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[(TMEDA)Li(μ -PPh₂)₂K(TMEDA)(THF)]: a heterobimetallic molecular lithium–potassium phosphide complex†

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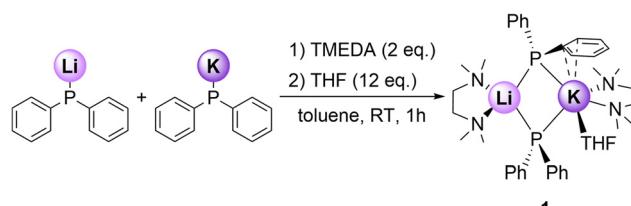
Made by a co-complexation reaction, heterobimetallic $[(\text{TMEDA})\text{Li}(\mu\text{-PPh}_2)_2\text{K}(\text{TMEDA})(\text{THF})]$ has been crystallographically and spectroscopically characterised, modelled by DFT calculations, and its performance compared against those of its homometallic phosphide components in preliminary studies of its application in catalytic hydrophosphination reactions of a representative alkene.

The beginning of organometallic compounds containing two distinct alkali metals can be traced back to Wittig’s 1950s discovery of di-organo-lithium–sodium compounds (here, organo is *n*-Bu or Ph).^{1–3} Brønsted basicity is a feature of these compounds and also of related early bimetallics such as potassium hydride–butyllithium.⁴ However, it was when Lochmann⁵ and Schlosser,⁶ building on studies by Morton,^{7,8} independently introduced the *n*-butyllithium–potassium-*t*-butoxide “superbase” that the synthetic community had found its first widely utilised bi-alkali-metal reagent. Significantly, hitherto none of these aforementioned bimetallics has been unequivocally structurally characterised, though assiduous work by Klett has uncovered a complexity of various $\text{Li}_x\text{K}_y\text{Np}_z(\text{OrBu})_{x+y-z}$ structures using neo-pentyl as an *n*-Bu substitute that almost certainly reveals the essential likeness of the Li–K superbase structure/s.^{9,10} Mixed alkali metal structures with organonitrogen ligands have also appeared such as guanidinide $\text{LiNa}_3[\text{O}=\text{P}(\text{NMe}_2)_3]_3[\text{N}=\text{C}(\text{NMe}_2)_2]_4$,¹¹ and the series of hexamethyldisilazides $[(\text{THF})_x\text{M}^1\text{M}^2\text{N}(\text{SiMe}_3)_2]$,¹² the first mixed bi-alkali-metal examples of a popular utility amide. Alkali metal amides have long been complementary useful reagents to their alkyl alkali metal counterparts, and they too have been incorporated into synergistically operative mixed alkali metal compounds,¹³ notably the LINK (*n*BuLi/KOtBu/TMP) system¹⁴ (TMP is 2,2,6,6-tetramethylpiperidine), as well as mixed mono-alkali-metal

bimetallics such as the turbo-Grignard reagents and inverse crown complexes,¹⁵ each of which incorporates a non-alkali metal, most typically magnesium.

In contrast to the sizable number of known organocarbon and organonitrogen mixed alkali metal compounds,^{16,17} organophosphorus examples are exceptionally rare. Westerhausen reported a phosphanediide example in $[\text{Li}_6\text{K}_6\text{Ba}\{\text{P}(\text{SiMe}_3)\}_6(\text{OSiPr}_3)_2]$,¹⁸ but to the best of our knowledge, hitherto there has been no secondary phosphide example. Here, we open this chemical space by the successful synthesis, NMR and X-ray crystallographic characterisation of the monomeric, dinuclear lithium–potassium phosphide, $[(\text{TMEDA})\text{Li}(\mu\text{-PPh}_2)_2\text{K}(\text{TMEDA})(\text{THF})]$, **1** (TMEDA is *N,N,N’,N’*-tetramethylethylenediamine).

Co-complexation reactions, such as in the addition of two different monometallic complexes, have become a facile and efficient way of generating heterobimetallic complexes.^{19–21} To access new mixed alkali metal organophosphorus compounds, we followed co-complexation procedures. Equimolar quantities of LiPPh₂ and KPPh₂ in toluene solution formed an orange suspension after 1 h at room temperature, which on adding two molar equivalents of Lewis donor TMEDA followed by twelve equivalents of THF gave an orange solution (Scheme 1). Volatiles were removed under reduced pressure to yield an orange oil, which upon trituration with hexane gave an isolable orange powder. THF was required to solubilise **1** in *d*₆-benzene for NMR characterisation. The ¹H spectrum revealed the expected singlet resonances for TMEDA at 1.97 ppm and 2.01 ppm, and



Scheme 1 Co-complexation synthesis of the title compound **1**.

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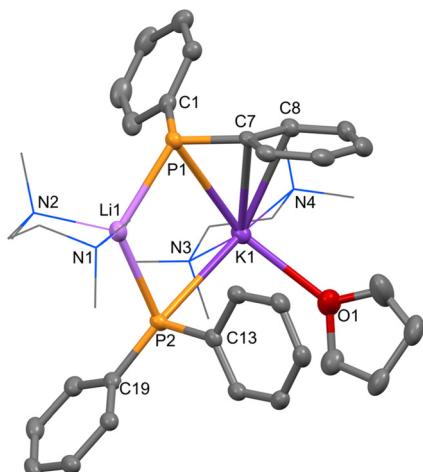


Fig. 1 Molecular structure of $\text{LiK}(\text{PPh}_2)_2(\text{TMEDA})_2\text{THF}$, **1**. Thermal ellipsoids have been drawn at 50% probability, H atoms omitted and TMEDA ligands drawn in wireframe for clarity. Selected bond lengths (Å) and angles (°): Li1–P1 2.602(2); Li1–P2 2.599(3); K1–P1 3.4466(5); K1–P2 3.2419(4); Li1–N1 2.130(3); Li1–N2 2.126(3); K1–N3 2.839(2); K1–N4 2.906(10); K1–O1 2.6892(14); K1–C7 3.2983(14); K1–C8 3.1566(14); P2–Li1–P1 116.36(9); P2–K1–P1 82.649(11); K1–P1–Li1 77.99(6); K1–P2–Li1 81.99(6).

resonances in the aromatic range 6.77–7.82 ppm. Both the ^7Li and ^{31}P NMR spectra showed one singlet at 1.48 ppm and –21.2 ppm, respectively. ^{31}P NMR analysis of solutions prepared of component monometallic complexes $[\text{LiPPh}_2(\text{TMEDA})]_2$ [–26.0 ppm] and $[\text{KPPh}_2(\text{TMEDA})]_n$ [–15.7 ppm]²² (see ESI,† p. 14–17) under the same conditions show that the resonance for the product of the co-complexation reaction (–21.2 ppm) lies near the midpoint of those for these compounds, suggestive of the desired formation of the heterobimetallic complex. The ^7Li NMR shift of $[\text{LiPPh}_2(\text{TMEDA})]_2$ [1.16 ppm] is also downfield with respect to that of the mixed-metal solution. Heating the orange suspension in toluene/THF and cooling the mixture at –30 °C, afforded orange crystals. An X-ray diffraction study confirmed these to be heterobimetallic monomer **1** (Fig. 1) crystallised in the triclinic space group $\bar{P}\bar{1}$.

The core feature of **1** is a four-membered LiPKP ring, which is near-planar (\sum endocyclic bond angles, 359°), with an obtuse angle at Li [116.36(9)°], acute angle at K [82.649(11)°] and dissimilar endocyclic angles at the two P bridges [77.99(6)°; 81.99(6)°]. Li–P bond distances [2.602(2) Å and 2.599(2) Å] are within experimental error of each other, while more asymmetry exists in the K–P bonds [3.4466(5) Å and 3.2419(4) Å]. These Li–P and K–P distances are within the range of literature values.²³ These metric differences reflect the greater coordinative asymmetry at K, whereas Li has a distorted tetrahedral geometry comprising two P and two (TMEDA) N atoms [Li1–N1 = 2.130(3) Å; Li1–N2 = 2.126(3) Å], the larger K atom has a coordination number of 7. This comprises two P, two (TMEDA) N and one (THF) O heteroatoms, with saturation completed by the π system of one Ph of the Ph₂P ligand *via* a $\eta^2\text{-C}_2$ (*ipso-ortho*) edge [K1–C7 3.2983(14); K1–C8 3.1566(14)]. This π coordination accounts for the unique Ph₂P ligand environments with P1 in a more distorted tetrahedral geometry than P2 (mean bond angles, 95.4° and 107.8°, respectively) (see Table S4 for selected bond metrics, ESI†). Here,

applying the criteria of Alvarez²⁴ for a geometric analysis of the hapticity of the aryl interactions in **1** (see ESI,† p. 19) predicts that K1 exhibits η^2 coordination to the π system reinforcing the crystallographic metric data.

To gain knowledge of the structure of **1** in solution, we studied it by ^1H diffusion-ordered NMR spectroscopy (DOSY) in d_8 -toluene (see ESI,† p. 12). Excess THF was required to dissolve **1**, since adding fewer equivalents, agitating or heating would cause **1** to precipitate from solution. The order of addition of reagents is also important, as when THF was added first, a mixed-metal species did not form and only the known polymeric $[\text{KPPh}_2]_n$ was isolable.²⁵ DOSY data imply that the $\text{LiK}(\text{PPh}_2)_2$ core is retained in the solution state. The diffusion coefficient D obtained for $\text{LiK}(\text{PPh}_2)_2$ (mean, $4.94 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) predicts that the LiK species in solution has an 18% higher experimental MW_{DOSY} (874 g mol^{–1}) than the theoretical MW of crystalline $\text{LiK}(\text{PPh}_2)_2(\text{TMEDA})_2(\text{THF})$ (721 g mol^{–1}). From our closest prediction to this theoretical MW in $[(\text{TMEDA})\text{Li}(\mu\text{-PPh}_2)_2\text{K}(\text{TMEDA})_2(\text{THF})_3]$ (MW_{diff} –1%), one could speculate that the K– π interactions in the crystal are replaced by two extra K–O (THF) bonds, especially as extra THF was added to dissolve the crystals in d_8 -toluene and since only one Ph₂P type ligand was seen in the ^{31}P NMR spectrum at temperatures as low as –40 °C (see ESI,† Fig. S8, p. 7). However, given that both TMEDA and THF have estimated MWs higher than their theoretical MWs (by –49 and –12%, respectively), complex equilibria are likely to be in play making it difficult to know with any certainty the species present in solution.

The most common alkali metal based structures in the Cambridge Structural Database (CSD)²⁶ are those of lithium compounds, with the greater interest in studying such structures stimulated mainly by the vast utility of organolithium compounds in synthesis. This detail holds true for alkali metal diorganophosphide compounds derived from secondary phosphines (R_2PH), with lithium examples particularly useful as diorganophosphido transfer agents.²⁷ In the case of diphenylphosphine, Ph₂PH, the phosphine used in this study, there are only a handful of Ph₂PLi structures in the database. Aligning well with the fundamental principles of and diversity within organolithium structural chemistry,²⁸ this small collection of structures contains, a solvent-separated ion pair, a monomer, a discrete dimer, and three one-dimensional chain polymers (Fig. 2), with the degree of aggregation controlled by the Lewis base donor solvent stabilising the Lewis acidic metal centre, namely, 12-crown-4, PMDETA, TMEDA, THF ($\times 2$), Et₂O, and DME, respectively. The key factor in this trend is clearly the denticity number of the Lewis base with the hexadentate, tridentate and bidentate donors dictating the solvent-separated ion pair, dimeric, and monomeric structures, respectively, while the weaker low denticity oxygen-based donors are not strong enough to cleave the infinite (P–Li) chain that presumably exists in donor-solvent free Ph₂PLi, which due to its lack of solubility in non-donor solvents has evaded its crystallographic characterisation. Lithium derivatives of other diorganophosphide structures are known, such as those from Cy₂PH,²⁹ t-Bu₂PH,^{30,31} Dipp₂PH,³² Mes₂PH,^{32,33} (Dipp)MesPH,³² $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PH}$ (technically from $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{PCl}$),³⁴ $[(\text{Me}_3\text{Si})_2\text{CH}](\text{Tipp})\text{PH}$,³⁵ $[(\text{Me}_3\text{Si})_2\text{CH}](\text{Dipp})\text{PH}$,³⁶ and $[(\text{Me}_3\text{Si})_2\text{CH}](\text{Ph})\text{PH}$.³⁷

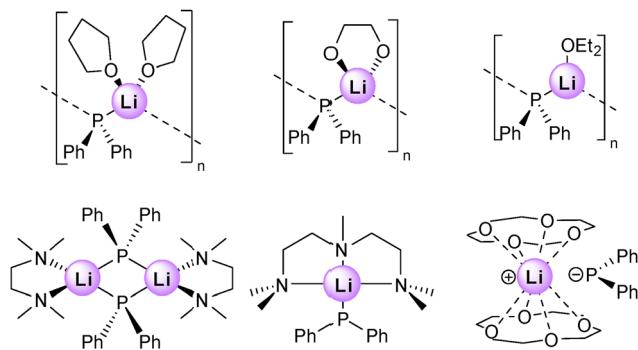


Fig. 2 Selection of reported crystallographically-characterised donor adducts of Ph_2PLi .

Noteworthy among these structures is $[\text{LiPt-Bu}_2(\text{THF})]_4$,³⁸ a discrete tetrameric molecule best described as a four Li-P rung ladder that is truncated by the presence of THF caps at the ladder end rungs. This structure is an early example of lithium organoelement structures that fit perfectly well into the ring-laddering concept³⁹ developed initially through the study of lithium organonitrogen compounds.

A search of the CSD revealed only four hits for Ph_2PK structures (Fig. 3). The larger coordination sphere of potassium⁴⁰ generally gives rise to more complexity in these structures compared to that of its lithium counterparts. Donor-solvent-free Ph_2PK ,²⁵ the product of an unplanned elimination reaction of Ph_2P from metallation of $\text{HC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{PPh}_2)$, exists as a complicated supramolecular network structure containing connected KPKP and KPKPKP four- and six-membered rings, respectively, which propagate mainly *via* K-Ph π -contacts. The bis-solvate $[\{\text{K}(\text{dioxane})_2\text{PPh}_2\}]_\infty$ ⁴¹ continues this 3-dimensional network connectivity through a combination of dioxane bridges, which have transoid type O donor centres and K-Ph π -contacts. In $[\{\text{Ph}_2\text{PK}(\text{PMDETA})\}]_\infty$ ⁴² the extra denticity provided by a tridentate PMDETA ligand reduces the supramolecular structure to a one-dimensional K-P bonded chain. Finally, the structure of $[\{\text{Ph}_2\text{P}\}[\text{K}_2(18\text{-crown-6})_2]^+[\text{PPh}_2^-]^\infty]$ ⁴³ is charge-separated comprising a Ph_2P^- anion sandwiched between two K(18-crown-6)⁺

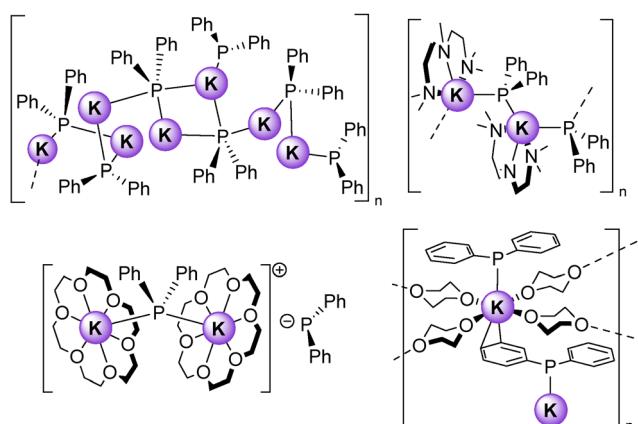


Fig. 3 Selection of reported crystallographically-characterised donor adducts of Ph_2PK .

cations as well as a second, separated Ph_2P^- anion. Potassium derivatives of other diorganophosphide structures are known including Dipp_2PH ,³² $t\text{-Bu}_2\text{PH}$,⁴⁴ $\text{Ph}(t\text{Bu})\text{PH}$,⁴⁵ and $(\text{Ter})\text{iPrPH}$.⁴⁶ Note that no mixed lithium–potassium diphenylphosphide structure was found in CSD searches.²⁶ Evidence that such structural knowledge is more important than just for curiosity value comes from our recent report on catalytic hydrophosphination reactions of alkynes.⁴⁷ Here, a clear correlation was found between the catalytic efficiency and the denticity of the donor and aggregation state of the NaPPh_2 -donor catalyst employed.

DFT calculations were performed to support the experimental findings in this study. QTAIM calculations reveal bond paths and critical points around the central Li-P-K-P core. Negative charges on the phosphorus extend in the direction of Li; however, the values of $\rho(r)$ and $\nabla^2\rho(r)$ between Li-P and K-P bonds are consistent with the expected closed-shell ionic interactions in each case (see ESI,† Fig. S19). ^{31}P NMR calculations were also performed and match the observed experimental trends, with the Li-K heterobimetallic ^{31}P calculated signal found between the two homometallic resonances. Energies of formation of **1** also support facile exchange processes between the three metal complexes (see ESI,† for details).

A preliminary investigation of the catalytic capability of **1** in a hydrophosphination reaction of an alkene was undertaken (Table 1). To aid with comparison of other systems reported by us,^{47,48} the conditions used with the substrate 1,1-diphenylethylene were 10 mol% catalyst loading at room temperature in d_8 -toluene. The conversion was calculated using adamantane as an internal standard. With **1** as a catalyst, 94% conversion occurred after only 20 minutes, with quantitative conversion after 1.25 h. This is in stark contrast to monometallic $[\text{LiPPh}_2(\text{TMEDA})]_2$, which under the same conditions could only reach 6% conversion after 1 h, and 21% even after 24 h. $[\text{KPPH}_2(\text{TMEDA})]_n$ was also tested, and quantitative conversion was reached after 0.5 h. This trend is reminiscent of that of $n\text{BuLi} < n\text{BuLi}.\text{KO}t\text{Bu} < n\text{BuK}$ found in Lochmann–Schlosser superbbase chemistry.⁵

Note, the dehydrocoupling of phosphines is a known competing reaction,^{49,50} but when tested in our system **1** showed no

Table 1 Catalytic hydrophosphination of 1,1-diphenylethylene

Catalyst	Time (h)	Conversion (%)
1 ^a	0.1	81
1 ^a	1.25	>99
$[\text{LiPPh}_2(\text{TMEDA})]_2$	1	6
$[\text{LiPPh}_2(\text{TMEDA})]_2$ ^a	24	21
$[\text{LiPPh}_2(\text{TMEDA})]_2$ ^a	6	56
$[\text{KPPH}_2(\text{TMEDA})]_n$	0.1	88
$[\text{KPPH}_2(\text{TMEDA})]_n$ ^a	0.5	>99
$[\text{KPPH}_2(\text{TMEDA})]_n$ ^a	0.5	>99

^a Contains 0.06 mL of THF. Adamantane (0.035 mmol) was added as an internal standard to calculate NMR conversion.



evidence of it after 24 h. Importantly, **1** was retained in solution during the dehydrocoupling control reactions indicating that it does not dissociate into its monometallic counterparts during hydrophosphination catalysis. This work has established a unique mixed lithium–potassium phosphide complex derived from a common phosphine. New base metal compounds of this type, heterometallic and homometallic, may become increasingly important for the chemical community in its quest towards more sustainable practices that avoid the use of precious transition metals.

MHC, investigation, writing – original draft; DOM, investigation; ARK, validation; REM, conceptualisation, writing – review & editing; CW, formal analysis, writing – review & editing.

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Data availability

NMR data, crystallographic data and XYZ files are available from the University of Strathclyde Knowledge Base at <https://doi.org/10.15129/a7b30f49-5910-417c-87ae-409ca2181178>.

Conflicts of interest

The authors have no conflicts of interest to declare.

Notes and references

- 1 G. Wittig, R. Ludwig and R. Polster, *Chem. Ber.*, 1955, **88**, 294–301.
- 2 G. Wittig and F. Bickelhaupt, *Chem. Ber.*, 1958, **91**, 865–872.
- 3 G. Wittig and E. Benz, *Chem. Ber.*, 1958, **91**, 873–882.
- 4 G. G. Eberhardt, *J. Org. Chem.*, 1964, **29**, 643–645.
- 5 L. Lochmann and M. Janata, *Cent. Eur. J. Chem.*, 2014, **12**, 537–548.
- 6 M. Schlosser, *Organometallics in Synthesis: A Manual*, John Wiley & Sons, Ltd, 2001, pp. 1–352.
- 7 A. A. Morton, E. E. Magat and R. L. Letsinger, *J. Am. Chem. Soc.*, 1947, **69**, 950–961.
- 8 A. A. Morton and M. E. T. Holden, *J. Am. Chem. Soc.*, 1947, **69**, 1675–1681.
- 9 P. Benrath, M. Kaiser, T. Limbach, M. Mondeshki and J. Klett, *Angew. Chem., Int. Ed.*, 2016, **55**, 10886–10889.
- 10 B. Jennwein, S. Kimpel, D. Thalheim and J. Klett, *Chem. – Eur. J.*, 2018, **24**, 7605–7609.
- 11 W. Clegg, R. E. Mulvey, R. Snaith, G. E. Toogood and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1986, 1740–1742.
- 12 P. G. Williard and M. A. Nichols, *J. Am. Chem. Soc.*, 1991, **113**, 9671–9673.
- 13 D. R. Armstrong, A. R. Kennedy, R. E. Mulvey and S. D. Robertson, *Chem. – Eur. J.*, 2011, **17**, 8820–8831.
- 14 P. Fleming and D. F. O’Shea, *J. Am. Chem. Soc.*, 2011, **133**, 1698–1701.
- 15 G. W. Honeyman, D. R. Armstrong, W. Clegg, E. Hevia, A. R. Kennedy, R. McLellan, S. A. Orr, J. A. Parkinson, D. L. Ramsay, S. D. Robertson, S. Towie and R. E. Mulvey, *Chem. Sci.*, 2020, **11**, 6510–6520.
- 16 D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1989, 57–58.
- 17 N. D. R. Barnett, R. E. Mulvey, W. Clegg and P. A. O’Neil, *Polyhedron*, 1992, **11**, 2809–2812.
- 18 M. Westerhausen, S. Weinrich, G. Kramer and H. Piotrowski, *Inorg. Chem.*, 2002, **41**, 7072–7076.
- 19 R. Campbell, E. Crosbie, A. R. Kennedy, R. E. Mulvey, R. A. Naismith and S. D. Robertson, *Aust. J. Chem.*, 2013, **66**, 1189–1201.
- 20 D. R. Armstrong, E. V. Brouillet, A. R. Kennedy, J. A. Garden, M. Granitzka, R. E. Mulvey and J. J. Trivett, *Dalton Trans.*, 2014, **43**, 14409–14423.
- 21 N. Jin, A. Logallo and E. Hevia, *Organometallics*, 2025, **44**, 197–206.
- 22 R. E. Mulvey, K. Wade, D. R. Armstrong, G. T. Walker, R. Snaith, W. Clegg and D. Reed, *Polyhedron*, 1987, **6**, 987–993.
- 23 As compared to all Li–P and K–P containing structures deposited with the Cambridge Structural Database (CSD).
- 24 A. Falceto, E. Carmona and S. Alvarez, *Organometallics*, 2014, **33**, 6660–6668.
- 25 A. G. Avent, D. Bonafoux, C. Eaborn, M. S. Hill, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2000, 2183–2190.
- 26 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, **72**, 171–179.
- 27 K. Issleib and E. Wenschuh, *Chem. Ber.*, 1964, **97**, 715–720.
- 28 V. H. Gessner, C. Däschlein and C. Strohmann, *Chem. – Eur. J.*, 2009, **15**, 3320–3334.
- 29 R. A. Bartlett, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1986, **25**, 1243–1247.
- 30 G. Rabe, J. Riede and A. Schier, *Acta Crystallogr. C*, 1996, **52**, 1350–1352.
- 31 G. Stiegritz, B. Neumüller and K. Dehnicke, *Z. Naturforsch., B*, 1993, **48b**, 156–160.
- 32 K. Izod, P. Evans and P. G. Waddell, *Dalton Trans.*, 2017, **46**, 13824–13834.
- 33 R. A. Bartlett, M. M. Olmstead, P. P. Power and G. A. Sigel, *Inorg. Chem.*, 1987, **26**, 1941–1946.
- 34 P. B. Hitchcock, M. F. Lappert, P. P. Power and S. J. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 1669–1670.
- 35 W. Clegg and R. W. Harrington, *CSD Commun.*, 2021, DOI: [10.5517/ccdc.csd.cc2736sc](https://doi.org/10.5517/ccdc.csd.cc2736sc).
- 36 K. Izod, P. Evans and P. G. Waddell, *Inorg. Chem.*, 2020, **59**, 863–874.
- 37 K. Izod, J. Stewart, E. R. Clark, W. Clegg and R. W. Harrington, *Inorg. Chem.*, 2010, **49**, 4698–4707.
- 38 R. A. Jones, A. L. Stuart and T. C. Wright, *J. Am. Chem. Soc.*, 1983, **105**, 7459–7460.
- 39 R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167–209.
- 40 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 186–197.
- 41 O. Kühl, J. Sieler and E. Hey-Hawkins, *Z. Kristallogr. – Cryst. Mater.*, 1999, **214**, 496–499.
- 42 K. Izod, W. McFarlane, B. V. Tyson, W. Clegg, R. W. Harrington and S. T. Liddle, *Organometallics*, 2003, **22**, 3684–3690.
- 43 F. Dornhaus, M. Bolte, H. W. Lerner and M. Wagner, *Eur. J. Inorg. Chem.*, 2006, 1777–1785.
- 44 M. Xu, A. R. Jupp and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2019, **58**, 3548–3552.
- 45 G. W. Rabe, S. Kheradmandan, H. Heise, I. A. Guzei, L. M. Liable-Sands and A. L. Rheingold, *Main Group Chem.*, 1998, **2**, 221–228.
- 46 J. Bresien, Y. Pilopp, A. Schulz, L. S. Szych, A. Villinger and R. Wustrack, *Inorg. Chem.*, 2020, **59**, 13561–13571.
- 47 M. T. Whitelaw, S. Banerjee, A. R. Kennedy, A. van Teijlingen, T. Tuttle and R. E. Mulvey, *Cell Rep. Phys. Sci.*, 2022, **3**, 100942.
- 48 V. A. Pollard, A. Young, R. McLellan, A. R. Kennedy, T. Tuttle and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2019, **58**, 12291–12296.
- 49 V. Naseri, R. J. Less, R. E. Mulvey, M. McPartlin and D. S. Wright, *Chem. Commun.*, 2010, **46**, 5000–5002.
- 50 S. Molitor, J. Becker and V. H. Gessner, *J. Am. Chem. Soc.*, 2014, **136**, 15517–15520.

