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Synthesis and Structure of Heavy Alkali Metal Pentalenides

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The solid-state structures of the first rubidium and caesium pentalenides $[Rb(THF)]_2[Ph_4Pn]$ and $[Cs(THF)]_2[Ph_4Pn]$ have been determined by single crystal X-ray diffraction. Both were found to be polymeric in the solid state through interactions of the cations with the phenyl substituents, in contrast to their lighter group 1 congeners which are monomeric for lithium and sodium, and THF-bridged for potassium. Both $[Rb(THF)]_2[Ph_4Pn]$ and $[Cs(THF)]_2[Ph_4Pn]$ displayed increased η^8 coordination,

1. Introduction

Pentalenide ($C_8H_6^{2-}$, **Pn**²⁻) is the bicyclic analogue of cyclopentadienide ($C_5H_5^-$, **Cp**⁻) and closely related to cyclooctatetraenide ($C_8H_8^{2-}$, **COT**²⁻) by a 1,5-transannular ring closure.^[1] However, in contrast to Cp⁻ and its derivatives, only the lithium, sodium and potassium salts have so far been reported for Pn²⁻ and its derivatives. This can be attributed to the difficulties in synthesising appropriate precursors to access pentalenide chemistry.^[2] Thus, interest in exploring the s-block chemistry of pentalenide has been limited to finding a suitable Pn²⁻ transfer reagent - frequently the lithium (Li2Pn^R, Li2Pn*, Li2[1,4-(SiMe₃)₂Pn]; R=H, Me, Et, ⁱPr, Pn*=1,2,3,4,5,6-Me₆Pn)^[3-7] or the potassium (K_2Pn^{\dagger} ; $Pn^{\dagger} = 1,4-(Si^{\dagger}Pr_3)_2Pn)^{[5]}$ salts used to explore fand *d*-block pentalenide chemistry.^[8,9] This has left the heavy alkali metals and (until recently) alkaline earth metals unexplored.^[10] In 2017, Merino and co-workers reported a computational study on the optimised geometries for the alkali

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demonstrating a shift towards higher hapticities down the group as previously predicted computationally for the parent $M_2[Pn]$ complexes (M=group 1 metal). The solid-state structures of the polydentate donor adducts [M(DME)_x]_2[Ph_4Pn] (M=Li, x=1; M=Na, x=2) and [M(Me_6TREN)]_2[Ph_4Pn] (M=K, Rb, Cs) were all monomeric and displayed increased metal-carbon distances and decreased ring slippage values relative to the THF adducts.

metal salts of the parent Pn²⁻ from Li to Cs, and found that as the size of the metal increased the positions of the cations shifted to sit more centrally over the bridgehead carbons in an η^{8} manner, as opposed to the predicted (and experimentally known) η^5 coordination for the smaller cations.^[11] Previously our group has introduced a family of tetra-arylated dihydropentalenes (1,3,4,6-Ar₄PnH₂),^[12] the parent of which, Ph₄PnH₂, has been used to synthesise the lithium and potassium salts as well as the first sodium pentalenide complex.^[13] As such, Ph₄Pn²⁻ is well suited to explore the chemistry of the heavy alkali metals (Figure 1) where the combination of aryl substituents and larger soft cations may lead to additional bonding interactions, such as in the related dibenzo[*a.e.*]cyclooctatetraenide (**DBCOT**²⁻) complexes where the cations engage in η^8 coordination to the central COT²⁻ unit with further coordination to the phenyl rings of neighbouring DBCOT²⁻ units.^[14] Herein we report the syntheses and solid-state structures of the first rubidium and caesium pentalenides as their THF solvates, and the DME/ Me₆TREN adducts of Li, Na, K, Rb, Cs, to complete the first



Figure 1. Known group 1 pentalenides and cyclooctatetraenides.



homologous series of group 1 pentalenides to analyse trends in structure and bonding across the group.

2. Results and Discussion

As with their lighter congeners, [Rb(THF)]₂[Ph₄Pn] and [Cs-(THF)]₂[Ph₄Pn] could be accessed via a double deprotonative metalation of the non-aromatic Ph_4PnH_2 with the appropriate HMDS bases in THF at room temperature (HMDS = 1,1,1,3,3,3hexamethyldisilazide, (Me₃Si)₂N⁻). Analogous to what had been reported for the lighter alkali metal Ph₄Pn²⁻ complexes, a bright red solution formed over the course of several hours which was accompanied by the disappearance of the NMR signals for Ph₄PnH₂. However, contrary to Li, Na, and K (as well as their combinations), with Cs and Rb no NMR signals assignable to Ph₄Pn²⁻ could be identified in solution even after an isolated sample was redissolved into THF (Figure S1). After standing in THF at -20 °C for two weeks a crop of single crystals suitable for X-ray diffraction experiments could be obtained in each case, confirming successful formation of the desired compounds. Figure 2 details the numbering of the pentalenide core as well as some of the key geometric parameters pertinent to the following structural discussion.

The solid-state structures of the new rubidium and caesium complexes (Figures 3 and S4) were isostructural and consisted of two independent molecules each with two cations bound to Ph_4Pn^{2-} in an *anti*-configuration with one THF unit coordinated to each metal. A one-dimensional polymeric chain arrangement was found in the solid state, with propagation through $M-\pi_{arene}$ interactions via the phenyl substituents. This is in contrast to $[K_2(THF)_4(Ph_4Pn)]_x$ which is also polymeric but where the propagation is achieved through bridging THF units.^[13] The metal- π_{arene} interactions in $[Rb(THF)]_2[Ph_4Pn]$ and $[Cs(THF)]_2[Ph_4Pn]$ could be quantified via the average Rb-Ph_{centroid} distances of 3.112 Å and Cs-Ph_{centroid} distances of 3.253 Å, respectively. These values are consistent with those found for the DBCOT²⁻ complexes [3.105(4)-3.308(4) Å (Rb) and 3.337 Å (Cs)] and the related group 1 aluminyl

dimers that feature similar metal- π_{arene} interactions ([M{Al- (NON^{Dipp})]₂ = 3.0966(9)-3.1428(10) Å (M = Rb),3.2474(14)-3.2688(15) Å (M = Cs);^[15] $[M{AI(BDI-H)}]_2 = 3.275 - 3.359$ Å (M = Rb), 3.652–3.884 Å (M = Cs);^[16] $[M{AI(SiN^{Dipp})}]_2 = 3.099 Å (M = Rb),$ 3.247 Å (M=Cs).^[17] As seen with the lighter group 1 Ph_4Pn^{2-} complexes, the phenyl rings in [Rb(THF)]₂[Ph₄Pn] and [Cs-(THF)]₂[Ph₄Pn] were twisted relative to the plane of the pentalenide so as to minimise steric clashing of the ortho C–H, yet still allow some degree of π conjugation with the core and charge delocalisation into the aryl groups.^[13,18] The extent of the aryl twist was of a similar magnitude, though a relatively wide range of angles (14.8°-29.3° for [Rb(THF)]₂[Ph₄Pn] and 16.0°-28.0° for [Cs(THF)]₂[Ph₄Pn]) were found in the single crystal XRD data, likely a consequence of the aforementioned M- π_{arene} interactions.

The shortest average metal-C₅-centroid (M-C_t) distances were 2.886 Å for [**Rb**(**THF**)]₂[**Ph**₄**Pn**] and 3.038 Å for [**Cs**-(**THF**)]₂[**Ph**₄**Pn**], with the average M-C_t distances to the other C₅ ring 3.260 Å and 3.298 Å for [**Rb**(**THF**)]₂[**Ph**₄**Pn**] and [**Cs**-(**THF**)]₂[**Ph**₄**Pn**] respectively, consistent with the analogous distances in [**Cs**(**THF**)₂][**Cp**^{BIG-IP}] (3.169–3.228 Å; Cp^{BIG-IP}r= C₅(*p*-^IPrPh)₅)^[19] and followed the expected increasing trend down the group.^[111] The cations in both structures sat more centrally over the central pentalenide core than the lighter alkali metals, as seen by the average M-Pn_{centroid} distances of 2.918 Å (Rb) and 3.016 Å (Cs) being similar to the shortest M-C_t distance. These distances were increased compared with the **DBCOT**²⁻ complexes which exhibit M-COT_{centroid} distances of 2.569(4)–2.662(4) Å (Rb) and 2.788(4) Å (Cs).^[14]

The heavier group 1 cations engaging in η^8 coordination with $\mathbf{Ph_4Pn^{2-}}$ was further reflected by the average metal-C₅centroid-wingtip carbon (M-C_t-C_w) angles of 98.3° (Rb) and 104.7° (Cs). An angle of 90° would signify the cation to be sat centrally over a C₅ ring in perfect η^5 coordination, an acute angle showing slippage towards η^3 and an obtuse angle signifying a coordination towards η^8 . The extent of ring slippage in pentalenide and other bicyclic systems may also be quantified with the parameter Δ , which is defined as the difference in the mean M-C_B and M-C_{NB} distances (C_B = bridge-



Figure 2. Definitions of ring slippage and hapticity (top), metal-C_{5-centroid}-wingtip angle (bottom left), metal-Pn_{centroid}-wingtip angle (bottom middle) and aryl twist (bottom right).





Figure 3. Single crystal XRD structure of $[Cs(THF)]_2[Ph_4Pn]$ with thermal ellipsoids at the 50% probability level (hydrogens omitted for clarity) (left) and its polymeric propagation (right).

head carbon, C_{NB} = non-bridgehead carbon; Figure 2).^[20-22] A value of $\Delta = 0$ would suggest a true η^5 system, positive values signify slippage towards the non-bridgehead carbons and η^3 coordination, whilst negative values point to deviation towards the bridgehead carbon and η^2/η^8 coordination. Applying this measure to $[Rb(THF)]_2[Ph_4Pn]$ and $[Cs(THF)]_2[Ph_4Pn]$ returns Δ values of -0.20 and -0.28 respectively, further signifying the greater η^8 coordination of the heavier group 1 Ph₄Pn²⁻ complexes. Whether this higher hapticity is a consequence of increasing ionic size or due to *d*-orbital involvement^[23] (as often invoked for the heavy alkaline earth metals^[24-27]) is currently unclear. Previous calculations on unsolvated M2[Pn] complexes revealed the bonding to be 84-92% ionic in nature,^[11] whilst calculations on Ph₄Pn²⁻ have shown the four phenyl substituents reduce charge density in the pentalenide core by up to 50%.^[18] Therefore, the bonding in $M_2[Ph_4Pn]$ may be expected to be more orbital-controlled and some level of *d*-orbital involvement may exist.

When the Δ values of all group 1 salts are quantitatively compared, the shift in the cation positions with respect to Ph_4Pn^{2-} becomes evident (Figure 4). $[Li(THF)_2]_2[Ph_4Pn]$ has a ring slippage value of $\Delta = 0.03$ and a M-Ct-C_w angle of 90° consistent with true η^5 coordination,^[13] whilst [Na-(THF)_3]_2[Ph_4Pn] exhibited a notable ring slippage of -0.28, similar to that of [Cs(THF)]_2[Ph_4Pn]. However, whereas [Cs-(THF)]_2[Ph_4Pn] can be considered as having a coordination mode closer to that of η^8 , the significantly smaller size of Na⁺ would lead to its coordination being described as predominantly η^5 . [K₂(THF)₄(Ph₄Pn)]_x showed noticeably reduced

slipped character with $\Delta = -0.11$ compared with [Na-(THF)₃]₂[Ph₄Pn] and the M-C_t-C_w angle was also 5° more acute (95.2° for K and 100.7° for Na). Whilst both would be considered η^5 , the observed differences in the two structural parameters are likely a consequence of [Na(THF)₃]₂[Ph₄Pn] being monomeric and [K₂(THF)₄(Ph₄Pn)]_x adopting a solvent-bridged polymeric structure.^[13]

In general, the structures of all $M_2[Ph_4Pn]$ complexes followed the expected trends, with increased metal-centroid distances down the group and the largest change observed between Li and Na (Figure 5, top).^[11] In all cases the M-C_t distances were found to be slightly longer than those predicted computationally for unsubstituted $M_2[Pn]$. This likely reflects the influence of the phenyl substituents which serve to remove electron density from the pentalenide core, thereby reducing the electrostatic contribution in the bonding of the cations to $Ph_4Pn^{2-.[18]}$

The change in the M-C_t-C_w angles (Figure 5, bottom), and by extension the change in coordination from η^5 to η^8 , also followed the trend expected from the computed results, although with smaller than expected values obtained for the heavier cations. A larger than predicted M-C_t-C_w angle was found for [Na-(THF)₃]₂[Ph₄Pn], but when considering only the Li, K, Rb and Cs structures the expected trend can be observed (Figure 5).

In order to examine the influence of donor ligands on the key $M_2[Ph_4Pn]$ structural parameters the DME (1,2-dimeth-oxyethane; M = Li, Na) and Me_6TREN (tris(*N*,*N*-dimethyl-2-aminoethyl)amine; M = K, Rb, Cs) adducts of $M_2[Ph_4Pn]$ were synthesised and characterised by X-ray diffraction. The lithium complex was found to accept a single bidentate donor of DME





Figure 4. Side-on view of $M_2[Ph_4Pn]$ complexes for M = Li, Na, K, Rb, Cs (top) and a plot of their ring slippage values (bottom). ESDs are within the size of each data point shown.

per metal cation in the form of [Li(DME)]₂[Ph₄Pn] (Figure 6, left). This complex exhibited close structural resemblance to the THF adduct as evidenced by an M-C_t distance of 1.913(3) Å and a M-C_t-C_w angle of 88.9° (0.065 Å shorter and 1.2° more acute than Li₂[Ph₄Pn]).^[13] Whilst the ring slippage value of $\Delta = 0.06$ was double that of $[Li(THF)_2]_2[Ph_4Pn]$ ($\Delta = 0.03$) it was still too small to describe the bonding as anything other than η^5 . Interestingly, the M-C_t distance in [Li(DME)]₂[Ph₄Pn] was close to the experimental value of the unsubstituted pentalenide complex [Li(DME)]₂[Pn] reported as 1.89 Å.^[4] The DME solvate of the sodium complex was shown to contain two equivalents of the bidentate donor coordinated to each alkali metal as [Na(DME)₂]₂[Ph₄Pn] (Figure 6, right). In contrast to the lithium complex, the sodium complex displayed noticeable structural differences compared with its THF adduct, with a larger M-C_t distance of 2.5883(8) Å (versus 2.4915(7) Å) and a significantly more acute M-C_t-C_w angle of 79.0° (versus 100.7°). As a consequence, the Na⁺ coordination to Ph_4Pn^{2-} with DME ligation is best described as η^3 ($\Delta = 0.31$) compared with the intermediate η^8/η^5 observed in $[Na(THF)_2]_2[Ph_4Pn]$, reflecting the increased number of Lewis donors coordinating to sodium in the former.^[13] This finding contrasts previous computational results on the effect of DME complexation to $M_2[Pn]$ which indicated that, beyond an increase in M-Pn distance, no significant structural changes were expected when compared to the parent unsolvated complexes.^[11]

All of the heavier $[M(Me_6TREN)]_2[Ph_4Pn]$ (M=K, Rb, Cs) complexes were found to be monomeric due to coordinative saturation of the heavy alkali metals by Me₆TREN (Figure 7).^[28-31] The K⁺ in $[K(Me_6TREN)]_2[Ph_4Pn]$ adopted a more η^8 coordination to Ph_4Pn^{2-} than in the THF adduct as evident by increased ring slippage values of $\Delta = -0.33$ and an M-C_t-C_w angle of 101.3°. Conversely, the Cs⁺ in $[Cs(Me_6TREN)]_2[Ph_4Pn]$ engaged in a more η^5 coordination to Ph_4Pn^{2-} with a calculated ring slippage value of -0.04 and an M-C_t-C_w angle of 92.3°. In the case of $[Rb-(Me_6TREN)]_2[Ph_4Pn]$ two molecules with different structural parameters were found in the unit cell, one engaging in a more η^5 coordination mode to Ph_4Pn^{2-} ($\Delta = -0.17$, M-C_t-C_w=97.8°, M-Pn-





Figure 5. Comparison of the metal-centroid distances (top) and metal-centroid-wingtip angles (bottom) between calculated ($M_2[Pn]$) and experimental ($M_2[Pn_4Pn]$) values. ESDs are within the size of each data point shown.



Figure 6. Single crystal XRD structures of $[Li(DME)]_2[Ph_4Pn]$ (left) and $[Na(DME)_2]_2[Ph_4Pn]$ (right) with thermal ellipsoids at the 50% probability level (hydrogens omitted for clarity).

 $\begin{array}{l} \mathsf{C}_{\mathsf{w}} \!=\! 77.9^{\circ}, \, \mathsf{M} \! \! - \! \mathsf{Pn}_{\mathsf{centroid}} \!=\! 2.960(3) \, \, \mathring{\mathsf{A}}, \, \mathsf{M} \! - \! \mathsf{C}_{\mathsf{t}} \!=\! 2.905(3) \, \, \mathring{\mathsf{A}}) \, \text{and the other} \\ \mathsf{more} \quad \eta^{\mathsf{8}} \, \, \mathsf{coordination} \, \, (\Delta \!=\! -0.49, \, \, \mathsf{M} \! - \! \mathsf{C}_{\mathsf{t}} \! - \! \mathsf{C}_{\mathsf{w}} \! =\! 108.4^{\circ}, \, \, \mathsf{M} \! - \! \mathsf{Pn} \! - \! \mathsf{C}_{\mathsf{w}} \! =\! 89.7^{\circ}, \, \mathsf{M} \! - \! \mathsf{Pn}_{\mathsf{centroid}} \! =\! 2.897(4) \, \, \mathring{\mathsf{A}}, \, \mathsf{M} \! - \! \mathsf{C}_{\mathsf{t}} \! =\! 3.046(4) \, \, \mathring{\mathsf{A}}). \end{array}$

As shown in Figure 8, the replacement of THF by either DME or Me_6TREN generally resulted in an increase in M-C_t distances, with the largest influence observed for the potassium and caesium complexes. The addition of Me_6TREN to the

heavier group 1 complexes resulted in a slight decrease in the M-C_t-C_w angle and ring slippage value signifying a gradual shift towards η^5 coordination as the group is descended. This contrasts with the THF systems where a shift towards η^8 coordination was observed, a difference likely caused by the polymeric nature of the THF adducts.





Figure 7. Single crystal XRD structures of $[M(Me_6TREN)]_2[Ph_4Pn]$ with thermal ellipsoids at the 50% probability level (hydrogens omitted for clarity).



Figure 8. Comparison of key structural parameters between the THF, DME and Me_{d} TREN adducts of $M_{2}[Ph_{d}Pn]$ (M = Li, Na, K, Rb, Cs). ESDs are within the size of each data point shown.

3. Conclusions

The solid-state structures of THF-solvated rubidium and caesium complexes of $Ph_{4}Pn^{2-}$, the first heavy group 1 pentalenide complexes reported, have been crystallographically determined. In keeping with their lighter congeners the cations adopted antigeometry, and similarly to $[K_2(THF)_4(Ph_4Pn)]_x$ were found to be polymeric in the solid state.^[13] However, instead of propagation through bridging THF groups $\text{M-}\pi_{\text{arene}}$ interactions between the cation and the phenyl groups of Ph₄Pn²⁻ were found as in the related DBCOT²⁻ complexes.^[14] In agreement with computational data for M₂[Pn], [Rb(THF)]₂[Ph₄Pn] and [Cs(THF)]₂[Ph₄Pn] showed increased η^8 character as evident by increased M-C_t-C_w angles (98.3° for Rb and 104.7° Cs) and more negative ring slippage values of $\Delta = -0.20$ and -0.28 for [Rb(THF)]₂[Ph₄Pn] and [Cs-(THF)]₂[Ph₄Pn] respectively. Their increased hapticity, along with the decreased ionic character of $Ph_4Pn_{\prime}^{2-[18]}$ may suggest some dorbital involvement in their bonding. The Me₆TREN adducts of the heavy group 1 complexes ([M(Me₆TREN]₂[Ph₄Pn], M=K, Rb, Cs) showed the opposite trend to the THF adducts with [K- $(Me_6TREN)]_2[Ph_4Pn]$ exhibiting greater η^8 coordination than [Cs-(Me₆TREN)]₂[Ph₄Pn], whilst the structure of [Na(DME)₂]₂[Ph₄Pn] revealed a significant change in the coordination mode of Ph₄Pn²⁻ from η^8/η^5 in the THF adduct to η^3 . However, in the case of [Rb(Me₆TREN)]₂[Ph₄Pn] two molecules with different hapticity were found within the same unit cell, demonstrating the variability of bonding and influence of packing effects in these compounds which calls for caution in interpreting structural parameters from XRD data. Nonetheless, the results reported add to the structural diversity of alkali-metal coordination to large π systems^[32] and may lead to application in transmetalation reactions.

Experimental

General: 1,3,4,6-Ph₄PnH₂, Li₂[Ph₄Pn], Na₂[Ph₄Pn], K₂[Ph₄Pn],^[13] Rb-(HMDS),^[33] Cs(HMDS)^[34] and Me₆TREN^[35] were synthesised according

to literature procedures. All reactions were carried out in an argonfilled glovebox.

Analysis: Single-crystal X-ray diffraction analysis was carried out using a Rigaku XtaLAB Synergy-S with monochromated Cu-K α (λ 1.5418 Å) radiation ([Rb(THF)]₂[Ph₄Pn], [Cs(THF)]₂[Ph₄Pn], [Rb-(Me₆TREN)]₂[Ph₄Pn], [Cs(Me₆TREN)]₂[Ph₄Pn]), a RIGAKU SuperNova Dual EoS2 ([Na(DME)₂]₂[Ph₄Pn], [K(Me₆TREN)]₂[Ph₄Pn]) and a Rigaku Xcalibur EosS2 single-crystal diffractometer ([Li(DME)]₂[Ph₄Pn]). For the rubidium and caesium structures, data collection and processing used CrysalisPro software.^[36] The structures were refined to convergence against F^2 using all independent reflections and the SHELXL program.^[37,38]

Note: The reactions reported herein focussed on obtaining highquality single crystals for structural analysis and as such do not allow reporting yields. However, preparative upscaling and isolation should be possible as for other group 1 pentalenide complexes if desired.

Synthesis of [Rb(THF)]₂[Ph₄Pn]

1,3,4,6-Ph₄PnH₂ (10.0 mg, 0.025 mmol) and Rb(HMDS) (31.0 mg, 0.125 mmol) were dissolved in 3 mL THF. The resulting solution was allowed to stir for 20 hours at room temperature and then cooled to -20 °C for two weeks. An orange crystalline solid was formed which provided a sample suitable for XRD analysis shown to be [Rb(THF)]₂[Ph₄Pn].

Synthesis of [Cs(THF)]₂[Ph₄Pn]

An identical procedure utilising $1,3,4,6-Ph_4PnH_2$ (10.0 mg, 0.025 mmol) and Cs(HMDS) (37.0 mg, 0.125 mmol) yielded an orange crystalline solid which provided a sample suitable for XRD analysis shown to be $[Cs(THF)]_2[Ph_4Pn]$.

Synthesis of [Li(DME)]₂[Ph₄Pn]

 $Li_2[Ph_4Pn]$ (20.0 mg, 0.028 mmol) was dissolved in 1,2-dimethoxyethane (2 mL) and the red solution stored at -30 °C for 4 days to yield crystals suitable for XRD analysis shown to be [Li-(DME)]₂[Ph₄Pn].

Synthesis of [Na(DME)₂]₂[Ph₄Pn]

 $Na_2[Ph_4Pn]$ (20.0 mg, 0.022 mmol) was dissolved in 1,2-dimeth-oxyethane (2 mL) and the red solution stored at $-30\,^\circ\text{C}$ for 4 days to yield crystals suitable for XRD analysis shown to be [Na-(DME)_2]_2[Ph_4Pn].

Synthesis of [K(Me₆TREN)]₂[Ph₄Pn]

1,3,4,6-Ph₄PnH₂ (20.0 mg, 0.05 mmol) was dissolved in 0.3 mL THF and K(HMDS) (50.0 mg, 0.24 mmol) in 0.3 mL THF was added. The resulting solution was stirred for 24 hours before Me₆TREN (0.066 mL, 0.24 mmol) was added and stirred for a further 10 minutes. The red solution was stored at -35 °C for 2 days to yield an orange crystalline solid suitable for XRD analysis shown to be [K(Me₆TREN)]₂[Ph₄Pn].

Synthesis of [Rb(Me₆TREN)]₂[Ph₄Pn]

1,3,4,6-Ph₄PnH₂ (10.0 mg, 0.025 mmol) and Rb(HMDS) (31.0 mg, 0.125 mmol) were dissolved in 3 mL THF. The resulting solution was allowed to stir for 15 hours at room temperature and Me₆TREN

(0.020 mL, 0.075 mmol) was added. The mixture was stirred for 10 mins and then stored at -20 °C for 1 week. An orange crystalline solid was formed which provided a sample suitable for XRD analysis shown to be [Rb(Me₆TREN)]₂[Ph₄Pn].

Synthesis of [Cs(Me₆TREN)]₂[Ph₄Pn]

1,3,4,6-Ph₄PnH₂ (10.0 mg, 0.025 mmol) and Cs(HMDS) (37.0 mg, 0.125 mmol) were dissolved in 3 mL THF. The resulting solution was allowed to stir for 15 hours at room temperature and Me₆TREN (0.020 mL, 0.075 mmol) was added. The mixture was stirred for 10 mins and then stored at -20 °C for 1 week. An orange crystalline solid was formed which provided a sample suitable for XRD analysis shown to be [Cs(Me₆TREN)]₂[Ph₄Pn].

Supporting Information

The Supporting Information is available free of charge at Additional analytical data (XRD, NMR). CCDC 2332849–2332851 and 2335734–2335737 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Pentalenides \cdot Rubidium \cdot Caesium \cdot Alkali Metal Coordination

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