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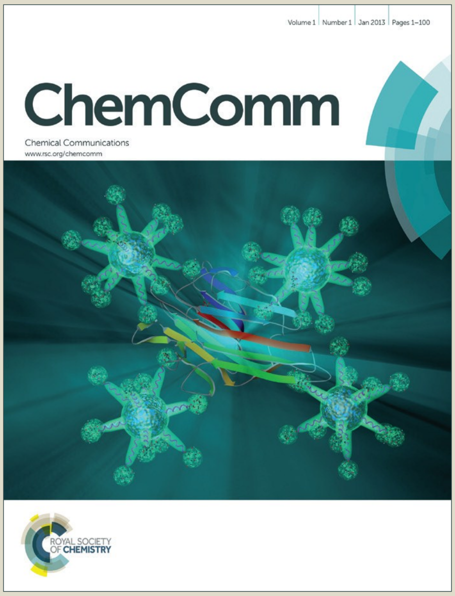

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Unique Group 1 Cations Stabilised by Homoleptic Neutral Phosphine Coordination

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Homoleptic coordination of the neutral diphosphines $Me_2P(CH_2)_2PMe_2$ and *o*-$C_6H_4(PMe_2)_2$ to the hard Li^+ and Na^+ cations is achieved using $Li[Al\{OC(CF_3)_3\}_4]$ and $Na[B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]$ as 'naked' cation sources. Crystallographic, solid state and solution multinuclear NMR studies confirm distorted octahedral coordination solely *via* three chelating diphosphines in these unique species.

Neutral phosphine ligands, PR_3 (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 have also developed substantially in recent years.[2] However, complexes involving coordination of neutral phosphine 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 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 phosphine co-ligand coordinated to an alkali metal cation, the organometallic silylamide dimer $[Li\{N(Ar)CC(R)Si(R)_2NAr\}(\mu\text{-}Me_2PCH_2CH_2PMe_2)]_2$ (mean d(Li–P) = 2.650(3) Å),[3] and two structurally authenticated species with PR_3 coordination to alkaline earth ions; $[BeCl_2(\kappa^1\text{-}Ph_2PCH_2PPh_2)_2]$ [4] and the dinuclear $[Be_2Cl_2(\mu\text{-}Cl)_2(PCy_3)_2]$,[5] both containing distorted tetrahedral Be(II).

A small number of *anionic* ligands bearing phosphine functions have been coordinated to s-block cations, including $[Mg\{C_6H_3\text{-}2,6\text{-}(CH_2PMe_2)_2\}_2]$, in which the Mg–P bonds are also stabilised by the anionic pincer ligand framework,[6] $[\{Li(2\text{-}PPh_2\text{-}C_6H_4)\}_2(OEt_2)_3]$ (d(Li–P) 2.69–2.75 Å),[7] hindered alkoxy-phosphine complexes, including $[Li(\mu\text{-}OC^tBu_2CH_2PR_2)]_2$ (R = Me or Ph) and $[Li(\mu\text{-}OC^tBu_2CH_2PPh_2)_2Li(OC^tBu_2)]$ d(Li–P) 2.50–2.65 Å, $[Na(H_2Al\{P(SiMe_3)_2\}_2)(dme)_2]$,[9] $[Li(solvent)_x\{Ph_2B(CH_2P^iPr_2)_2\}]$ (solvent = thf, x = 2; Et_2O, x = 1) (d(Li–P) = 2.596(3), 2.608(3) Å),[10] 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 reported[12] that complexes of Na^+ with polyamines and aza macrocycles, including the $[Na(Me_3\text{-}tacn)_2]^+$ sandwich cation and the distorted five-coordinate $[Na(thf)(Me_4\text{-}cyclam)]^+$ cation (Me_3-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, Me_4-cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), could be prepared readily by using $Na[BAr^F]\cdot 2thf$ ($[BAr^F]^- = [B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]^-$). This $[BAr^F]^-$ salt[13] has good solubility in weak-donor solvents such as CH_2Cl_2 and toluene. Very recently we extended this chemistry by reporting the homoleptic octathia coordination to Na^+ in the macrocyclic complex, $[Na([24]aneS_8)][BAr^F]$ ($[24]aneS_8$ = 1,4,7,10,13,16,19,22-octathiacycloctetracosane), 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 aza and thioether chemistry. To achieve this we have used both the $[BAr^F]^-$ [15] and $[Al\{OC(CF_3)_3\}_4]^-$ 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 $Li[Al\{OC(CF_3)_3\}_4]$ [19] with three mol. equivs. of $Me_2PCH_2CH_2PMe_2$ (dmpe) or *o*-$C_6H_4(PMe_2)_2$ (diphos) in anhydrous toluene gives $[Li(dmpe)_3][Al\{OC(CF_3)_3\}_4]$ and $[Li(diphos)_3][Al\{OC(CF_3)_3\}_4]$, respectively as white solids in very good yield. The corresponding $[Na(dmpe)_3][BAr^F]$ and $[Na(diphos)_3][BAr^F]$ salts were obtained similarly from a 3:1 diphosphine : $Na[BAr^F]$

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Electronic Supplementary Information (ESI) available: a packing diagram for $[Na(diphos)_3][BAr^F]$ and MAS NMR data (^7Li, ^{23}Na and ^{31}P) for the phosphine complexes reported. See DOI: 10.1039/x0xx00000x ratio. Attempts to prepare the analogous K$^+$ complexes by reaction of the diphosphine with K[BAr^F] in a 3:1 molar ratio failed, while the weaker donor and sterically bulkier *o*-$C_6H_4(PPh_2)_2$, and the diarsine, *o*-$C_6H_4(AsMe_2)_2$ (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)$_3$][BAr^F] contains discrete Na$^+$ cations coordinated to three chelating dmpe ligands, in a distorted octahedral environment (Fig. 1), with discrete [BAr^F]$^-$ 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)$_3$]BAr^F],§ 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). Like 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(H$_2$Al{P(SiMe$_3$)$_2$}$_2$)(dme)$_2$] (d(Na−P) = 3.052(1), 3.092(1) Å).[9] 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 [BAr^F]$^-$ anions remain discrete, but interleave between the cations (Fig. S1).

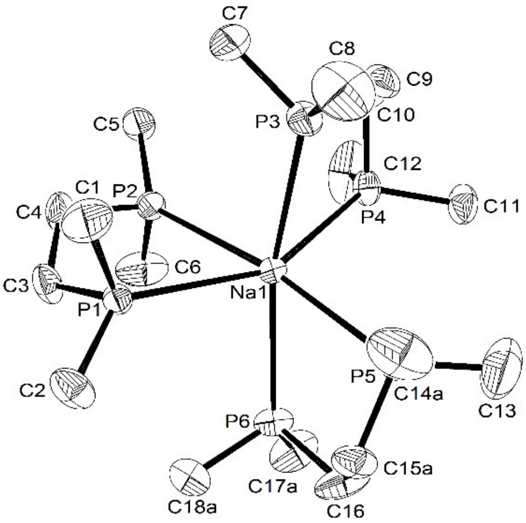

Figure 1. View of the structure of the [Na(dmpe)$_3$]$^+$ cation with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Na1−P1 3.0287(8), Na1−P2 3.0035(8), Na1−P3 2.9621(8), Na1−P4 2.9459(8), Na1−P5 2.9718(8), Na1−P6 2.9960(8), P1−Na1−P2 69.801(18), P3−Na1−P4 73.40(2), P5−Na1−P6 71.48(2).

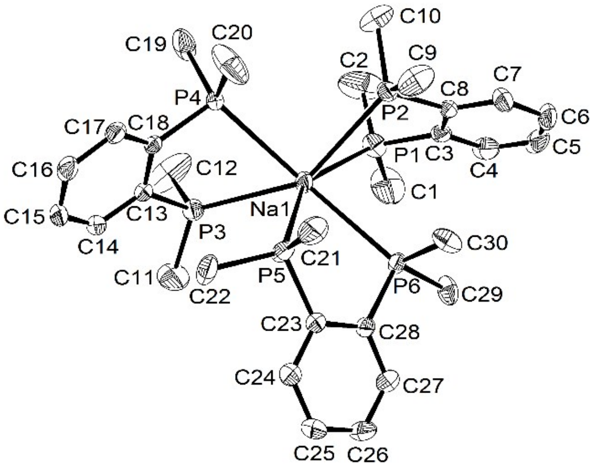

Figure 2. View of the structure of the [Na(diphos)$_3$]+ cation with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitte clarity. Selected bond lengths (Å) and angles (°): Na1−P1 2.9216(12), Na1−P2 3.0677(12), Na1−P3 3.0087(12), Na1−P4 2.9937(12), Na1−P5 2.9992(12), Na 3.0400(12), P1−Na1−P2 65.36(3), P3−Na1−P4 65.49(3), P5−Na1−P6 65.57(3).

The structure§ of the lithium-diphosphine comp [Li(diphos)$_3$][Al{OC(CF$_3$)$_3$}$_4$] was also determined from a sma weakly diffracting crystal. While the weak diffraction data mean that detailed geometric comparisons require caution, the presenc of three chelating neutral diphos ligands at Li$^+$, giving homolepti P$_6$-coordination, is unequivocal (Fig. 3). The aluminate anio provides charge balance, but does not interact with the cation. Th Li−P bond distances are considerably shorter (by *ca.* 0.4 Å) tha d(Na−P) in these systems, while the P−Li−P angles within th chelate rings are correspondingly larger (*ca*. 75º), as expected du to the smaller ionic radius.

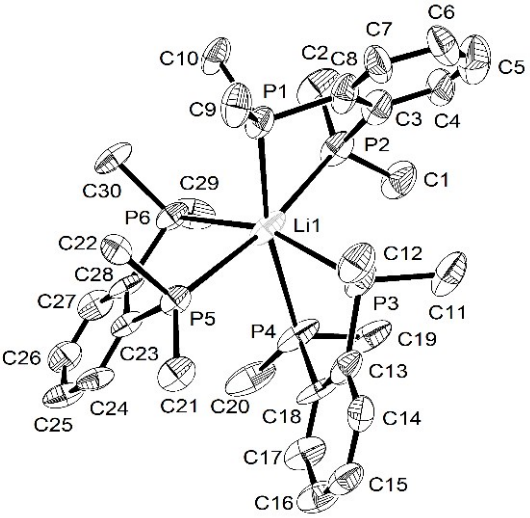

Figure 3. View of the structure of the [Li(diphos)$_3$]$^+$ cation with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted fo clarity.

To investigate the properties of these unusual complexes further, we report the MAS NMR spectroscopic data (^{31}P, ^{23}Na and ^{7}Li) 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, Figs. S2–S4). The ^{31}P 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 in solution (–48 ppm).[20] This is further confirmed by ^{31}P 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.

Complex	δ^{31}P/ppm		δ^{7}Li/ppm		δ^{23}Na/ppm^{c}	
	solid	sol$^{n\ b}$	solid	sol$^{n\ b}$	solid	sol$^{n\ b}$
$[Li(diphos)_3]$-$[Al\{OC(CF_3)_3\}_4]$	–59.2	–53.0	+0.4	–0.1	–	–
$[Li(dmpe)_3]$-$[Al\{OC(CF_3)_3\}_4]$	–54.5	–45.9	–0.7	–1.3	–	–
$[Na(diphos)_3]$-$[BAr^F]$	–61.5, –59.0 (1:1)	–50.3	–	–	+3.8	+5.5
$[Na(dmpe)_3]$-$[BAr^F]$	–57.4	–49.7	–	–	+8.9	+2.5

Table 1 Selected solid state and solution NMR spectroscopic data^{a}

^{a} small amounts of uncomplexed ligand (literature δ^{31}P = –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^{8}-toluene solution (298 K); Na complexes recorded in CD_2Cl_2 solution (298 K); ^{c} δ^{23}Na measured for $Na[BAr^F]$ = –35.5 (s).

The chemical shift differences between 'free' and coordinated diphosphine (Δ) are small and negative for all four 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.[22] No ^{7}Li-^{31}P / ^{23}Na-^{31}P 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 ^{7}Li NMR data for $[Li(dmpe)_3][Al\{OC(CF_3)_3\}_4]$, showing a single peak at –0.7 ppm.

Solution ^{1}H and ^{31}P{^{1}H} NMR spectra (d^{8}-toluene or CD_2Cl_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 ^{7}Li and ^{23}Na 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 ^{7}Li and ^{23}Na 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.

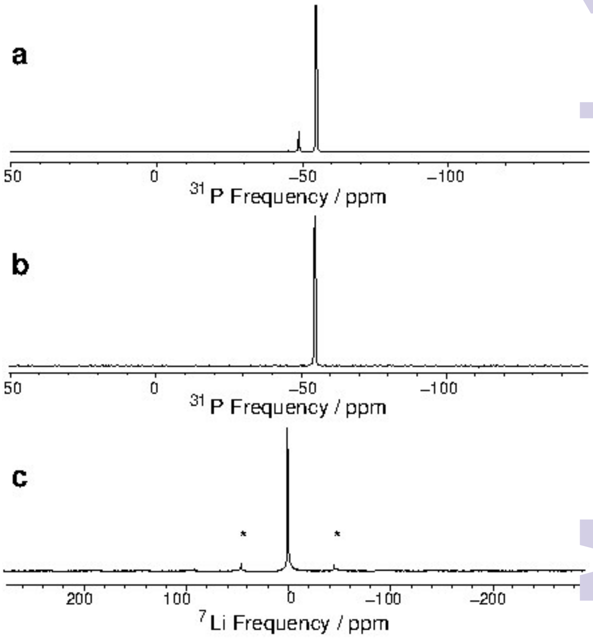

Figure 4. Solid state MAS NMR measurements at 9.4 T and 7.1 kHz spinning freque on $[Li(dmpe)_3][Al\{OC(CF_3)_3\}_4]$. Spinning sidebands are labelled with asterisks. (a) Direct acquisition ^{31}P NMR spectrum. The spectrum is an average of 8 scans with inter-pulse delay of 60 s. The main peak at –54.5ppm is due to the complex, while the small peak at –48.5 ppm corresponds to 'free' dmpe (due to a small amount of decomposition of the complex during data acquisition). (b) ^{31}P CP MAS NMR spectrum, where the peak from the very mobile reagent ('free' dmpe) is absent. The spectrum is an average of 1 scans with inter-pulse delay of 10 s. (c) Direct excitation ^{7}Li NMR spectrum. The spectrum is an average of 32 scans with inter-pulse delay of 15 s. The signal is at –0.7 ppm.

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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.

$[Li(diphos)_3][Al\{OC(CF_3)_3\}_4]$: $Li[Al\{OC(CF_3)_3\}_4]$ (121 mg, 0.125 mmol) in 3 mL toluene was added o-$C_6H_4(PMe_2)_2$ (74 mg, 0.375 mmol) with stirring. After 5 mins, 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 $C_{46}H_{48}AlF_{36}LiO_4P_6$ (1568.5): C, 35.2%; H, 3.0%. Found: C, 35.2 %; H, 3.0 %. ^{1}H NMR (CD_2Cl_2, 298 K): 1.35 (s, [36H], Me), 7.37-7.43 (m, [6H], o-C_6H_4), 7.47-7.53 (m, [6H], o-C_6H_4) ppm.

$[Na(diphos)_3][B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]$: Method as above, using $Na[B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4]$ (110 mg, 0.125 mmol) o-$C_6H_4(PMe_2)$ (74 mg, 0.375 mmol. White solid. Yield: 160 mg, 86%. Colourless single crystals were grown by slow evaporation from a toluene solution under N_2. Anal, required for $C_{62}H_{60}BF_{24}NaP_6$ (1480.7): C, 50.3; H, 4.0%. Found: C, 50.4; H, 4.0%. ^{1}H NMR (CD_2Cl_2, 298 K): 1.20 (s, [36H], Me), 7.34-7.37 (m, [6H], o-C_6H_4), 7.42-7.48 (m, [10H], overlapping o-C_6H_4 and $[BAr^F]^-$ H4), 7.62 (s, [8H], $[BAr^F]^-$ H2/6) ppm.

[Li(dmpe)$_3$][Al{OC(CF$_3$)$_3$}$_4$]: Li[Al{OC(CF$_3$)$_3$}$_4$] (121 mg, 0.125 mmol) in 5 ml toluene was added dmpe (58 mg, 0.375 mmol) with stirring. After 5 mins, the volatiles were removed *in vacuo*. The white solid residue was washed with anhydrous pentane and dried *in vacuo*. Yield: 164 mg, 91%. Anal, required for $C_{34}H_{48}AlF_{36}LiO_4P_6$ (1424.4): C, 28.6; H, 3.3%. Found: C, 28.7; H, 3.0%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): 1.30 (br s, [36H], Me), 1.85 (br s, [12H], CH$_2$) ppm.

[Na(dmpe)$_3$][B{3,5-(CF$_3$)$_2$-C$_6$H$_3$}$_4$]: As above, using Na[B{3,5-(CF$_3$)$_2$-C$_6$H$_3$}$_4$] (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 N$_2$. Anal, required for $C_{50}H_{60}BF_{24}NaP_6$ (1336.6): C, 44.9; H, 4.5%. Found: C, 44.8; H, 4.5%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): 1.01 (br s, [36H], Me), 1.45 (br s, [12H], CH$_2$), 7.46 (s, [4H], [BAr^F]$^-$ H4), 7.62 (s, [8H], [BAr^F]$^-$ H2/6) ppm.

[§] Crystal data for [Na(dmpe)$_3$][BAr^F]: $C_{50}H_{60}BF_{24}NaP_6$, MWt = 1336.60, monoclinic, P2$_1$/c (no. 14), a = 18.4514(10), b = 13.2631(10), c = 26.133(2) Å, β = 90.826(3)°, U = 6394.6(8) Å^3, Z = 4, μ = 0.277 mm^{-1}, T = 100 K, 35720 total reflections, 12513 unique reflections, R$_{int}$ = 0.059, R1 ($I > 2\sigma(I)$) = 0.068, R1 (all data) = 0.105, wR2 ($I > 2\sigma(I)$) = 0.169, wR2 (all data) = 0.197. Crystal data for [Na(diphos)$_3$][BAr^F]: $C_{62}H_{60}BF_{24}NaP_6$, MWt = 1480.72, triclinic, P−1 (no. 2), a = 12.5084(10), b = 16.4798(10), c = 17.5637(10) Å, α = 79.047(4), β = 78.403(4), γ = 81.625(4)º, U = 3460.2(4) Å^3, Z = 2, μ = 0.264 mm^{-1}, 31294 total reflections, 13561 unique reflections, R$_{int}$ = 0.033, R1 ($I > 2\sigma(I)$) = 0.053, R1 (all data) = 0. 063, wR2 ($I > 2\sigma(I)$) = 0.143, wR2 (all data) = 0.149.

Crystal data for [Li(diphos)$_3$][Al{OC(CF$_3$)$_3$}$_4$]: $C_{46}H_{48}AlF_{36}LiO_4P_6$, MWt = 1568.58, orthorhombic, Pna2$_1$ (no. 33), a = 15.092(2), b = 27.737(5), c = 15.405(3) Å, U = 6449.1(19) Å^3, Z = 4, μ = 0.325 mm^{-1}, 38663 total reflections, 12559 unique reflections, R$_{int}$ = 0.093, R1 ($I > 2\sigma(I)$) = 0.101, R1 (all data) = 0. 150, wR2 ($I > 2\sigma(I)$) = 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_1 = 0.71073 Å) with VHF *Varimax* optics (70 µm focus). The crystals were held at 100 K in a nitrogen gas stream. Structure solution and refinement on the Na complexes were mostly straightforward,[23,24] except for some disorder in the CF$_3$ groups of the [BAr^F]$^-$ anions which was modelled satisfactorily. For [Li(diphos)$_3$][Al{OC(CF$_3$)$_3$}$_4$], 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 a riding model. The H atoms on the disordered CH$_2$ and CH$_3$ group were not located. CCDC 1044099-1044101 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data request/cif

§§ **Solid state NMR Experiments.** All 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 oxide 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 N$_2$ gas flow for bearing and drive. The chemical shift scales were referenced by setting at 0 ppm the signals of LiCl 1M, NaCl 1M and 85% H$_3$PO$_4$, respectively for ^{7}Li, ^{23}Na and ^{31}P. Spectra were recorded with direct excitation using a 90 ° pulse followed by acquisition, without proton decoupling. For ^{31}P NMR, additional measurements were also performed with ramped CP methods with 3 ms contact time.

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