has become vital to modern synthetic chemistry.^{1,2} Their use as strong σ -donor ligands spans not only the transition metals but also increasingly into main group coordination chemistry, particularly in the stabilisation of reactive low oxidation state species that had previously been inaccessible via conventional routes.³ While NHCs have become one of the most commonly encountered ligand systems, their application in Group 1 metal complexes has remained largely confined to lithium,^{4–8} with only a select few examples of sodium and potassium NHC complexes reported in the literature.^{9–13} Notably, the only structurally characterised NHC complexes of Rb (**1c**) and Cs (**1d**) were very recently detailed by Tamm and co-workers, who utilised a trimethylsilyl-protected anionic NHC to afford the complete series of alkali metal salt complexes via reaction with the corresponding alkali metal *tert*-butoxides (Fig. 1a).¹⁴ This scarcity of heavier alkali metal NHC complexes is unsurprising based on the trend of decreasing metal-carbene bond strength upon descending the group.¹⁵

Tethered NHC ligands – a typical carbene moiety bound to an ancillary donor group such as neutral N or P based groups,^{16–18} anionic groups such as aryl/alkoxide^{19,20} or polycyclic aromatic hydrocarbons *e.g.*, fluorenyl, indenyl²¹ – have emerged as a versatile ligand subclass.²² Early notable examples using these anionic tethered NHC ligands in Group 1 metal complexes include a report from Arnold and co-workers

in 2003 of the first structurally characterised, amido functionalised, NHC–Li complex.²³ This was followed in 2005 by the same group where they describe the synthesis of the first potassium NHC complexes featuring an alkoxy-tethered NHC ligand (Fig. 1b).²⁴ In the solid state, these form tetrameric [K–NHC] aggregates, where each potassium cation coordinates to three alkoxy-groups and one carbene centre. The Danopoulos group subsequently reported in 2007 a series of NHC–potassium complexes using fluorenyl- and indenyl-tethers (Fig. 1c), which served as effective ligand transfer reagents in the synthesis of various transition metal complexes.^{25–27} More recently, Mansell and co-workers were able to extend the use of fluorenyl-tethered saturated NHCs to access homobimetallic

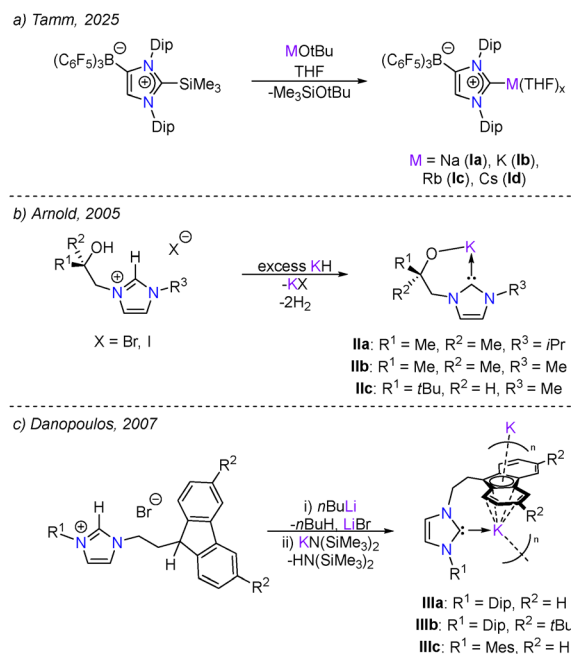


Fig. 1 Reported examples of NHC Rb and Cs complexes (a) and tethered NHC alkali metal complexes (b) and (c). Dip = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl.

^a Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, UK. E-mail: catherine.weetman@strath.ac.uk

^b Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK. E-mail: s.mansell@hw.ac.uk



While the reported synthesis of imidazolium salt **1** requires heating dioxane solutions of mesitylimidazole and 9-(2-bromoethyl)-9H-fluorene to 100 °C for 5 days (79%),^{26,36} improved yields (85%) and similar purity (as judged by ¹H NMR spectroscopy) could be obtained by simply heating the aforementioned starting materials to 100 °C overnight in the absence of solvent. In line with previous reports, addition of one equivalent of *n*BuLi to –80 °C toluene solutions of **1** affords the corresponding free carbene *in situ*, which upon subsequent addition to toluene solutions of RbN(SiMe₃)₂ or CsN(SiMe₃)₂, respectively, yields the Rb and Cs complexes **2** and **3** (Scheme 1). Complexes **2** and **3** were isolated as air- and moisture-sensitive red powders in yields of 25% and 34%, respectively. Both are essentially insoluble in typical non-donor hydrocarbon solvents (hexane, benzene, toluene) but dissolve readily in THF. NMR spectroscopic analysis of both suggested structures consistent with those proposed in Scheme 1, with only minor shifts observed in the resonances between the two spectra (*e.g.* Mes-*o*-CH₃ appears at 1.63 ppm for **2** and 1.67 ppm for **3**). The carbenic carbon gives rise to a very weak resonance at 210.0 ppm in the ¹³C{¹H} NMR spectrum of **2**, while no chemical shifts attributable to the carbenic carbon were observed for **3**. However, coupling was observed between the ethyl-bridge CH₂ and a weak resonance at 212.7 ppm in its ¹H-¹³C HMBC NMR spectrum (Fig. S10), allowing for assignment of the carbene centre in **3**. These are noticeably at higher chemical shift when compared with similar carbene chemical shift ranges in related fluorenyl-tethered alkali



Scheme 1 Synthesis of fluorenyl-tethered NHC Rb (**2**) and Cs (**3**) complexes.

metal complexes (*cf.* **IIa** at 198.7 ppm and **IIIa** at 206.9 ppm)^{24,25} but are slightly upfield relative to Tamm's anionic NHC complexes (216.9 ppm Rb (**Ic**) and 216.2 ppm Cs (**Id**), respectively).¹ Complex **2** shows good stability in solution – heating THF-*d*₈ solutions to 80 °C for three days results in only minor decomposition. In contrast, complex **3** exhibits more notable decomposition under the same conditions (approximately 60% of **3** remaining), with formation of at least two new mesityl-containing fragments observed in the ¹H NMR spectrum (Fig. S11). No resonances were observed in the ¹³³Cs NMR spectrum of **3** between the range of –200 ppm and +200 ppm, likely due to issues arising from the quadrupolar nature of ¹³³Cs.

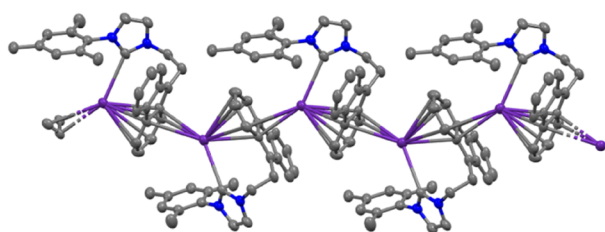
Recrystallisation of **2** from a layered THF/pentane solution, and **3** from a layered THF/benzene solution, afforded single crystals suitable for analysis by X-ray diffraction. The molecular structures of both are shown in Fig. 2 and are consistent with their spectroscopic data. Both complexes **2** and **3** crystallise in the monoclinic $P2_1/c$ space group as a polymeric species, due to the cation- π interaction between the central Rb/Cs cation and the fluorenyl-tether, with the hapticity of the metal-aryl interactions ranging from η^3 to η^6 depending on the aryl substituent. No interaction between the metal centre and the mesityl substituent was observed, similar to the potassium derivatives reported by Danopoulos.²⁵ The Rb-C_{carbene} (3.067(3) Å and 3.088(3) Å) and Cs-C_{carbene} (3.220(2) Å and 3.183(2) Å) bond lengths are among the longest reported for NHC-alkali metal bonds, as expected with the large ionic radii of both alkali metals, and represent some of the longest reported of the fluorenyl-tethered NHC alkali metal complexes.³⁷ These are also in line with those reported for Tamm's NHC Rb and Cs complexes (Rb (**1c**): 3.066(5) Å and 3.078(2) Å; Cs (**1d**): 3.3815(16) Å). As would be expected, the deviation from linearity of the M-NHC bond (pitch angle)³⁸ increases from 17.8° in **2** to 21.6° in **3**. A similar trend is noted across the series of alkali metal NHC complexes reported by Tamm.¹⁴

From one such attempted synthesis of **3** a red crystalline solid was obtained, which was revealed to be the heterobimetallic Cs/Li complex **4** by single crystal X-ray diffraction analysis (Fig. 3). The formation of **4** likely arises from contamination of the CsN(SiMe₃)₂ used in this synthesis. A previous report from O'Hara and co-workers showed that altering the ratio of LiN(SiMe₃)₂ to CsF in the synthesis of CsN(SiMe₃)₂ affords a mixed metal [Cs/Li{N(SiMe₃)₂}]_∞ species.³⁹ The aforementioned molecular structure of **4** showed poor quality and thus is only included here for completeness, although the connectivity is consistent with solution state spectroscopic data (*vide infra*).

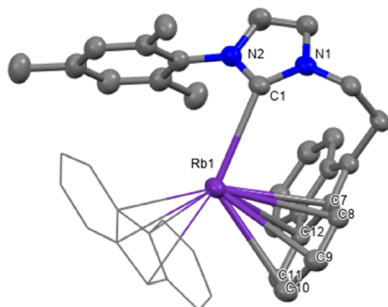
Complex **4** could be independently synthesised using a mixture of pure CsN(SiMe₃)₂ and LiN(SiMe₃)₂ in a 2:1 ratio (Scheme 2). Similarly, addition of preformed [CsLi{N(SiMe₃)₂}₂] to benzene-d₆ suspensions of **3** resulted in the formation of **4** as judged by ¹H NMR spectroscopy, albeit at a slower rate than the aforementioned method due to the poor solubility of **3** in benzene-d₆. **4** was isolated as a red crystalline solid and showed good solubility in toluene and benzene. No decomposition of **4** was observed after heating benzene-d₆ solutions to 80 °C for 3 days.

All expected chemical shifts based on the solid-state structure were observed in the ^1H NMR spectrum of **4**, with similar

(A) Rb Polymer network



(B) Rb Monomeric unit



(C) Cs Monomeric unit

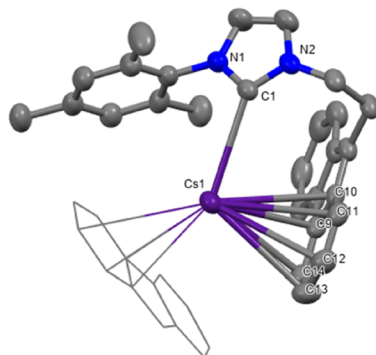


Fig. 2 Molecular structures (50% thermal ellipsoids) of **2** (polymer expansion of Rb2 network (A) and monomeric unit of Rb1 network (B)) and **3** (monomeric unit (C)). The fluorenyl ring system of the connecting unit in B and C is displayed in wireframe. Hydrogen atoms have been omitted from both for clarity. Selected bond lengths (Å) and angles (°): Complex **2** – Rb1–C1: 3.067(3), Rb1'–C6: 3.277(3), Rb1'–C7: 3.088(3), Rb1–C7: 3.284(3), Rb1–C8: 3.402(4), Rb1–C9: 3.421(4), Rb1–C10: 3.342(4), Rb1–C11: 3.251(3), Rb1'–C12: 3.238(3), Rb1–C12: 3.209(3), Rb1'–C13: 3.528(3), Rb1–C18: 3.543(3), Rb2–C28: 3.088(3), Rb2'–C34: 3.157(3), Rb2–C34: 3.327(4), Rb2'–C35: 3.363(4), Rb2–C35: 3.430(4), Rb2–C36: 3.472(4), Rb2–C37: 3.414(4), Rb2–C38: 3.310(4), Rb2–C39: 3.241(3), Rb2'–C39: 3.438(3), Rb1–C1–N1: 136.4(2), Rb1–C1–N2: 116.8(2). Complex **3** – Cs1–C1: 3.220(2), Cs1–C9: 3.361(2), Cs1'–C9: 3.523(2), Cs1–C10: 3.439(2), Cs1'–C10: 3.293(2), Cs1–C11: 3.562(2), Cs1'–C11: 3.405(2), Cs1–C12: 3.625(3), Cs1'–C12: 3.687(3), Cs1–C13: 3.589(3), Cs11–C14: 3.454(3), Cs2–C28: 3.183(2), Cs2'–C33: 3.524(2), Cs2–C40: 3.410(2), Cs2'–C40: 3.352(2), Cs2–C41: 3.410(3), Cs2–C42: 3.568(3), Cs2–C43: 3.651(3), Cs2–C44: 3.594(3), Cs2'–C44: 3.521(2), Cs2–C45: 3.426(2), Cs2'–C45: 3.186(2), Cs1–C1–N1: 110.6(15), Cs1–C1–N2: 140.2(16).

environments observed for the mesityl- and fluorenyl-substituents as those observed in **3**, while exhibiting a notable downfield shift at 0.33 ppm of the N(Si(CH)₃)₂ group in comparison to that previously reported for [CsLi{N(SiMe₃)₂}₂] (0.27 ppm). Similar to **3**, no resonance for the carbene centre

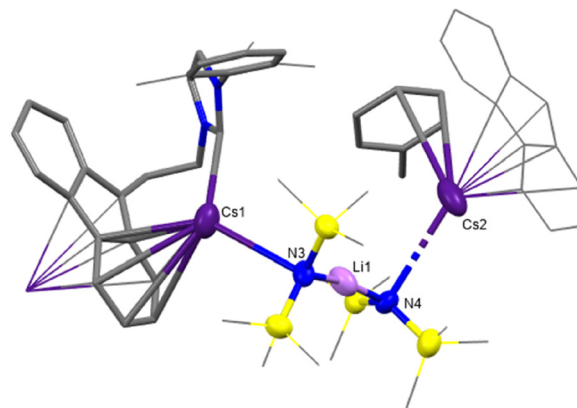
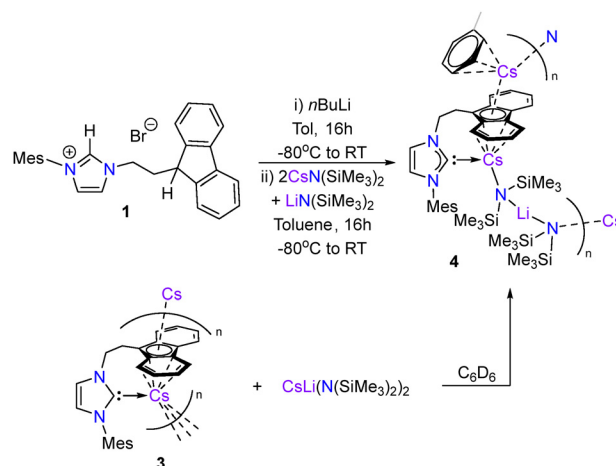


Fig. 3 Molecular structure of **4**. Central Cs, Li, Si and N atoms shown with 50% thermal ellipsoids, carbon in capped sticks, methyl groups and connecting fluorenyl unit displayed in wireframe. Connectivity data only.



Scheme 2 Synthesis of Cs/Li heterobimetallic NHC complex **4**.

was observed in the ¹³C{¹H} NMR spectrum of **4**, however, coupling was again seen in the ¹H–¹³C HMBC spectrum between the ethyl-bridged CH₂ and a weak resonance at 210.9 ppm. Only one broad resonance was observed in the ¹³³Cs NMR spectrum (Fig. S18) as opposed to the expected two, again likely due to the quadrupolar nature of ¹³³Cs, or the presence of a dynamic process in solution.

It is of note that the resonances attributable to the coordinated toluene molecule are observed at the same chemical shift as free toluene, suggesting dissociation in solution. Subsequent analysis by ¹H-DOSY NMR spectroscopy confirms this (Fig. S19), whereby notable separation of the resonances attributable to monomeric complex **3**, [CsLi{N(SiMe₃)₂}₂] and toluene was observed. Multiple attempts to crystallise and analyse complex **4** by single crystal X-ray diffraction resulted in unit cell checks matching that found for **3**, again affirming the ease with which **4** can dissociate in solution.

Using a fluorenyl-tethered NHC system, we have synthesised and structurally characterised only the second examples of N-heterocyclic carbene-stabilised Rb and Cs complexes, and



the first examples of such heavy alkali metals stabilised by a fluorenyl-tethered NHC donor. A related Cs/Li heterobimetallic species could also be synthesised using a combination of the respective metal amide bases. As expected, these species contain some of the longest reported alkali metal-carbene bond lengths due to the large ionic radii of the metals involved. These species also highlight the importance of π -interactions in the stabilisation of such heavy alkali metal complexes whereas conventional monodentate-NHC ligands have in the past fallen short. With the rise of well-defined organocaesium complexes in catalytic applications, these compounds represent a significant synthetic achievement and one for future reactivity studies.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. SB: writing – original draft, formal analysis, data curation. ARK: writing – review & editing, validation, formal analysis. SMM: writing – review & editing, validation, formal analysis, conceptualization. CEW: writing – review & editing, validation, supervision, project administration, funding acquisition, formal analysis, conceptualization.

We thank Craig Irving for assistance with NMR spectroscopy and Janie-Anne Pickrell for technical support. This work was supported by the EPSRC New Investigator Award [EP/Y015754/1]. CEW would like to thank the University of Strathclyde for the award of a Chancellor's Fellowship.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data that supports the findings of this study are available from the University of Strathclyde Knowledge Base Pure data repository at <https://doi.org/10.15129/c6ec8b54-de92-4b76-9eb2-bb54af4c2fb4>.

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: general synthetic experimental details, NMR spectra, X-ray crystallography. See DOI: <https://doi.org/10.1039/d5cc06477e>.

CCDC 2501678–2501680 contain the supplementary crystallographic data for this paper.^{40a–c}

References

- 1 F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172.
- 2 M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485–496.
- 3 V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, *Chem. Rev.*, 2018, **118**, 9678–9842.
- 4 R. Fränkel, C. Birg, U. Kernbach, T. Haberer, H. Nöth and W. P. Fehlhammer, *Angew. Chem., Int. Ed.*, 2001, **40**, 1907–1910.
- 5 A. J. Arduengo, M. Tamm, J. C. Calabrese, F. Davidson and W. J. Marshall, *Chem. Lett.*, 1999, 1021–1022.
- 6 M. Brendel, J. Wenz, I. V. Shishkov, F. Rominger and P. Hofmann, *Organometallics*, 2015, **34**, 669–672.
- 7 J. Obenlünenschloß, N. Boysen, K. Rönnyby, A. Muriqi, V. Hoffmann, C. Abad, D. Rogalla, U. Brokmann, E. Rädlein, M. Nolan and A. Devi, *Angew. Chem., Int. Ed.*, 2025, e202513066.
- 8 A. Stasch, S. P. Sarish, H. W. Roesky, K. Meindl, F. Dall'Antonia, T. Schulz and D. Stalke, *Chem. – Asian J.*, 2009, **4**, 1451–1457.
- 9 M. S. Hill, G. Kociok-Köhn and D. J. MacDougall, *Inorg. Chem.*, 2011, **50**, 5234–5241.
- 10 D. R. Armstrong, S. E. Baillie, V. L. Blair, N. G. Chabloz, J. Diez, J. Garcia-Alvarez, A. R. Kennedy, S. D. Robertson and E. Hevia, *Chem. Sci.*, 2013, **4**, 4259.
- 11 R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. Guy Orpen and M. J. Quayle, *Chem. Commun.*, 1999, 241–242.
- 12 S. Bellemín-Laponnaz and S. Dagorne, *Chem. Rev.*, 2014, **114**(18), 8747–8774.
- 13 M. Bhandari and S. Yruegas, *Eur. J. Inorg. Chem.*, 2025, e202400560.
- 14 L. J. Groth, D. Bockfeld and M. Tamm, *Chem. Commun.*, 2025, **61**, 15806–15809.
- 15 K. C. Edwards, M. Vasiliu, J. W. Maxwell, C. E. Castillo, D. M. Marion, R. Craciun, J. F. Hall, D. Tapu and D. A. Dixon, *J. Phys. Chem. A*, 2023, **127**, 10838–10850.
- 16 D. Pugh and A. A. Danopoulos, *Coord. Chem. Rev.*, 2007, **251**, 610–641.
- 17 O. Köhl, *Chem. Soc. Rev.*, 2006, **36**, 592–607.
- 18 T. Simler, L. Karmazin, C. Bailly, P. Braunstein and A. A. Danopoulos, *Organometallics*, 2016, **35**, 903–912.
- 19 S. Hameury, P. De Frémont and P. Braunstein, *Chem. Soc. Rev.*, 2017, **46**, 632–733.
- 20 D. Zhang and G. Zi, *Chem. Soc. Rev.*, 2015, **44**, 1898–1921.
- 21 K. J. Evans and S. M. Mansell, *Chem. – Eur. J.*, 2020, **26**, 5927–5941.
- 22 B. Royo and E. Peris, *Eur. J. Inorg. Chem.*, 2012, 1309–1318.
- 23 P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.*, 2003, **42**, 5981–5984.
- 24 P. L. Arnold, M. Rodden and C. Wilson, *Chem. Commun.*, 2005, 1743.
- 25 S. P. Downing and A. A. Danopoulos, *Organometallics*, 2006, **25**, 1337–1340.
- 26 S. P. Downing, S. C. Guadaño, D. Pugh, A. A. Danopoulos, R. M. Bellabarba, M. Hanton, D. Smith and R. P. Tooze, *Organometallics*, 2007, **26**, 3762–3770.
- 27 S. P. Downing, P. J. Pogorzelec, A. A. Danopoulos and D. J. Cole-Hamilton, *Eur. J. Inorg. Chem.*, 2009, 1816–1824.
- 28 K. J. Evans and S. M. Mansell, *Chem. – Eur. J.*, 2019, **25**, 3766–3769.
- 29 K. J. Evans, C. L. Campbell, M. F. Haddow, C. Luz, P. A. Morton and S. M. Mansell, *Eur. J. Inorg. Chem.*, 2019, 4894–4901.
- 30 M. G. Davidson, D. Garcia-Vivo, A. R. Kennedy, R. E. Mulvey and S. D. Robertson, *Chem. – Eur. J.*, 2011, **17**, 3364–3369.
- 31 T. X. Gentner and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2021, **60**, 9247–9262.
- 32 S. D. Robertson, M. Uzelac and R. E. Mulvey, *Chem. Rev.*, 2019, **119**, 8332–8405.
- 33 P. A. Macdonald, S. Banerjee, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2023, **62**, e202304966.
- 34 H.-Z. Du, J.-Z. Fan, Z.-Z. Wang, N. A. Strotman, H. Yang and B.-T. Guan, *Angew. Chem., Int. Ed.*, 2023, **62**, e202214461.
- 35 F. Krämer, M. H. Crabbe, I. Fernández and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2025, **64**, e202516376.
- 36 J. Kukral, P. Lehmus, M. Klinga, M. Leskelä and B. Rieger, *Eur. J. Inorg. Chem.*, 2002, 1349–1356.
- 37 Based on a search of the Cambridge Structural Database (CSD). Accessed 10th November 2025.
- 38 N. Schwarz, X. Sun, R. Yadav, R. Köppe, T. Simler and P. W. Roesky, *Chem. – Eur. J.*, 2021, **27**, 12857–12865.
- 39 A. I. Ojeda-Amador, A. J. Martínez-Martínez, A. R. Kennedy and C. T. O'Hara, *Inorg. Chem.*, 2016, **55**, 5719–5728.
- 40 (a) CCDC 2501678: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2pz696](https://doi.org/10.5517/ccdc.csd.cc2pz696); (b) CCDC 2501679: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2pz6b7](https://doi.org/10.5517/ccdc.csd.cc2pz6b7); (c) CCDC 2501680: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2pz6c8](https://doi.org/10.5517/ccdc.csd.cc2pz6c8).

