could have a high preparative value. The stage is now set for the discovery of new stereoconvergent reactions orchestrated by stereoselection at the steady state.

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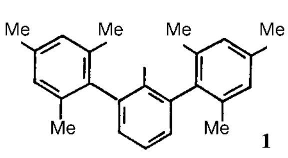
[5] The following rate constants were used for the calculation: $k_{\text{fast}} = 4.6 \times 10^7\,\text{s}^{-1}$; $k_{\text{slow}} = 1.0 \times 10^7\,\text{s}^{-1}$; $k_{\text{H}} = 2.0 \times 10^7\,\text{s}^{-1}$.

Phosphanides of the Heavier Alkali Metals

J. David Smith*

Much of the fascination of inorganic chemistry lies in the study of trends in the periodic table, up and down groups, across periods, and diagonally. Compounds of the same stoichiometry are compared, similarities noted, and attempts made to understand subtle differences. It has been commonplace in teaching inorganic chemistry to cover the marked changes from carbon to lead or from nitrogen to bismuth in considerable detail, and to pass rather quickly over some of the other groups—for example, the alkali metals, alkaline earths, or halogens—because the variation from the top to the bottom of the periodic table is much smaller. In these groups near the sides of the table the chemistry is dominated by one oxidation state, but it is rash to assume that the chemistry of those elements which have been less fully studied will simply mirror that of the compounds that are well known. Factors other than oxidation state, for example size and polarizability, have to be considered, and these may give much greater variety in the chemistry of, for example, elements from Groups 1, 2, 3, or 17 than is sometimes acknowledged.

This point is illustrated for the chemistry of the Group 1 elements in the recent paper by Rabe et al.[1] on the structure of the rubidium and cesium phosphanides MPHR (M = Rb, Cs, R = 2,6-dimesitylphenyl (**1**)). General interest in the reactions of alkali metals with phosphanes comes from their widespread use in the synthesis of phosphorus-containing ligands. The lithium phosphanides of general formula LiPHR or $LiPR_2$ show a wide variety of structures that were summarized recently by Becker et al.[2] A few compounds—especially those in which the lithium atom is complexed by large ligands, for example, [12]crown-4—are ionic,[2, 3] that is, $[LiL_n][PR_2]$. Monomeric molecular structures are rare. More commonly, the molecules associate to give ladder or helical structures which may be oligomeric or polymeric[2, 4] (Figure 1) like the corresponding amido compounds.[5] Information on the structures of sodium and potassium phosphanides is sparse, but the few examples that have been reported show that they fit into the same overall pattern. Polymeric ladder structures, based on alkali metal–phosphorus bonds, predominate.[6]



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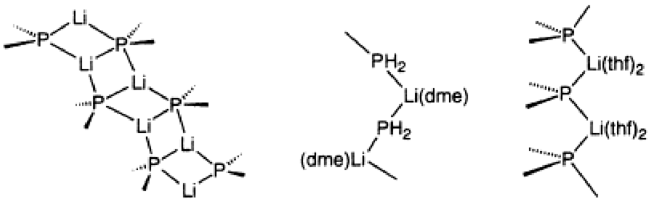

Figure 1. Some structures of lithium phosphanides (taken from reference [4]). dme = 1,2-dimethoxyethane.

The general principles underlying this pattern of structures were defined in a seminal paper[7] many years ago, and they apply to most groups of oligomeric compounds containing an element from Groups 1–3 (M) and one from Groups 15–17 (E). Firstly, for the formation of higher from lower oligomers, the enthalpy change associated with the formation of additional M–E bonds must be sufficient to overcome the unfavorable entropic contribution to the free energy. Secondly, the oligomerization or polymerization is curtailed by the attachment of large groups to either element. In the last few years very bulky aryl groups such as **1** have been used for this purpose, and a range of main group compounds showing highly unusual structural features have been obtained.[3, 8]

Rabe et al.[1] studied the reactions of the heavier alkali metals rubidium and cesium with the very bulky 2,6-dimesi-

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tylphenylphosphane. Yellow crystals of the rubidium compound RbPHR were obtained from toluene, and crystals of the cesium compound from toluene containing the bases tetrahydrofuran (THF) or *N*-methylimidazole (*N*-MeIm). X-ray studies showed that the solid-state structures differed from those of previously described alkali metal salts of primary phosphanes.

The rubidium compound adopts a cubane structure $[RbPHR]_4$ (Figure 2a) of the kind that is common among the alkoxo, thiolato, and imido derivatives of main group elements. For compounds in which M = alkali metal examples of $(MCl)_4$ and $(MOR)_4$ are known: $[RbPHR]_4$ (**2**) extends the isoelectronic series. However, whereas many halides and alkoxo derivatives require lone pairs from bases such as THF to complete the coordination sphere of the alkali metal, for example $[Li\{OP(NMe_2)_3\}Cl]_4$ or $[Li(thf)OCtBu{=}CH_2]_4$,[9] these are excluded in **2**, and electrons are donated instead from the mesityl rings from phosphanido ligands encapsulating the rubidium atoms (Figure 2a). The metal–aryl interactions must therefore compete successfully with the metal–lone pair interactions.

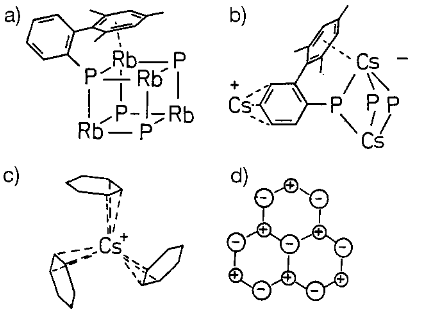

Figure 2. Partial structures of the rubidium and cesium phosphanides **2** and **3**. a) Partial structure of **2**; b) partial structure of **3**; c) coordination of the cation in **3**; d) the two-dimensional net in **3** showing the cavities occupied by solvent.

The cesium compound forms a two-dimensional ionic structure described by the formula $Cs^+[Cs_2(PHR)_3]^-$ (**3**). Within the anion the two cesium atoms are linked by three PHR bridges and protected by mesityl groups on the periphery of the ligands R, rather like the rubidium atoms in **2** (Figure 2b). The cesium cations are coordinated by the central phenyl groups of the phosphane ligands at the 3-, 4-, and 5-positions. The two-dimensional structure as a whole has threefold symmetry about axes through the two cesium atoms of the anion. Since each cesium cation is bound to ligands from three separate anions, its coordination resembles that of a paddle wheel (Figure 2c). The net of cations and anions has a series of holes which accommodate toluene solvate molecules as in a host–guest compound (Figure 2d). The toluene molecules are readily removed under reduced pressure to leave a solid which will not redissolve in toluene without the addition of a base such as THF, pyridine, or *N*-MeIm; however, upon crystallization the metal–aryl interactions are, as in **2**, sufficiently strong to exclude the base from the cesium coordination sphere.

What other general points can be made about these two unexpected new structures? Firstly, they provide examples of a general pattern which is now recognized to be widely applicable. In a series of compounds with the same overall stoichiometry, for example $M^+[EAr_n]^-$, the lighter alkali metals lithium and sodium tend to make bonds with the electronegative elements E, whereas the heavier, softer, more polarizable alkali metals rubidium and cesium frequently interact most strongly with aryl groups on the ligand periphery. There are exceptions to this rule, but the general tendency is clear as shown by data on organometallic compounds[10] as well as aryloxo and arylthiolato derivatives.[11] This is illustrated here by just one example chosen from many others in the literature. The structure of the mixed alkoxide $Cs_2La(OAr)_5$ (Ar = 2,6-diisopropylphenyl)[12] consists of layers of two-dimensional sheets containing cesium cations and $La(OAr)_5$ anions linked by cesium–aryl interactions, and the sheets are linked by additional cesium–aryl contacts into a three-dimensional framework leaving channels which can accommodate toluene solvate molecules (c.f. **2**). The coordination sphere of each of the three independent cesium atoms in the complex structure is made up entirely of 19 Cs–C contacts, and there is no Cs–O distance that is smaller than 450 pm.

Secondly, the structures suggest that the balance between metal–aryl and metal–phosphorus interactions is subtle. A small change from rubidium to cesium can produce a drastic change in structure. Since the ligand remains the same the difference must arise from the relative strengths of metal–phosphorus and metal–aryl interactions. It would be interesting to know whether systematic changes in structure can be induced by changes in substituents on the aryl rings, and what part is played by the steric requirements of the ligand in determining the structures of compounds in which there are lithium–aryl interactions, for example $[LiR'LiPHR']_2$ (**4**, R' = 2,4,6-$tBu_3C_6H_2$;[12] Figure 3). The increased importance of metal–aryl interactions for the heavier alkali metals has been demonstrated in a number of computational studies.[13]

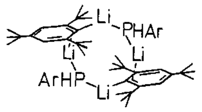

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Figure 3. Aryl–lithium interactions in **4**.

Thirdly, structures studied by X-ray diffraction are those of compounds which crystallize; they do not necessarily indicate the species in solution, though they may provide strong pointers. The development of modern gloveboxes and improvements in equipment for vacuum lines allow rigorous control of blanket-gas composition so that very air- and moisture-sensitive organo, alkoxo, amido, and phosphanido compounds may be safely manipulated. It is likely that many more compounds of the heavier alkali and alkaline earth metals will be studied in the next few years. The incentive will come both from interest in the new structures themselves and from those engaged in the preparation of phosphanes for incorporation into catalysts for asymmetric syntheses or polymerization.[14] If the compounds of rubidium and cesium prove to be more reactive than the analogous compounds of lithium and sodium, they could be used as ligand transfer reagents at lower temperatures and therefore with fewer side reactions and less racemization. The extent to which the metal–aryl interactions can be broken down in solution is not yet clear. Compounds **2** and **3** proved to be insoluble in organic solvents in the absence of base. Is this a general characteristic for such compounds?

Good research answers some questions but raises others. There is considerable scope for further investigation before the chemistry of the heavier alkali metal phosphanides is understood.

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