Unique Group 1 cations stabilised by homoleptic neutral phosphine coordination†

Marina Carravetta, Maria Concistre, William Levason, Gillian Reid* and Wenjian Zhang

Homoleptic coordination of the neutral diphosphines $\text{Me}_2\text{P(CH}_2\text{)}_2\text{PMe}_2$ and $\sigma$-$\text{C}_6\text{H}_4\text{PMe}_2\text{J}_2$ to the hard Li$^+$ and Na$^+$ cations is achieved using $\text{Li}[\text{OC(CF}_3\text{)}_2\text{J}_2]$ and $\text{Na}[\text{B(3,5-OC(CF}_3\text{)}_2\text{C}_6\text{H}_4\text{J}_2]$ as ‘naked’ cation sources. Crystalllographic, solid state and solution multinuclear NMR studies confirm distorted octahedral coordination solely via three chelating diphosphines in these unique species.

Neutral phosphate ligands, $\text{PR}_3$ ($\text{R} = \text{alkyl, aryl}$), are ubiquitous in transition metal chemistry, owing to their capacity to tune the electronic and steric properties, and hence the reactivity, of the complexes, and to the strong $\sigma$-donor properties of the soft phosphine donor functions. This has led to wide utilisation of phosphate co-ligands in many transition metal reagents and catalysts. Phosphine complexes of many p-block acceptors have also developed substantially in recent years. However, complexes involving coordination of neutral phosphate ligands towards the strongly electropositive s-block elements, particularly the Group 1 cations, have remained extremely elusive, and there are no reported examples with exclusively $\text{PR}_3$ coordination. This is no doubt in part due to the high affinity of the alkali metal and alkaline earth cations for hard, electronegative Lewis bases such as water, alkoxide, amide etc., their high lability, as well as the high lattice energies often associated with many Group 1 and 2 salts, which severely limit their solubilities in non-competitive organic media. Thus, to-date there has been only one reported example of a neutral phosphate co-ligand coordinated to an alkali metal cation, the organometalllic silylamide dimer $[\text{Li}{\text{N(Ar)}\text{C}(\text{SiMe}_3)\text{2}}](\text{dme})_2$ (solvent = thf, $x = 2$; Et$_3$O, $x = 1$) ($d(\text{Li} – \text{P}) = 2.596(3), 2.608(3)$ Å), as well as a small number of Li$^+$ complexes with phosphinomethylaluminate ligands. The negative charge on the anionic ligands in these species brings a significant electrostatic component to the bonding, and contrasts the covalet metal–phosphine bonding present in the d- and p-block acceptor ions.

In recent work we reported that complexes of Na$^+$ with polyamines andaza macrocycles, including the $[\text{Na}(\text{Me}_2\text{tacn})_2]^+$ sandwich cation and the distorted five-coordinate $[\text{Na}(\text{thf})(\text{Me}_4\text{-cyclam})]^+$ cation ($\text{Me}_2\text{-tacn} = 1,4,7,10\text{-tetramethyl-1,4,7,10-tetraazacyclododecane}$, $\text{Me}_2\text{-cyclam} = 1,4,8,11\text{-tetramethyl-1,4,8,11-tetraazaacyclotetradecane}$), could be prepared readily by using $[\text{Na}(\text{BAR})_2]^+$ [BAR$^+$ = $[\text{B}(\text{3,5-OC(CF}_3\text{)}_2\text{C}_6\text{H}_4\text{J}_2]$]. This $\text{BAR}^+$ salt has good solubility in weak-donor solvents such as $\text{CH}_2\text{Cl}_2$ and toluene. Very recently we extended this chemistry by reporting the homoleptic octahthia coordination to Na$^+$ in the macrocyclic complex, $[\text{Na}(\text{[24]aneS}_8)][\text{BAR}^+]$ ($[\text{24]aneS}_8 = 1,4,7,10,13,16,19,22\text{-octaaza-}
\text{cyclotetradecane}$), containing distorted dodecahedral coordination. To develop this chemistry further we sought to establish whether it would be possible to induce coordination of softer, neutral phosphate ligands towards Group 1 cations without the additional stability offered by the macrocyclic frameworks employed in the aza and thioether chemistry. To achieve this we have used both the $\text{BAR}^+$ and $[\text{Al}(\text{OC(CF}_3\text{)}_2\text{J}_4)]^{15}$ weakly coordinating anions.

We describe here the first series of Group 1 cations coordinated only to neutral phosphate ligands, in the form of distorted octahedral Li$^+$ and Na$^+$ cations containing tris-diphosphine coordination.

Reaction of $[\text{Li}[\text{OC(CF}_3\text{)}_2\text{J}_4]$ with three mol. equiv. of $\text{Me}_2\text{PCH}_2\text{C}_6\text{H}_4\text{PMe}_2$ (dmpe) or $\sigma$-$\text{C}_6\text{H}_4\text{PMe}_2\text{J}_2$ (diphos) in anhydrous...
toluene gives [Li(dmpe)₃][Al{OC(CF₃)₃}₄] and [Li(diphos)₃][Al{OC(CF₃)₃}₄], respectively as white solids in very good yield.† The corresponding [Na(dmpe)₃][BARF] and [Na(diphos)₃][BARF] salts were obtained similarly from a 3:1 diphosphine:Na[BARF] ratio. Attempts to prepare the analogous K+ complexes by reaction of the diphosphine with K[BARF] in a 3:1 molar ratio failed, while the weaker donor and sterically bulkier o-C₆H₄(PPh₂)₂ and the diarsine, o-C₆H₄(AsMe₂)₂ (the direct analogue of diphos), did not coordinate to Li⁺ or Na⁺ under similar conditions.

The coordination environments present in the new complexes were established unambiguously from X-ray crystallographic studies on three examples. The structure§ of [Na(dmpe)₃][BARF] contains discrete Na⁺ cations coordinated to three chelating dmpe ligands, in a distorted octahedral environment (Fig. 1), with discrete [BARF]⁻ anions providing charge balance. The Na–P bond distances lie in the range 2.95–3.03 Å, suggesting relatively weak coordination, and the P–Na–P angles within the five-membered chelate rings are very acute (69.8–73.4°). A similar structure is present in [Na(diphos)₃][BARF],§ with coordination at Na⁺ through six P-donor atoms from three chelating diphos ligands, with d(Na–P) = 2.92–3.07 Å (Fig. 2). As in the dmpe complex, these are considerably longer than the sum of the ionic radius for Na (1.02 Å) and the covalent radius for P (1.06 Å). They compare with [Na[H₂Al{P(SiMe₃)₂}₂](dmpe)] d(Na–P) = 3.052(1), 3.092(1) Å.³ The P–Na–P angles within the chelate rings are even more acute, ca. 65°, reflecting the smaller bite angle associated with the rigid o-phenylene diphosphine cf. the dimethylene-linked dmpe. The large [BARF]⁻ anions remain discrete, but interleave between the cations (Fig. S1, ESI†).

The structure§ of the lithium–diphosphine complex, [Li(diphos)₃][Al{OC(CF₃)₃}₄] was also determined from a small, weakly diffracting crystal. While the weak diffraction data mean that detailed geometric comparisons require caution, the presence of three chelating neutral diphos ligands at Li⁺, giving homoleptic P₆-coordination, is unequivocal (Fig. 3). The alaninate anion provides charge balance, but does not interact with the cation. The Li–P bond distances are considerably shorter (by ca. 0.4 Å) than d(Na–P) in these systems, while the P–Li–P angles within the chelate rings are correspondingly larger (ca. 75°), as expected due to the smaller ionic radius.

To investigate the properties of these unusual complexes further, we obtained the MAS NMR spectroscopic data (³¹P, ²³Na and ⁷Li) from the powdered solids. The NMR data are summarised in Table 1. The spectra for [Li(dmpe)₃]⁺ are shown in Fig. 4 (the other spectra are provided as ESI† Fig. S2–S4). The ³¹P NMR data from direct excitation (Fig. 4(a)) exhibits two peaks, the main one at −54.5 ppm is attributed to the six equivalent P-donor atoms in the complex cation; the minor peak at −48.5 ppm is consistent with the chemical shift for ‘free’ dmpe...
Na complexes recorded in CD$_2$Cl$_2$ solution (298 K). [Na(diphos)$_3$][BArF]$_3$

Some sample degradation during spectral acquisition. b Selected solid state and solution NMR spectroscopic data

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta^{31P}$/ppm</th>
<th>$\delta^7Li$/ppm</th>
<th>$\delta^{23Na}$/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Li(diphos)$_3$][Al{OC(CF$_3$)$_3$}$_4$]</td>
<td>59.2</td>
<td>+0.4</td>
<td>+3.8</td>
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<tr>
<td>[Li(dmpe)$_3$][Al{OC(CF$_3$)$_3$}$_4$]</td>
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<td>-0.1</td>
<td>+5.5</td>
</tr>
<tr>
<td>[Na(diphos)$_3$][BArF]$_3$</td>
<td>-61.5, -59.0 (1:1)</td>
<td>—</td>
<td>+8.9</td>
</tr>
<tr>
<td>[Na(dmpe)$_3$][BArF]$_3$</td>
<td>-57.4</td>
<td>—</td>
<td>+2.5</td>
</tr>
</tbody>
</table>

a Small amounts of uncomplexed ligand (literature $\delta^{31P} = -48$ (dmpe)$^{20}$ and $-55$ (diphos)$^{20}$) were also observed in the solid state spectra in some of the samples, arising from some sample degradation during spectral acquisition. b Li complexes recorded in d$_2$-toluene solution (298 K); Na complexes recorded in CD$_2$Cl$_2$ solution (298 K). c $\delta^{23Na}$ measured for Na[BArF]$_3$ = -35.5 (s) ppm.

in solution (−48 ppm)$^{20}$ This is further confirmed by $^{31P}$ cross-polarization (CP) MAS$^{21}$ data (Fig. 4(b)), where the second peak is absent, in accord with the highly mobile nature of ‘free’ dmpe.

The chemical shift differences between ‘free’ and coordinated diphosphine (J) are small and negative for all complexes; (L = dmpe: Δ = −6 ppm for Li$^+$; −9.4 ppm for Na$^+$; L = diphos: Δ = −5 ppm for Li$^+$; ca. −6 ppm for Na$^+$). These contrast with the large, positive Δ values typically observed in transition metal phosphine complexes which contain five-membered chelate rings. No $Li^{31P}$ or Na$^{31P}$ couplings are evident in the spectra, presumably due to the small magnitude of the J values, which fall within the line width.

Fig. 4(c) shows the $^7Li$ NMR data for [Li(dmpe)$_3$][Al{OC(CF$_3$)$_3$}$_4$], showing a single peak at −0.7 ppm.

Solution $^1$H and $^{31P}$($^1$H) NMR spectra (d$_8$-toluene or CD$_2$Cl$_2$) on the four compounds also show very small coordination shifts, although in these spectra the resonances are closer to the respective ‘free’ ligand. These, as well as the $^7Li$ and $^{23Na}$ solution spectra, are essentially unchanged upon cooling to 183 K (it seems likely that the low temperature-limiting spectrum is not reached at the freezing point of the solvent). These observations may indicate that in solution the complexes are partially dissociated, leading to chemical shifts closer to the free ligand values. Sharp singlets are observed by $^7Li$ and $^{23Na}$ NMR spectroscopy, with chemical shifts similar to those from the solid state spectra (Table 1).

These results demonstrate that unusual homoletic neutral phosphine complexes of the Group 1 cations can be readily accessed in (non-polar) organic media through the use of the strong σ-donating bidentate ligands with ‘naked’ metal cation sources.

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Notes and references

† Synthetic procedures. Schlenk techniques and a glove-box were used for all manipulations, which were conducted under anhydrous and anaerobic conditions.

[Li(diphos)$_3$][Al(OC(CF$_3$)$_3$)$_4$]; Li[Al(OC(CF$_3$)$_3$)$_4$] (121 mg, 0.125 mmol) in 3 mL toluene was added o-C$_6$H$_4$(PMe$_2$)$_2$LiO(P$_3$) (1568.5): C, 35.2%; H, 3.0%. Found: C, 35.2 %; H, 3.0 %. $^1H$ NMR (CD$_2$Cl$_2$, 298 K): 1.35 [s, (36H), Me], 7.37–7.43 [m, (6H), o-C$_6$H$_4$].

[Na(dmpe)$_3$][B{3,5-(CF$_3$)$_2$-C$_6$H$_4$}$_4$]: method as above, using Na[B{3,5-(CF$_3$)$_2$-C$_6$H$_4$}$_4$] (110 mg, 0.125 mmol) in 3 mL toluene under N$_2$. Analytical required for C$_{46}$H$_{48}$AlF$_{36}$LiO$_4$P$_6$: C, 28.6; H, 3.3%. $^1H$ NMR (CD$_2$Cl$_2$, 298 K): 1.85 [br s, (12H), CH$_2$] ppm.

[Na(dmpe)$_3$][B{3,5-(CF$_3$)$_2$-C$_6$H$_4$}$_4$]: method as above, using Na[B{3,5-(CF$_3$)$_2$-C$_6$H$_4$}$_4$] (121 mg, 0.125 mmol) in 5 mL toluene was added dmpe (58 mg, 0.375 mmol) with stirring. After 5 min, the volatiles were removed in vacuo. The white solid residue was washed with pentane and dried in vacuo. Yield: 181 mg 92%. Colourless single crystals were grown by slow evaporation from a toluene solution under N$_2$. Anal, required for C$_{46}$H$_{48}$AlF$_{36}$LiO$_4$P$_6$: C, 28.7; H, 3.0%. $^1H$ NMR (CD$_2$Cl$_2$, 298 K): 1.30 (br s, [36H], Me), 7.37–7.43 (m, [6H], o-C$_6$H$_4$), 7.53 (m, [6H], o-C$_6$H$_4$) ppm.

[Na(dmpe)$_3$][B{3,5-(CF$_3$)$_2$-C$_6$H$_4$}$_4$]: method as above, using Na[B{3,5-(CF$_3$)$_2$-C$_6$H$_4$}$_4$] (110 mg, 0.125 mmol) in 3 mL toluene under N$_2$. Analytical required for C$_{46}$H$_{48}$AlF$_{36}$LiO$_4$P$_6$: C, 28.6; H, 3.3%. $^1H$ NMR (CD$_2$Cl$_2$, 298 K): 1.85 [br s, (12H), CH$_2$] ppm.
White solid. Yield: 143 mg, 85%. Colourless single crystals were grown by slow evaporation from a toluene solution under N2. Anal, required for C60H60BF24NaP6 (1336.6): C, 44.9; H, 4.5%. Found: C, 44.8; H, 4.5%. The ORTEP drawing of (1) is shown in Fig. 3 along with the atom numbering. The CCDC Structures deposited in the Cambridge Structural Database under the deposition numbers 1044099–1044101.

Crystal data for [Na(dmpe)3][BArF]: C60H60BF24NaP6, MW = 1336.60, monoclinic, P21/c (no. 14), a = 18.4514(10), b = 13.2631(10), c = 26.1323(2) A, β = 98.8263(2), U = 6394.6(8) Å3, Z = 4, µ = 0.277 mm−1, θ = 100 K, 35720 total reflections, 12559 unique reflections, Rint = 0.059, R1 = (I > 2σ(I)) = 0.068, R2 (all data) = 0.165, wR2 (I > 2σ(I)) = 0.169, wR2 (all data) = 0.197.

Crystal data for [Li(diphos)3][Al{OC(CF3)3}4]: C40H48AlF36LiO4P6, MW = 1480.72, triclinic, P1 (no. 2), a = 12.5084(10), b = 16.4799(10), c = 17.5637(10) Å, α = 79.47(4), β = 78.804(4), γ = 81.625(4), U = 3460.2(4) Å3, Z = 2, µ = 0.264 mm−1, 31294 total reflections, 13561 unique reflections, Rint = 0.033, R1 = (I > 2σ(I)) = 0.053, R1 (all data) = 0.063, wR2 (I > 2σ(I)) = 0.143, wR2 (all data) = 0.149.

Crystal data for [Li(diphos)3][Al(OC(CF3)3)3]: C66H56AlF18LiOP6, MW = 1568.58, orthorhombic, Pna21 (no. 33), a = 15.092(2), b = 27.737(5), c = 15.405(3) Å, U = 6449.1(19) Å3, Z = 4, µ = 0.325 mm−1, 38663 total reflections, 12559 unique reflections, Rint = 0.093, R1 = (I > 2σ(I)) = 0.101, R1 (all data) = 0.150, wR2 (I > 2σ(I)) = 0.210, wR2 (all data) = 0.236. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E Superbright molybdenum rotating anode generator (λ = 0.71073 Å) with VHF Varimax optics (70 µm f/0.95). The crystals were held at 100 K in a nitrogen gas stream. Structure solution and refinement on the Na complexes were mostly straightforward, except for some disorder in the CF3 groups of the [BArF]− anions which was modelled satisfactorily. For [Li(diphos)][Al(OC(CF3)3)], despite several attempts, only very small crystals could be obtained. This led to weak diffraction, particularly at high angle, and hence higher R-factors and a less well-defined structure. The H atoms were placed in calculated positions and refined using ariding model. The H atoms on the disordered CH and CH3 group were not located. CCDC 1044099–1044101.

Additional measurements were performed on a Bruker 9.4 T magnet with a Chemagnetics Infinity console using a double-resonance 4 mm APEX probe. Solid powdered samples were transferred into 4 mm zirconium thin wall rotors within the glovebox, using special end caps with o-rings to exclude air. Magic angle spinning (MAS) conditions have been applied with a spinning speed of 7.1 kHz at room temperature, using N2 gas flow for bearing and drive. The chemical shift scales were referenced by setting at 0 ppm the signals of LiCl 1 M, NaCl 1 M and 85% H3PO4, respectively for 6Li, 23Na and 31P. Spectra were recorded with direct excitation using a 90° pulse followed by acquisition, without proton decoupling. For 31P NMR, additional measurements were also performed with ramped CP methods with 3 ms contact time.