Unique Group 1 cations stabilised by homoleptic neutral phosphine coordination†

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Homoleptic coordination of the neutral diphosphines Me₂P(CH₂)₂PMe₂ and σ-C₆H₄[PMé₂]₂ to the hard Li⁺ and Na⁺ cations is achieved using Li[Al(OCl)(CF₃)₂]₂ and Na[B(3,5-(CF₃)₂C₆H₄)]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 phoshpine ligands, PR₃ (R = 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 σ-donor properties of the soft phosphine donor functions. This has led to wide utilisation of phosphine co-ligands in many transition metal reagents and catalysts.¹ Phosphine complexes of many p-block acceptors towards the strongly electropositive s-block elements, particularly the Group 1 cations, have remained extremely elusive, and there are no reported examples with exclusively PR₃ 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, alkoide, 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 phosphine co-ligand coordinated to an alkali metal cation, the organometallic silylamide dimer [Li{N(Ar)CC(R)–Si(R)₂NAr}₂](dme)₂, containing distorted dodecahedral coordination.¹⁴

A small number of anionic ligands bearing phosphine functions have been coordinated to s-block cations, including [Mg(C₆H₄–2,6-(CH₂PMé₂)₂)₂]₂ in which the Mg–P bonds are also stabilised by the anionic pincer ligand framework,⁵ [(Li[2-PPh₂-C₆H₄]₂)(OB₃)]₂ (d(Li–P) = 2.69–2.75 Å),⁶ hindered alkoxy–phosphine complexes, including [Li[μ-OCBu₂CH₂PR₂]]₂ (R = Me or Ph) and [Li[μ-OCBu₂CH₂PPh₂]Li(OCBu₃)] (d(Li–P) = 2.50–2.65 Å),⁷ [Na[H₂Al{P(SiMe₃)₂}₂](dme)]₉ [Li(solvent)]₂[Ph₃B–(CH₂P₃Pr₂)₂]₉ (solvent = thf, x = 2; Et₂O, x = 1) (d(Li–P) = 2.596(3), 2.608(3) Å),⁸ as well as a small number of Li⁺ complexes with (phosphinomethyl)aluminate ligands.¹¹ The negative charge on the anionic ligands in these species brings a significant electrostatic component to the bonding, and contrasts the covalent metal–phosphine bonding present in the d- and p-block acceptor ions.

In recent work we reported¹² that complexes of Na⁺ with polyanimes andaza macrocycles, including the [Na(Me₂-tacn)₂⁺ sandwich cation and the distorted five-coordinate [Na(thf)[Me₂-cyclam]]⁺ cation (Me₂-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, Me₂-cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), could be prepared readily by using Na[BAR⁺]·2thf ([BAR⁺] = [B(3,5–CF₃)₂–C₆H₄]⁺). This [BAR⁺]⁺ salt¹³ has good solubility in weak-donor solvents such as CH₂Cl₂ and toluene. Very recently we extended this chemistry by reporting the homoleptic octahidia coordination to Na⁺ in the macrocyclic complex, [Na([24]aneS₈)]⁺[BAR⁺]¹⁶ ([24]aneS₈ = 1,4,7,10,13,16,19,22-octahediazacyclotetradecane), containing distorted dodecahedral coordination.¹⁴ To develop this chemistry further we sought to establish whether it would be possible to induce coordination of softer, neutral phosphine ligands towards Group 1 cations without the additional stability offered by the macrocyclic frameworks employed in the azo and thioether chemistry. To achieve this we have used both the [BAR⁺]⁺¹⁵ and [Al(OC(CF₃)₂)]⁺ weakly coordinating anions.¹⁶–¹⁹

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

Reaction of Li[Al[OC(CF₃)₂]₄] with three mol. equiv. of Me₂PCH₂CH₂PMe₂ (dmpe) or σ-C₆H₄[PMé₂]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. 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 aluminato 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...
Table 1  Selected solid state and solution NMR spectroscopic data.a

| Complex                                      | δ31P/ppm | δ7Li/ppm | δ23Na/ppm |
|----------------------------------------------|----------|----------|-----------|
| [Li(dmpe)3][Al{OC(CF3)3}4]                  | −54.5    | −45.9    | −5.7      |
| [Na(dmpe)3][BArF4]                          | −57.4    | +4.0     | +5.8      |
| [Li(dmpe)3][Al{OC(CF3)3}4]                  | −54.5    | −45.9    | −5.7      |
| [Na(dmpe)3][BArF4]                          | −57.4    | +4.0     | +5.8      |
| [Na(dmpe)3]                                  | −61.3.   | −50.3    | +3.8      |
| [Na(dmpe)3][BArF4]                          | −49.7    | +8.9     | +2.5      |

a  Small amounts of uncomplexed ligand (literature δ31P = −48 (dmpe)) and −55 (diphos) were also observed in the solid state spectra in some of the samples, arising from some sample degradation during spectral acquisition. δ Li complexes recorded in d8-toluene solution (298 K); Na complexes recorded in CD2Cl2 solution (298 K). δ23Na measured for Na[BArF4] = −35.5 (s) ppm.

in solution (−48 ppm). This is further confirmed by 31P cross-polarization (CP) MAS 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 diphenylphosphine (diphos) 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 31P−31P or 31P−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(CF3)3}4], showing a single peak at −0.7 ppm.

Solution 1H and 31P{1H} NMR spectra (d8-toluene or CD2Cl2) 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 homoleptic 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 procedure. Schlenk techniques and a glove-box were used for all manipulations, which were conducted under anhydrous and anaerobic conditions.

[Li(dmpe)3][Al{OC(CF3)3}4]: As above, using Na[B{3,5-(CF3)2-C6H3}4]: method as above, using Na[B{3,5-(CF3)2-C6H3}4]: (110 mg, 0.125 mmol) and dmpe (58 mg, 0.375 mmol). 7Li NMR (CD2Cl2, 298 K): 1.35 (s, [36H], Me), 7.37–7.43 (m, [6H], o-C6H4), 7.53 (m, [6H], o-C6H4 and [BArF]), 7.62 (s, [8H], [BArF]). Anal, required for C46H48AlF36LiO4P6 (1424.4): C, 28.6; H, 3.3%. Found: C, 28.7; H, 3.0%. 1H NMR (CD2Cl2, 298 K): 1.30 (br s, [36H], Me), 7.62 (s, [8H], [BArF]).

[Na(dmpe)3][B{3,5-(CF3)2-C6H3}4]: As above, using Na[B{3,5-(CF3)2-C6H3}4]: (110 mg, 0.125 mmol) and dmpe (58 mg, 0.375 mmol),
White solid. Yield: 143 mg, 85%. Colourless single crystals were grown by slow evaporation from a toluene solution under N₂. Anal, required for C₃₀H₄₀BF₂₄Na₆P₆ (1336.6): C, 44.9; H, 4.5%. Found: C, 44.8; H, 4.5%. 

§ Crystal data for [Na(dmpe)₃][BAR⁷]: Cₙ₀H₄₀BF₂₄Na₆P₆, Mₒ = 1336.60, monoclinic, P₂₁/c (no. 14), a = 18.4514(10), b = 13.2631(10), c = 26.133(2) Å, β = 108.826(3)°, V = 6394.6(8) Å³, Z = 4, μ = 0.277 mm⁻¹, T = 100 K, 35720 total reflections, 12513 unique reflections, Rint = 0.059, R₁ (I > 2σ(I)) = 0.068, R₁ (all data) = 0.165, wR₂ (I > 2σ(I)) = 0.169, wR₂ (all data) = 0.197.

Crystal data for [Li(diphos)₃][BAR⁷]: C₃₀H₃₆BF₂₄Na₆P₆, Mₒ = 1480.72, triclinic, P1 (no. 2), a = 12.5084(10), b = 16.4798(10), c = 17.5637(10) Å, α = 79.047(4), β = 78.625(4), γ = 81.625(4), V = 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(O(CF₃)₃)₃]: C₳₆H₴₆AlLiO₃P₆, Mₒ = 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 (μ = 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 (μ = 0.236.

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