

# Diversity of Structures and Bonding in Alkali Metal Ureaphosphanes

Michelle H. Crabbe,<sup>a</sup> Alan R. Kennedy,<sup>a</sup> Catherine E. Weetman,<sup>\*a</sup> and Robert E. Mulvey<sup>\*a</sup>

<sup>a</sup> Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK  
E-mail: and, e-mail: Catherine.weetman@strath.ac.uk; r.e.mulvey@strath.ac.uk

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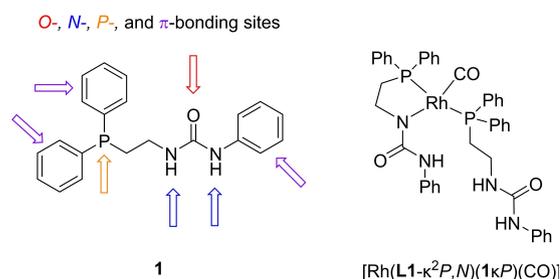
While organoelement compounds of lithium, sodium and potassium have been much studied for decades and consequently have found forests of applications, those of the heavier alkali metals, rubidium and caesium would barely manage to fill a tree. However, recently the literature has seen some little growth spurts with these metals, hinting at a possible fertile future in areas such as homogeneous catalysis provided more work is put into their fundamental development. Here we report the synthesis and crystal structures of lithium, rubidium and caesium derivatives of the ureaphosphane  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NHC(=O)NHPh}$ , chosen because it offers *O*, *N*, *P*, and  $\pi$ -coordination sites. Though one may expect such alkali metal compounds to be essentially similar, the caesium complex has novel features where  $\text{Cs}^+$  engages in a side-on coordination to the  $\text{C}=\text{O}$  bond and in a weak bond to the *P* centre, both of which are absent in the *Rb* structure. Less surprisingly, the lithium derivative is tetrameric in contrast to the infinite networks of the rubidium and caesium structures. All alkali metal derivatives were made with deprotonating the ureaphosphane by a suitable base, including the sodium and potassium complexes though these two complexes could not be obtained in a crystalline form.

**Keywords:** Alkali metals, metalation, structure elucidation, synthesis, ureaphosphanes.

## Introduction

Introduced by Reek and co-workers, the ureaphosphane 1-[2-(diphenylphosphanyl)ethyl]-3-phenylurea, **1** (Figure 1),<sup>[1]</sup> was prepared as the simplest member and model compound for a family of *P*, *O*-bidentate ligands for exploitation in rhodium-catalysed asymmetric hydrogenation applications. Since this achiral pro-ligand (with respect to its lack of metalation) contains three distinct heteroatoms (*N*, *O*, *P*), two distinct unsaturated groups ( $\text{C}=\text{O}$  and  $\text{Ph}$ ) with linear and cyclic  $\pi$ -bonding features respectively, as well as two acidic *N*–*H* bonds, we considered it could be a good ligand to investigate in metalation reactions to study comparisons and contrasts in its behaviour towards, and bonding to, alkali metals.

Recently we have carried out homogeneous catalytic studies including all the non-radioactive alkali



**Figure 1.** (LHS) Ureaphosphane **1** with multiple binding sites highlighted and (RHS) previous crystallographically characterised rhodium ureaphosphane.

metals ( $\text{Li}$ – $\text{Cs}$ )<sup>[2,3]</sup> and found that results down the group can significantly deviate from each other meaning that it is not prudent to treat these alkali metals as merely generic counterions in such cases as each can display their own unique reactivity profile. The whole group of alkali metals are increasingly being included in synthetic and structural studies,<sup>[3–5]</sup> most pertinently illustrated by the alkali metal ureates where

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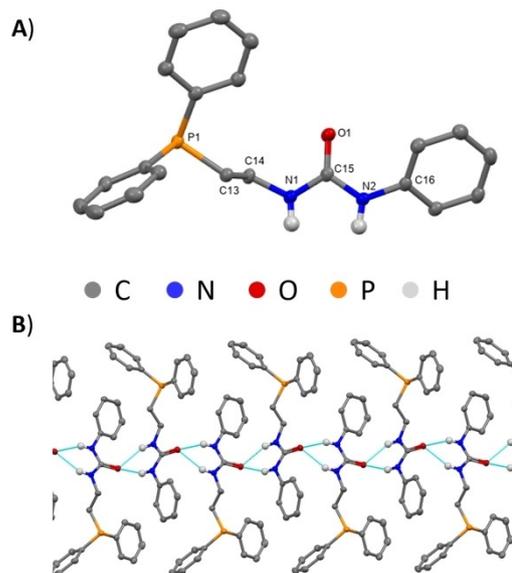
one NH has been deprotonated.<sup>[6,7]</sup> To the best of our knowledge pro-ligand **1** has rarely been metalated where the product has been crystallographically characterised, though related ureaphosphane compounds, some with known crystal structures, have been reported.<sup>[8–14]</sup> A search of the Cambridge Structural Database<sup>[15]</sup> (CSD) revealed only one hit, namely for the rhodium complex  $[\text{Rh}(\text{L}1-\kappa^2\text{P},\text{N})(1\kappa\text{P})(\text{CO})]^{[16]}$  (Figure 1) prepared by treatment of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  with two equivalents of **1**. One equivalent of **1** retains its two N–H bonds and binds to the transition metal only through its P atom, while the remaining N–H unit forms a hydrogen bond N–H...O to **L1**. Such hydrogen bonds are common in structures where **1** acts as a neutral ligand. Deprotonated at its  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NH}$  site, the second equivalent of **1** (now **L1**) chelates to the Rh centre via its P and N heteroatoms to close a 5-membered (PCCNRh) ring.

By reporting the crystal structures of **1** and the synthesis and crystal structures of three distinctly different alkali metalated derivatives of it, the present study furthers understanding of the diverse nature of bonding found within the alkali metal family. This information can help those researchers endeavouring to design new alkali metal catalysts/pre-catalysts, especially in the cases of rubidium and caesium, the structural chemistry of which remains meagrely studied in comparison to those of their lighter congeners.

## Results and Discussion

Given the importance of the individuality of each alkali metal in its organoelement chemistry, we were interested to examine their coordination chemistry with the ureaphosphane ligand on account of its multiple coordination options. Here, there is potential for *O*-, *N*-, *P*- coordination as well as  $\pi$ -bonding interactions. We started the study by synthesising and attempting to grow crystals of the proligand **1**. In the original literature preparation **1**<sup>[1]</sup> was isolated as a colourless powder, but we were successful in growing colourless crystals of it suitable for single crystal X-ray diffraction (SC-XRD) by slow vapour diffusion of *n*-hexane into a concentrated THF solution at  $-30^\circ\text{C}$  (Figure 2).

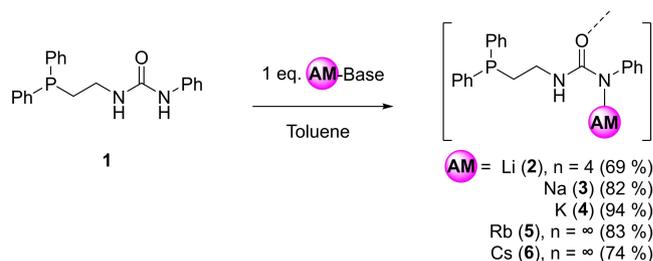
Compound **1** crystallises in the monoclinic  $\text{P}2_1/n$  space group with one molecule in the asymmetric unit. However, the extended network reveals hydrogen bonding between the acyclic urea NH (donor) and the carbonyl (acceptor) moieties. These are intercon-



**Figure 2.** **A)** Asymmetric unit of proligand **1** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms other than those on N(1) and N(2) have been omitted for clarity. Atom colour code also shown. Selected bond lengths (Å) and angles ( $^\circ$ ): N(1)–C(15) 1.3535(16), N(2)–C(15) 1.3741(15), C(15)–O(1) 1.2406(15), N(1)–C(15)–N(2) 113.86(10). **B)** Hydrogen bonding network of compound **1**, graph set notation  $\text{R}_2^1(6)$ .

nected  $\text{R}_2^1(6)$  motifs that link together to give a one-dimensional hydrogen bonded chain that propagates parallel to the crystallographic *b* axis.<sup>[17,18]</sup>

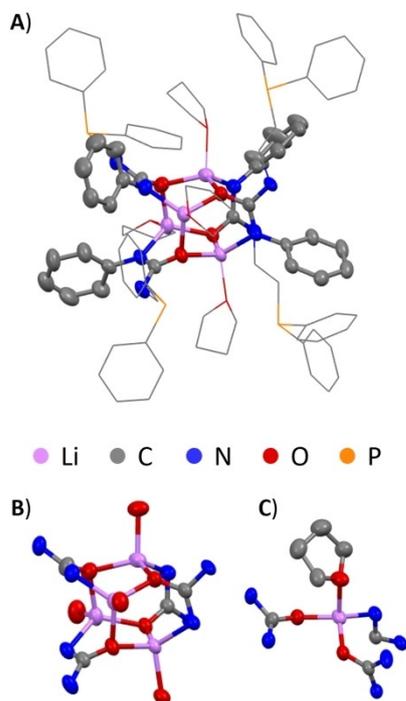
With the proligand in hand, we probed the coordination chemistry of **1** by reacting it with an equivalent of alkali metal base. In all cases, reactions proceeded with clean metalation at the N(2) site and compounds **2–6**  $[\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NHC(=O)N(Ph)AM-M}(\text{THF})_m\}_n]$  (AM = Li (**2**), Na (**3**), K (**4**), Rb (**5**), Cs (**6**)) were isolated in good yields (Scheme 1). This was



**Scheme 1.** General synthetic strategy and isolated yields for alkali metal ureaphosphanes **2–6**. Owing to the diverse structural motifs across **2**, **5**, and **6**, the chemdraw is not representative of the crystal structures, rather a general simplified view showing the site of deprotonative metalation. For this reason, coordinated THFs are also not shown for simplification purposes.

initially confirmed by  $^1\text{H-NMR}$  spectroscopy as loss of the  $\text{NHPh}$  resonance at  $\delta$  7.71 ppm, and retention of the  $\text{NHCH}_2$  resonance in the range  $\delta$  4.5–6.5 ppm [Li (**2**) 4.42 ppm; Na (**3**) 6.45 ppm; K (**4**) 6.33 ppm; Rb (**5**) 5.90 ppm; Cs (**6**) 5.42 ppm]. Inspection of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, revealed a common resonance at  $\delta$   $-21$  ppm throughout the series **1–6**, consistent with a lack of alkali metal coordination at the phosphane [P(III)] centre in solution. It is of note that attempts to dimetalate compound **1** (that is, at both NH sites) in the presence of excess  $n\text{-BuLi}$ , LiTMP (TMP = 2,2,6,6-tetramethylpiperidine) or LiHMDS (HMDS = hexamethyldisilazide) failed.<sup>[19]</sup> Whilst the NMR spectra (see the Supporting Information for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  data) are similar across the alkali metal series, solid-state studies reveal structures with notable differences between them.

Using the same procedure that worked well with **1**, crystals suitable for SC-XRD of **2** were grown by slow vapour diffusion of  $n$ -hexane into a concentrated THF solution at  $-30^\circ\text{C}$  (Figure 3). This study revealed

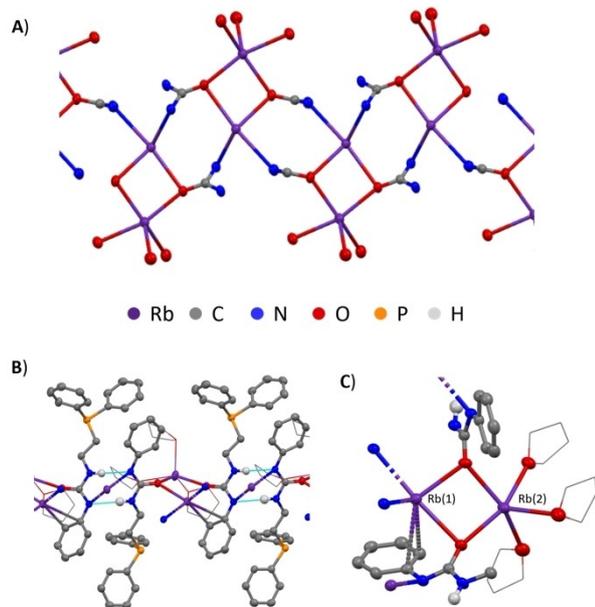


**Figure 3.** **A)** Molecular structure of compound **2** with thermal ellipsoids drawn at 50% probability level. Solvent molecules and hydrogen atoms have been omitted for clarity, whilst coordinated solvent and the ethyldiphosphane unit are depicted in wireframe. Atom colour code also shown. **B)** Central  $\text{Li}_4(\text{urea})_4(\text{THF})_4$  core with coordinated solvent, ethyldiphosphane unit and phenyl removed for clarity. **C)** Lithium coordination environment.

compound **2** to be a discrete molecular tetrameric lithium cage (Figure 3), with the general formula  $\text{Li}_4(\mathbf{L1})_4(\text{THF})_4$  (where **L1** = the deprotonated ureaphosphane ligand **1**). In line with NMR observations, metalation has occurred exclusively at the N(2) position and the absence of phosphane-lithium coordination persists in the solid state with the alkylphosphane arm exo-cyclic to the central  $\text{Li}_4$  core. Figures 3B and 3C show the central core of complex **2** and the coordination of each Li centre, respectively. The cage is formed via a urea carbonyl unit bridging two Li centres. Each lithium centre is pseudo-tetrahedral within an  $\text{NO}_3$  coordinative environment, as it is bound to three ureaphosphanes and one THF solvent molecule which sits exo-cyclic to the central core. Here both  $O$ - and  $N$ -bound coordination modes are observed with average  $\text{Li-O}$  (1.926 Å) and  $\text{Li-N}$  (2.030 Å) bond lengths in the ballpark of literature values.<sup>[20]</sup>

The average carbonyl  $\text{C-O}$  bond lengths within **2** indicate mainly retention of the double bond [**2** 1.283 vs. **1** 1.2406(15) Å], whilst the average  $\text{C-N}(2)$  bond length decreases with respect to that in the starting proligand in line with metalation at this position [**2** 1.311 vs. 1.3741(15) Å]. Despite several attempts, crystals suitable for SC-XRD with Na (**3**) and K (**4**) could not be obtained.

Since generally heavier alkali metals show a greater preference for  $\pi$ -bonding interactions,<sup>[21–31]</sup> we were interested to ascertain if this  $\pi$ -philicity featured here. Following reaction of one equivalent of the bulky amides RbHMDS or CsHMDS with **1**, crystals suitable for SC-XRD were again grown by vapour diffusion of  $n$ -hexane into a concentrated THF solution at  $-30^\circ\text{C}$ . Rubidium complex **5** was found to crystallise in the  $\text{P}2_1/c$  monoclinic space group as an infinite polymeric network (Figure 4). Matching up with the solution NMR data, again there is no phosphorus-alkali metal contact observed within compound **5**, with the closest Rb–P separation distance being 5.63 Å, (for reference the longest Rb–P bond structurally characterised in the CSD is 3.840(2) Å,<sup>[32]</sup> sum of covalent radii = 3.21 Å,<sup>[33]</sup> and sum of Van der Waals radii = 4.83 Å).<sup>[34]</sup> However, **5** consists of an infinite network containing two Rb centres in the asymmetric repeating unit, which form part of a four-membered  $(\text{RbO})_2$  ring. The  $(\text{RbO})_2$  ring is nearly planar, with the sum of endocyclic angles being  $358.0^\circ$  and a dihedral angle of  $164.7^\circ$ . The 3D infinite network extends out through Rb(1), the  $N$ -bound ureas in which Rb(1) bridges are both deprotonated, but interestingly N(2) also partakes in hydrogen bonding forming a secondary 2D network (Figure 4B).

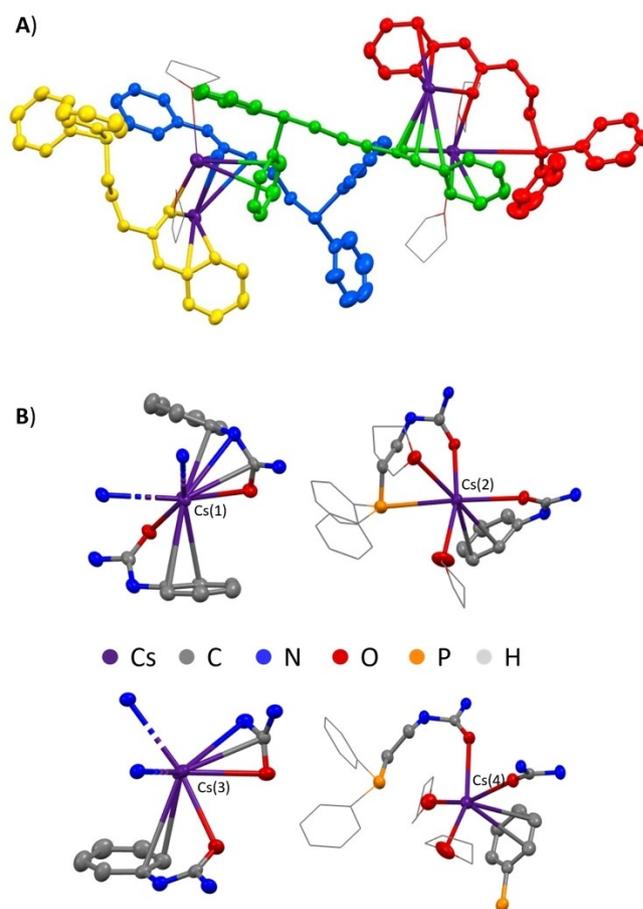


**Figure 4.** **A)** Solid state structure of compound **5** with thermal ellipsoids drawn at 50% probability level. Carbon atoms, except the urea C, hydrogen and phosphorus atoms have been omitted for clarity. Atom colour code also shown. **B)** Hydrogen bonding within **5**, graph set notation  $R_7^1(8)$ , **C)** Coordination environments at both Rb centres, coordinated solvent drawn in wireframe.

Both Rb(1) and Rb(2) are *pseudo*-trigonal bipyramidal (Figure 4C) in featuring axial ligands close to  $180^\circ$  [ $O_{\text{urea}}\text{-Rb(1)-N}$   $172.0^\circ$  and  $O_{\text{THF}}\text{-Rb(2)-O}_{\text{urea}}$   $153.9^\circ$ ] with an average equatorial ligand angle of  $116.6^\circ$  Rb(1) and  $119.2^\circ$  Rb(2). Rb(1) lies within a  $N_2O_2C$  environment as it has an  $\eta^2$   $\pi$ -interaction with the phenyl ring, two *N*-bound and two *O*-bound urea fragments, whilst Rb(2) is within an  $O_5$  environment via coordination to two *O*-bound ureas and three THF ligands.

Caesium complex **6** crystallises in the P-1 triclinic space group as an infinite network (Figure 5), featuring four ligands and four Cs atoms within the asymmetric unit. Compound **6** propagates through Cs–N interactions, and also features hydrogen bonding with the formal graph set notation of  $R_2^2(8)$ ,  $C_1^1(6)$  (see SI for further information). Whilst the solution studies revealed little change across the alkali metal series, here in the solid-state structural diversity and binding preferences across the alkali metals are evident, as compound **6** uniquely features Cs–P interactions and side-on urea  $\pi$ -interactions.

The Cs(2)–P(1) distance of  $3.895(1)$  Å and the notably longer Cs(4)–P(3) distance of  $4.1426(8)$  Å, are in line with previously reported Cs–P bond distances in the CSD (average  $3.733$  Å), and the longest being



**Figure 5.** **A)** Asymmetric unit of compound **6** with thermal ellipsoids drawn at 50% probability level. Solvent molecules and hydrogen atoms have been omitted for clarity, whilst coordinated solvent is depicted in wireframe. Each of the four ligands in the asymmetric unit shown in four different colours to highlight the alternative coordination modes. **B)** Coordination environments at the four distinct Cs centres. Atom colour code also shown.

$4.442(3)$  Å.<sup>[35]</sup> Both Cs–P interactions are longer than the sum of the covalent radii ( $3.43$  Å)<sup>[33]</sup> implying they are weak interactions, but they still lie well within the Van der Waals radii ( $5.23$  Å).<sup>[34]</sup> This increased preference for a Cs–P interaction is reflected in the overall structure of **6**. In **2** and **5** the ethylphosphane unit is exocyclic to the central LiO or RbO cores with the average AM–P separation distances of  $5.27$  Å and  $5.78$  Å, respectively. Here in compound **6**, *P,O*-coordination is observed in two of the four ligand environments [Figure 5 red and yellow coloured ligands, Cs(2) and Cs(4)], whilst the remaining two ligand environments feature side-on  $\pi$ -coordination with the urea unit and  $\eta^2$ -coordination to the *N*-phenyl group (Fig-

ure 5 blue and green coloured ligands, Cs(1) and Cs(3)).

The differences in the urea coordination modes (end-on *O*-coordination vs. side-on  $\pi$ -coordination) are best observed in Cs(1) or Cs(3) (Figure 5B), whilst the bond lengths in the urea unit remain similar across the two ligands the differences lie in the Cs-urea distances and angles, as highlighted in Table 1. As expected, end-on *O*-coordination results in a shorter Cs–O bond with longer separation distances, whilst side-on  $\pi$ -coordination features similar Cs–O/C/N distances across the urea fragment. The Cs(1)–O–C angles of 117.0(2) vs. 76.1(2)° in the red and green ligands, respectively, support the different coordination modes with the C=O unit (end-on; red ligand) and perpendicular (side-on  $\pi$ ; green ligand) to the Cs atom. This highlights the diverse binding modes available to Cs and, by default, across the alkali metal series.

Whilst it is relatively well-known that the heavier alkali metals prefer aryl  $\pi$ -interactions, to the best of our knowledge it is the first time that side-on C=O  $\pi$ -bonding has been crystallographically observed. Examination of the CSD, revealed four structures where the Cs–O–C bond angle was less than 100° (See SI for further information).<sup>[36–39]</sup> However, on close examination of the key structural metrics no  $\pi$ -coordination

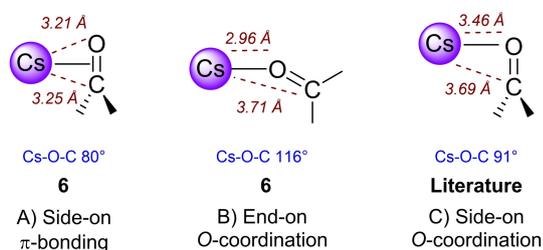
was observed, rather a slipped side-on *O*-coordination noted. Figure 6 highlights the different coordination modes of C=O to Cs, with side-on  $\pi$ -bonding (type A) exemplified by a close to 1 ratio of Cs–C:Cs–O bond lengths (0.98) indicating that Cs is situated at the midpoint of the C=O bond. The asymmetry in type C coordination yields a ratio of 0.93, highlighting the slipped nature and weaker Cs–C interaction (for reference type B has a ratio of 0.80).

## Conclusions

The organoelement chemistries of the heavier alkali metals rubidium and caesium are underdeveloped in comparison to those of their lighter alkali metal congeners. Unlike for salts, studies of the whole group are relatively rare for organoelement compounds. This fundamental study reports a conformity in the reactions of selected bases of all non-radioactive group members with the ureaphosphane Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>NHC(=O)NPh, where deprotonation occurs selectively at the N(H) site of the N(H)Ph terminal in good to high yields. However, the crystal structures of the lithium, rubidium, and caesium products reveal interesting distinctions. The side-on  $\pi$ -coordination of the Cs<sup>+</sup> cation to the C=O group is a standout feature. Moreover, contrasting structural results for the rubidium and caesium products show that these heavier alkali metals should not be classed together as mere gengenions in organoelement chemistry. Such differences in structures and bonding, however small, need to be logged more now that the reaction chemistry of organoelement rubidium and caesium compounds especially in homogeneous catalysis is starting to attract interest. Combined with solution studies, this knowledge will aid theoreticians in modelling such compounds employed in catalysis to compute possible reactions mechanisms.

**Table 1.** Selected bond lengths (Å) and angles (°) for Cs(1) and Cs(3) in Compound 6.

	Cs(1) Ligand 1 (Red)	Ligand 2 (Green)	Cs(3) Ligand 3 (Blue)	Ligand 4 (Yellow)
Cs–O	2.990(2)	3.272(3)	3.152(3)	2.925(2)
Cs–C	3.744(3)	3.211(4)	3.287(4)	3.672(3)
Cs–N	3.978(3)	3.327(3)	3.877(3)	4.029(3)
Cs–N(H)	4.897(3)	3.750(3)	3.577(3)	4.729(3)
Cs– <i>ip</i> - soC	3.422(3)	3.719(4)	4.233(4)	3.704(3)
Cs–O–C	117.0(2)	76.1(2)	84.8(2)	116.6(2)



**Figure 6.** Different C=O binding modes to Cs. Average bond lengths and angles for coordination modes A and B are from compound 6, whilst mode C metrics are average values from literature.<sup>[36–39]</sup>

## Experimental Section

Synthetic protocols and characterization of the new compounds are reported in the electronic supporting information. CCDC deposition numbers 2351927 to 2351930, contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[40–49]</sup>

## Author Contribution Statement

M.H.C. carried out the experimental work including the synthesis and characterisation of all materials. A.R.K. and M.H.C. performed the X-ray diffraction studies. R.E.M. and C.E.W. supervised the work and all authors contributed to producing the manuscript.

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## Data Availability Statement

The data that support the findings of this study are openly available in PURE at <https://doi.org/10.15129/b56c24a9-a533-48ca-bea5-6d9ee91f83b4>, reference number 201794242.

## References

- [1] J. Meeuwissen, R. J. Detz, A. J. Sandee, B. de Bruin, J. N. H. Reek, 'Rhodium-P,O-Bidentate Coordinated Ureaphosphine Ligands for Asymmetric Hydrogenation Reactions' *Dalton Trans.* **2010**, 39, 1929–1931.
- [2] T. X. Gentner, A. R. Kennedy, E. Hevia, R. E. Mulvey, 'Alkali Metal (Li, Na, K, Rb, Cs) Mediation in Magnesium Hexamethyldisilazide [Mg(HMDS)<sub>2</sub>] Catalysed Transfer Hydrogenation of Alkenes' *ChemCatChem* **2021**, 13, 2371–2378.
- [3] M. P. Coles, M. J. Evans, 'The emerging chemistry of the alumanyl anion', *Chem. Commun.* **2022**, 59, 503–519.
- [4] L. Brieger, C. Unkelbach, C. Strohmam, 'THF-solvated Heavy Alkali Metal Benzyl Compounds (Na, Rb, Cs): Defined Deprotonation Reagents for Alkali Metal Mediation Chemistry', *Chem. Eur. J.* **2021**, 27, 17780–17784.
- [5] S. Banerjee, P. A. Macdonald, S. A. Orr, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle, R. E. Mulvey, 'Hydrocarbon soluble alkali-metal-aluminium hydride surrog[ATES]', *Chem. Eur. J.* **2022**, 28, e202201085.
- [6] H. Sawinski, R. Dronskowsk, 'The First Structurally Characterized Salts of Deprotonated Urea: M(CN<sub>2</sub>H<sub>3</sub>O) with M = Na, K, Rb, and Cs' *Z. Anorg. Allg. Chem.* **2014**, 640(5), 846–850.
- [7] H. Sawinski, R. Dronskowsk, 'Synthesis and Crystal Structure of a "High-temperature" Phase of Li[H<sub>2</sub>NC(O)NH], the Missing Alkali-Metal Ureate', *Z. Naturforsch.* **2014**, 69b, 651–654.
- [8] P. A. Macdonald, S. Banerjee, A. R. Kennedy, A. van Teijlingen, S. D. Robertson, T. Tuttle, R. E. Mulvey, 'Alkali Metal Dihydropyridines in Transfer Hydrogenation Catalysis of Imines: Amide Basicity versus Hydride Surrogacy', *Angew. Chem. Int. Ed.* **2023**, 62, e202304966.
- [9] J. Meeuwissen, R. Detz, A. J. Sandee, B. de Bruin, M. A. Siegler, A. L. Spek, J. N. H. Reek, 'Ureaphosphanes as Hybrid, Anionic or Supramolecular Bidentate Ligands for Asymmetric Hydrogenation Reactions' *Eur. J. Inorg. Chem.* **2010**, 2992–2997.
- [10] P. A. Duckmanton, A. J. Blake, J. B. Love, 'Palladium and Rhodium Ureaphosphine Complexes: Exploring Structural and Catalytic Consequences of Anion Binding', *Inorg. Chem.* **2005**, 22, 7708–7710.
- [11] A. Franchino, À. Martí, S. Nejrótti, A. M. Echavarrén, 'Silver-Free Au(I) Catalysis Enabled by Bifunctional Urea- and Squaramide-Phosphine Ligands via H-Bonding', *Chem. Eur. J.* **2021**, 27, 11989–11996.
- [12] J. Wassenaar, J. N. H. Reek, 'Hybrid bidentate phosphorus ligands in asymmetric catalysis: Privileged ligand approach vs. combinatorial strategies' *Org. Biomol. Chem.* **2011**, 9, 1704–1713.
- [13] A. J. Sandee, A. M. van der Burg, J. N. H. Reek, 'UREAphos: supramolecular bidentate ligands for asymmetric hydrogenation' *Chem. Commun.* **2007**, 864–866.
- [14] L. K. Knight, Z. Freixa, P. W. N. M. van Leeuwen, J. N. H. Reek, 'Supramolecular trans-Coordinating Phosphine Ligand' *Organometallics* **2006**, 25, 954–960.
- [15] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, 'The Cambridge Structural Database', *Acta Cryst.* **2016**, B72, 171–179.
- [16] D. Rageot, D. H. Woodmansee, B. Pugin, A. Pfaltz, 'Proline-Based P,O Ligand/Iridium Complexes as Highly Selective Catalysts: Asymmetric Hydrogenation of Trisubstituted Alkenes' *Angew. Chem. Int. Ed.* **2011**, 50, 9598–9601.
- [17] J. Bernstein, R. E. Davis, L. Shimoni, N.-L. Chang, 'Patterns in Hydrogen Bonding: Functionality and Graph Set Analysis in Crystals' *Angew. Chem. Int. Ed.* **1995**, 34, 1555–1573.
- [18] M. C. Etter, 'Encoding and decoding hydrogen-bond patterns of organic compounds' *Acc. Chem. Res.* **1990**, 23, 120–126.
- [19] R. E. Mulvey, S. D. Robertson, 'Synthetically Important Alkali-Metal-Utility Amides: Lithium, Sodium, and Potassium Hexamethyldisilazides, Diisopropylamides and Tetramethylpiperidides', *Angew. Chem. Int. Ed.* **2013**, 52, 11470–11487.
- [20] Based on statistical analysis of all Li–O and Li–N containing structures deposited with the Cambridge Structural Database (CSD). See ESI for descriptive statistics and histograms. Accessed March 4<sup>th</sup>, 2024.

- [21] T. X. Gentner, R. E. Mulvey, 'Alkali-Metal Mediation: Diversity of Applications in Main-Group Organometallic Chemistry' *Angew. Chem. Int. Ed.* **2021**, *60*, 9247–9262.
- [22] M. G. Davidson, D. Garcia-Vivo, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, 'Exploiting  $\sigma/\pi$  Coordination Isomerism to Prepare Homologous Organoalkali Metal (Li, Na, K) Monomers with Identical Ligand Sets' *Chem. Eur. J.* **2011**, *17*, 3364–3369.
- [23] A. Rae, K. M. Byrne, S. A. Brown, A. R. Kennedy, T. Krämer, R. E. Mulvey, S. D. Robertson, 'Sigma/pi Bonding Preferences of Solvated Alkali-Metal Cations to Ditopic Arylmethyl Anions' *Chem. Eur. J.* **2022**, *28*, e202104260.
- [24] J. Wacker, J. R. Lynch, S. Banerjee, P. A. Macdonald, A. R. Kennedy, B. Sarkar, R. E. Mulvey, 'Isolable rubidium and caesium derivatives of common organic carbonyl compounds' *Chem. Commun.* **2024**, *60*, 91–94.
- [25] C. Schade, P. v. R. Schleyer, 'Sodium, Potassium, Rubidium, and Cesium: X-Ray Structural Analysis of Their Organic Compounds' *Adv. Organomet. Chem.* **1987**, *27*, 169–278.
- [26] D. Hoffmann, W. Bauer, P. v. R. Schleyer, U. Pieper, D. Stalke, 'Cation-induced structural alterations in the organo alkali metal derivatives of triphenylmethane: a combined x-ray and NMR study of the potassium-caesium salts' *Organometallics* **1993**, *12*(4), 1193–1200.
- [27] D. Hoffmann, W. Bauer, F. Hampel, N. J. R. van Eikema Hommes, P. v. R. Schleyer, P. Otto, U. Pieper, D. Stalke, D. S. Wright, R. Snaith, '.eta.3 and .eta.6 Bridging cations in the N,N,N',N'-pentamethyldiethylenetriamine-solvated complexes of benzylpotassium and benzylrubidium: an x-ray, NMR, and MO study' *J. Am. Chem. Soc.* **1994**, *116*(2), 528–536.
- [28] J. Hicks, P. Vasko, J. M. Goicoechea, S. Aldridge, 'The Alumanyl Anion: A New Generation of Aluminium Nucleophile' *Angew. Chem. Int. Ed.* **2021**, *60*, 1702–1713.
- [29] T. X. Gentner, M. J. Evans, A. R. Kennedy, S. E. Neale, C. L. McMullin, M. P. Coles, R. E. Mulvey, 'Rubidium and Caesium Alumynyls: Synthesis, Structures and Reactivity in C–H bond Activation of Benzene' *Chem. Commun.* **2022**, *58*, 1390–1393.
- [30] S. F. McWilliams, P. L. Holland, 'Dinitrogen Binding and Cleavage by Multinuclear Iron Complexes' *Acc. Chem. Res.* **2015**, *48*(7), 2059–2065.
- [31] S. M. Bhutto, P. L. Holland, 'Dinitrogen Activation and Functionalization Using  $\beta$ -Diketiminato Iron Complexes', *Eur. J. Inorg. Chem.* **2019**, 1861–1869.
- [32] C. Frenzel, F. Somoza Jr., S. Blaurock, E. Hey-Hawkins, 'Syntheses and solid-state structures of  $[\{K(THF)_2(PHTipp)K(THF)(\mu\text{-}THF)(PHTipp)\}_x]_2$  and  $[Rb(THF)(PHTipp)]_x$  (Tipp = 2,4,6-Pr<sup>i</sup><sub>3</sub>C<sub>6</sub>H<sub>2</sub>)' *J. Chem. Soc. Dalton Trans.* **2001**, 3115–3118.
- [33] P. Pyykkö, M. Atsumi, 'Molecular Single-Bond Covalent Radii for Elements 1–118' *Chem. Eur. J.* **2009**, *15*, 186–197.
- [34] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, 'Consistent van der Waals Radii for the Whole Main Group', *J. Phys. Chem. A* **2009**, *113*, 5806–5812.
- [35] G. W. Rabe, H. Heise, G. P. A. Yap, L. M. Liable-Sands, I. A. Guzei, A. L. Rheingold, 'Molecular Structures of the Heavier Alkali Metal Salts of Supermesitylphosphane: A Systematic Investigation' *Inorg. Chem.* **1998**, *37*(17), 4235–4245.
- [36] V. Lorenz, P. Liebing, L. Hilfert, L. Schröder, F. T. Edlmann, 'Synthesis and Structural Investigation of a Complete Series of Brightly Colored Alkali Metal 1,3-Dimethylviolurates' *Z. Anorg. Allg. Chem.* **2020**, *646*, 1854–1860.
- [37] A. N. Bilyachenko, A. A. Korlyukov, A. V. Vologzhanina, V. N. Khrustalev, A. N. Kulakova, J. Long, J. Larionova, Y. Guari, M. S. Dronova, U. S. Tsareva, P. V. Dorovatovskii, E. S. Shubina, M. M. Levitsky, 'Tuning linkage isomerism and magnetic properties of bi- and tri-metallic cage silsesquioxanes by cation and solvent effects' *Dalton Trans.* **2017**, *46*, 12935–12949.
- [38] X. Meng, F. Liang, J. Tang, K. Kang, T. Zeng, W. Yin, R. Guo, Z. Lin, M. Xia, 'Parallel Alignment of  $\pi$ -Conjugated Anions in Hydroisocyanurates Enhancing Optical Anisotropy' *Inorg. Chem.* **2019**, *58*(14), 8948–8952.
- [39] A. A. Korlyukov, A. V. Vologzhanina, M. I. Buzin, N. V. Sergienko, B. G. Zavin, A. M. Muzafarov, 'Cu(II)-Silsesquioxanes as Secondary Building Units for Construction of Coordination Polymers: A Case Study of Cesium-Containing Compounds' *Cryst. Growth Des.* **2016**, *16*(4), 1968–1977.
- [40] D. F. Shriver, 'The manipulation of air-sensitive compounds', McGraw-Hill, New York, 1969.
- [41] M. V. Gradiski, A. N. Kharat, M. S. E. Ong, A. J. Lough, S. A. M. Smith, R. H. Morris, 'A One-Step Preparation of Tetradentate Ligands with Nitrogen and Phosphorus Donors by Reductive Amination and Representative Iron Complexes' *Inorg. Chem.* **2020**, *59*, 11041–11053.
- [42] A. I. Ojeda-Amador, A. J. Martínez-Martínez, A. R. Kennedy, D. R. Armstrong, C. T. O'Hara, 'Monodentate coordination of the normally chelating chiral diamine (R,R)-TMEDA' *Chem. Commun.* **2017**, *53*, 324–327.
- [43] P. G. Williard, 'Structure of potassium hexamethyldisilazide toluene solvate' *Acta Crystallogr. Sect. C* **1988**, *44*, 270–272.
- [44] S. Kriek, P. Schüler, H. Görls, M. Westerhausen, 'Straightforward synthesis of rubidium bis(trimethylsilyl)amide and complexes of the alkali metal bis(trimethylsilyl)amides with weakly coordinating 2,2,5,5-tetramethyltetrahydrofuran' *Dalton Trans.* **2018**, *47*, 12562–12569.
- [45] A. I. Ojeda-Amador, A. J. Martínez-Martínez, A. R. Kennedy, C. T. O'Hara, 'Structural Studies of Cesium, Lithium/Cesium, and Sodium/Cesium Bis(trimethylsilyl)amide (HMDS) Complexes' *Inorg. Chem.* **2016**, *55*, 5719–5728.
- [46] Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, Oxfordshire, England. 2014.
- [47] G. M. Sheldrick, 'SHELXT – Integrated space-group and crystal-structure determination' *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [48] G. M. Sheldrick, 'Crystal structure refinement with SHELXL' *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
- [49] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, 'OLEX2: a complete structure solution, refinement and analysis program' *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

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