Azaphosphaallyl anion lithium [ArNC(Bu^t)PAr]$^-$Li$^+$(THF)$_4$ and its monomeric potassium and thallium complexes (Ar = 2, 6-iPr$_2$C$_6$H$_3$)†

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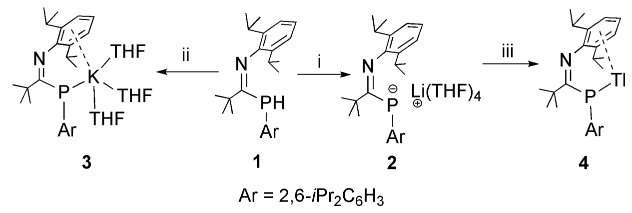
The super azaphosphaallyl free anion and its monomeric potassium and thallium complexes stabilized by M–arene interactions were synthesized and structurally characterized.

Amidinate family of ligands is one of the best explored ligands in organometallic chemistry and catalysis.[1] The ligands could support varieties of very interesting transition metal,[2] main group[3] and lanthanide[4] complexes with unusual bonding and reactivity. It could be expected that the "hybrid" type of azaphophaallyl ligands [R^{1}NC(R^2)PR^3]$^-$, in which one of the "hard" nitrogen atoms in the amidinate backbone was replace by a "soft" phosphorus atom, was also promising supporting ligands for a range of metals with unique structures and reaction patterns. However, the chemistry of this type of ligands has been much less documented in the literature. There are only a very limited number of azaphophaallyl lithium, potassium and alkaline earth metal complexes that have been reported and structurally characterized.[5] Very recently, Bertrand[6] and Boere's groups[7] independently reported general synthetic routes to the super-NCP type ligands with the bulky 2,6-iPr$_2$C$_6$H$_3$ (Ar) group on N and P atoms, and the crystal structures of their Li and K complexes have been reported. The available structural data revealed that only two type bonding modes, *i.e.*, N-η^1 coordination to alkaline ions or chelating coordination mode to alkaline earth ions, have been observed for this type of NCP ligands.

Herein, we report on the synthesis and structures of the lithium anionic azaphosphaallyl [ArNC(Bu^t)PAr]$^-$ (**2**) and its monomeric potassium (**3**) and thallium derivatives (**4**) (Scheme 1).‡ Notably, the structure of **2** consists of well separated non-interacting cations and anions, and the potassium and thallium complexes display η^1-coordination mode to the phosphorus atom. The results demonstrated that the electronic and steric properties of the substituents on the NCP ligand backbone have substantial effects on the coordination modes and electron distribution of the ligands. The thallium complex **4**, to the best of our knowledge, represents the first univalent thallium phosphides albeit a number of structurally characterized thallium complexes supported by nitrogen[3,8] and carbon-based[9] ligands are known.



Scheme 1 Preparation of **2**, **3** and **4**. Reagents and conditions: (i) n-BuLi, in THF; (ii) KN(SiMe$_3$)$_2$, in THF; (iii) TlCl, in Et$_2$O.

Reaction of the iminochloride ArNC(Bu^t)Cl with ArPHLi in refluxing THF afforded the phosphino imine ArNC(Bu^t)PAr(H) (**1**) as white needle crystals in modest yield. Alternatively, **1** can also be obtained by treatment of the primary phosphine ArPH$_2$ with ArNC(Bu^t)Cl in refluxing xylenes.[7] Its iminophosphine structure was deduced from ^{1}H, ^{31}P, and ^{13}C NMR and IR spectrometry and elemental analysis. A doublet resonance for the P–H group was observed in the ^{1}H NMR spectrum at δ 4.74 ppm ($^1J_{PH}$ = 251 Hz). The IR spectrum displays an absorption band centered at 2354 cm^{-1}, characteristic of a P–H stretch vibration. The central carbon resonance for the NCP backbone was observed at δ 182.0 ppm (d, J = 61 Hz) in the ^{13}C NMR spectrum. The ^{31}P NMR spectrum of **1** showed a singlet at δ –84.3 ppm.

Reaction of **1** with n-BuLi and KN(SiMe$_3$)$_2$ in THF yielded the lithium anion [ArNC(Bu^t)PAr]$^-$[Li(THF)$_4$]$^+$ (**2**) and the potassium salt [ArNC(Bu^t)PAr][K(THF)$_3$] (**3**) as orange crystals in high yields, respectively. Compounds **2** and **3** have been characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopies. The ^{1}H NMR spectrum of **2** indicates that four THF molecules are present. The ^{31}P NMR spectrum of **2** displays a quadruple resonance centred at δ –42.4 ppm (J = 106 Hz). The ^{13}C resonance of the imine carbon is observed at δ 154.2 ppm (d, J = 8.53), which is a marked shift to upper field relative to that of **1** (*ca.* δ 182 ppm) due to the location of negative charge. The ^{1}H NMR spectrum of **3** disclosed that the presence of three THF molecules. The singlet resonance in the ^{31}P NMR spectrum falls at δ –43.3 ppm and the doublet resonance for the imine carbon is observed at δ 154.0 ppm (d, J = 11.1 Hz) in the ^{13}C NMR spectrum. In order to disclose the coordination environments of the alkali ions, X-ray single-crystal analyses were carried out for **2** and **3**.

Single crystals of **2** suitable for an X-ray diffraction study were obtained from THF at –40 °C. The structure of **2** reveals the separated solvated lithium ion as [Li(THF)$_4$]$^+$, leaving the free [ArNC(Bu^t)PAr] anion (Fig. 1). The N1–C13 bond length of 1.317(3) Å is longer than a typical C–N double bond while the P1–C13 bond length of 1.796(3) Å is shorter than a P–C single bond (1.85 Å). These structural parameters and the almost co-planarity of P1–C13–N1–C18 indicate the delocalized structure of the anion. It is noteworthy that **2** is the first structurally characterized free azaphosphaallyl anion. The known lithium

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† CCDC reference numbers 736328 (**2**), 736329 (**3**) and 736327 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b916501k

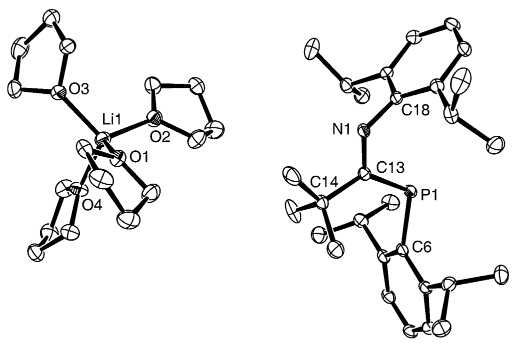

Fig. 1 Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C13 1.796(3), P1–C6 1.875(3), N1–C13 1.317(3), N1–C18 1.411(3), Li1–O1 1.909(6); C6–P1–C13 111.59(12), P1–C13–N1 118.8(2), C13–N1–C18 121.9(2).

azaphosphaallylic derivatives either adopt η^1 N-coordination or η^2 chelating coordination mode.

The molecular structure of **3** (Fig. 2) shows that the potassium atom is bonded to the phosphorus atom and three THF molecules with an additional contact to the aryl ring on the nitrogen atom. The potassium cation deviates slightly from the NCP plane with the K1–P1–C13–N1 torsion angle of 10.5(3)°. The P1–K1 bond length of 3.1718(17) Å is in the short range on record for K–arene intramolecular interactions. The short P–K bond distances have been found in the cluster $[KP(H)Dmp]_4$ (3.043 and 3.162 Å)[10] and in $(KP)_n$ (3.08 Å).[11] The N1–C13 bond length of 1.304(5) Å and the P1–C13 bond length of 1.790(4) Å are only marginally shorter than those found in **2**.

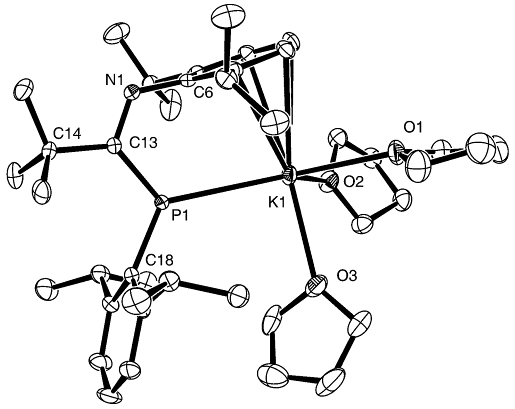

Fig. 2 Molecular structure of **3**. Hydrogen atoms and one disordered THF molecule in the crystal have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–K1 3.1718(17), P1–C13 1.790(4), P1–C18 1.856(4), N1–C13 1.304(5), N1–C6 1.402(5), C13–P1–K1 120.13(12), N1–C13–P1 118.5(3), C6–N1–C13 121.5(3).

Reaction of **2** with TlCl in diethyl ether at low temperature yielded the monomeric thallium(I) complex **4** in high yield. Complex **4** is a red-black, crystalline solid. It is very sensitive towards moisture and air. **4** is thermally stable (95 °C dec.) in the solid state, and it can be stored in solution at dark at −25 °C for several weeks. However, the solution of **4** in toluene at room temperature decomposes in a couple of hours to give black metal powder. The ^{13}C NMR spectrum displays the single resonance for the NCP backbone carbon at δ 155.3 ppm and the ^{31}P NMR spectrum shows a double resonance at δ −71.70 ppm ($J = 252.3$ Hz). The UV-vis spectrum shows absorptions centered at 334 and 513 nm, which probably due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

The X-ray structure analysis reveals that **4** is monomeric with the quasi one-coordinated thallium atom (Fig. 3). The most notable structural feature is that the thallium ion is coordinated to the phosphorus atom and has significant intramolecular interactions with the Ar ring on the nitrogen atom. The P1–Tl1 bond length of 2.8335(11) Å is shorter than those in $Tl_2[P_4(Ar')_2]$ (Ar' = 2,6-$Ar_2C_6H_3$, 3.032(3)–3.168(3) Å),[12] diarylamido-based (PNP)Tl (2.971 and 3.108 Å)[13] and polymeric Tl(μ-η^5:η^5-1,4,2-$P_2SbC_2Bu^t{}_2$) (3.246(9) and 3.301(8) Å),[14] but longer than those in trivalent thallium phosphanide $[Me_2TlP(SiMe_3)_2]_2$(2.695 and 2.688 Å).[15] The Tl atom adopts a slightly slipped π-coordination to the aryl ring with Tl$\cdots$C distances lying in the range of 3.03–3.32 Å, which are within the normal range for intramolecular arene–Tl(I) interactions.[3a,16] The shorter N1–C1 bond length of 1.288(4) Å and longer P1–C1 bond length of 1.822(3) Å than those observed in **2** and **3** indicates the more localized structure of **4** and more imino-phosphide character. The thallium ion deviates slightly from the NCP plane with the Tl1–P1–C1–N1 torsion angle of 23.7(3)°.

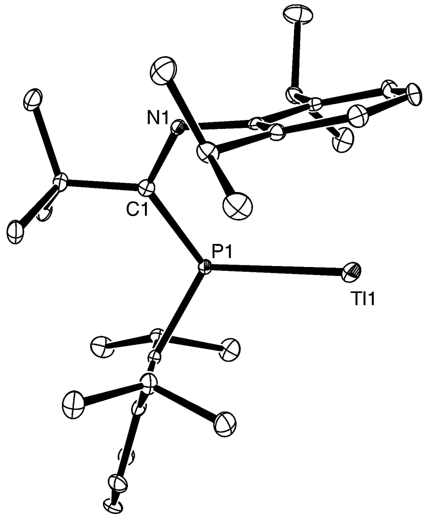

Fig. 3 Molecular structure of **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Tl1–P1 2.8335(11), P1–C1 1.822(3), P1–C18 1.855(3), N1–C1 1.288(4), N1–C6 1.402(4); C1–P1–C18 113.95(15), C1–P1–Tl1 111.86(11), C1–N1–C6 124.0(3), N1–C1–P1 119.6(2).

In conclusion, we have prepared and fully characterized lithium, potassium and thallium derivatives of the bulky azaphosphaallylic ligand. The results demonstrated, for the first time, that the slight modification of the substituents on the NCP ligand backbone would result in the remarkable changes in the structures of lithium and potassium salts. The monomeric thallium complex appears to be the first univalent phosphanide thallium complex. Future work in this line will focus on exploring the reactions of these ligand transfer reagents for the preparation of other metal complexes with this ligand.

Acknowledgements

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Notes and references

‡ Spectroscopic data for **1**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.06 (d, 3 H, CH*Me*$_2$), 1.11 (d, 6 H, CH*Me*$_2$), 1.17 (d, 3 H, CH*Me*$_2$), 1.19 (d, 6 H, CH*Me*$_2$), 1.22 (s, 9 H, C*Me*$_3$), 1.23 (d, 3 H, CH*Me*$_2$), 1.38 (d, 3 H, CH*Me*$_2$), 2.80 (sept, 1 H, C*H*Me$_2$), 2.93 (sept, 1 H, C*H*Me$_2$), 3.55 (sept, 2 H, C*H*Me$_2$), 4.74 (d, 1 H, P*H*), 6.97–7.04 (m, 2 H, Ar*H*), 7.08–7.13 (m, 3 H, Ar*H*), 7.31 (t, 1 H, Ar*H*). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 21.5, 23.3, 24.0 (s, CH*Me*$_2$), 24.1 (br s, CH*Me*$_2$), 28.1 (d, *C*HMe$_2$), 28.6 (s, *C*HMe$_2$), 29.1 (s, C*Me*$_3$), 33.4 (d, *C*HMe$_2$), 45.1 (d, *C*Me$_3$), 122.5, 122.8, 123.1, 123.2, 128.4 (d), 130.6, 134.3, 134.7, 146.4 (d), 154.3 (d, Ar-C), 182.0 (N*C*P). ^{31}P NMR (162 MHz, CDCl$_3$): δ –84.3 (s). MS: *m/z* 436.2 ([ArNC(Bu^t)PAr]$^+$). IR (cm^{-1}): υ 2354 (P*H*). Anal. calcd for $C_{29}H_{44}NP$ (437.32): C 79.59, H 10.13, N 3.20. Found: C 79.52, H 10.25, N 3.04. For **2**: ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.22 (d, 6 H, CH*Me*$_2$), 1.37 (d, 6 H, CH*Me*$_2$), 1.44 (d, 6 H, CH*Me*$_2$), 1.53 (d, 6 H, CH*Me*$_2$), 1.29 (m, 16 H, THF), 1.60 (s, 9 H, C*Me*$_3$), 3.43 (t, 16 H, THF), 3.64 (sept, 2 H, C*H*Me$_2$), 4.82 (sept, 2 H, C*H*Me$_2$), 6.66 (t, 1 H, Ar*H*), 7.11 (d, 1 H, Ar*H*), 7.20–7.25 (m, 4 H, Ar*H*). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 21.7, 22.8, 23.2, 24.0, 26.2, 28.1 (CH*Me*$_2$), 25.6 (THF), 29.4 (*C*HMe$_2$), 31.2 (C*Me*$_3$), 33.9 (d, *C*HMe$_2$), 45.3 (s, *C*Me$_3$), 67.9 (s, THF-O*C*H$_2$), 119.6, 122.5, 124.0, 131.2, 139.0 (s, Ar-*C*), 154.2 (P*C*N). ^{31}P NMR (162 MHz, C$_6$D$_6$): δ –42.4 (q, J = 106.2). Anal. calcd for $C_{45}H_{75}LiNO_4P$ (731.97): C 73.84, H 10.33, N 1.91. Found: C 73.55, H 10.29, N 2.07. UV-vis (THF): λ_{max}/nm: 335.5 (297.3), 276.5 (4476.5), 235.0 (14 040.0). For **3**: ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.99 (d, 6 H, CH*Me*$_2$), 1.27 (d, 6 H, CH*Me*$_2$), 1.28 (d, 6 H, CH*Me*$_2$), 1.37 (d, 6 H, CH*Me*$_2$), 1.39 (m, 8 H, THF), 1.49 (s, 9 H, C*Me*$_3$), 3.55 (t, 8 H, THF), 3.47 (sept, 2 H, C*H*Me$_2$), 4.67 (sept, 2 H, C*H*Me$_2$), 6.60 (t, 1 H, Ar*H*), 6.83 (d, 2 H, Ar*H*), 6.95 (d, 2 H, Ar*H*), 7.03 (d, 1 H, Ar*H*). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 22.9, 23.9, 24.3, 26.3 (CH*Me*$_2$), 25.8 (THF), 28.0 (*C*HMe$_2$), 31.6 (s, C*Me*$_3$), 34.00 (d, *C*HMe$_2$), 45.8 (s, *C*Me$_3$), 67.8 (s, THF), 100.3, 118.2, 122.3, 122.8, 140.1 (s, Ar-*C*), 154.0 (P*C*N). ^{31}P NMR (162 MHz, C$_6$D$_6$): δ –43.3 (br s). Anal. calcd for $C_{37}H_{59}KNO_2P$ (619.39): C 71.68, H 9.59, N 2.26. Found: C 71.77, H 9.65, N 2.13. UV-vis (THF): λ_{max}/nm: 357.0 (62.56), 326.5 (238.46), 248.5 (985.44), 244.0 (1044.29). For **4**: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.23 (d, 6 H, CH*Me*$_2$), 1.26 (d, 6 H, CH*Me*$_2$), 1.36 (d, 6 H, CH*Me*$_2$), 1.40 (d, 6 H, CH*Me*$_2$), 1.45 (s, 9 H, C*Me*$_3$), 3.36 (sept, 2 H, C*H*Me$_2$), 4.37 (br s, 2 H, C*H*Me$_2$), 6.60 (t, 1 H, Ar*H*), 7.06 (d, 1 H, Ar*H*), 7.25 (d, 2 H, Ar*H*), 7.35 (d, 2 H, Ar*H*). ^{13}C NMR (75.4 MHz, C$_6$D$_6$): δ 22.8, 23.2, 24.1, 28.3 (CH*Me*$_2$), 29.3 (*C*HMe$_2$), 31.3 (C*Me*$_3$), 34.2 (*C*HMe$_2$), 48.3 (*C*Me$_3$), 122.2, 123.3, 126.7, 129.0, 136.7 (Ar-*C*), 155.3 (P*C*N). ^{31}P NMR (121.4 MHz, C$_6$D$_6$): δ –71.7 (d, J = 252.3 Hz). Anal. calcd for $C_{29}H_{43}NPTl$ (640.98): C 54.34, H 6.76, N 2.19. Found: C 54.25, H 6.96, N 2.23. UV-vis (THF): λ_{max}/nm: 513.0 (602.8), 333.5 (4117.5), 281.0 (10 320.7), 257.0 (8350.4), 240.0 (7922.0).§

§ Crystal data for **2**: $C_{45}H_{75}LiNO_4P$, $M = 731.97$, monoclinic, space group $P2_1/n$, $a = 14.626(7)$, $b = 18.619(8)$, $c = 16.409(7)$ Å, $\beta = 91.021(6)°$, $V = 4468(3)$ Å^3, $Z = 4$, $D_c = 1.088$ g cm^{-3}, $F(000) = 1608$, $\mu = 0.101$ mm^{-1} (Mo Kα, $\lambda = 0.71070$ Å), $T = 113(2)$ K, 7880 unique reflections (38 506 measured, $R_{int} = 0.0892$), $R_1 = 0.0814$ [$I > 2\sigma(I)$], w$R_2 = 0.1798$ (all data). For **3**: $C_{45}H_{75}KNO_4P$, $M = 764.13$, monoclinic, space group $P2_1/n$, $a = 9.885(4)$, $b = 23.726(10)$, $c = 19.383(8)$ Å, $\beta = 91.308(7)°$, $V = 4545(3)$ Å^3, $Z = 4$, $D_c = 1.117$ g cm^{-3}, $F(000) = 1672$, $\mu = 0.191$ mm^{-1} (Mo Kα, $\lambda = 0.71070$ Å), $T = 113(2)$ K, 8025 unique reflections (39 550 measured, $R_{int} = 0.0707$), $R_1 = 0.0767$ [$I > 2\sigma(I)$], w$R_2 = 0.2081$ (all data). For **4**: $C_{29}H_{43}NPTl$, $M = 640.98$, monoclinic, space group $P2_1/n$, $a = 14.442(3)$, $b = 10.787(2)$, $c = 18.310(4)$ Å, $\beta = 103.105(4)°$, $V = 2778.1(11)$ Å^3, $Z = 4$, $D_c = 1.533$ g cm^{-3}, $F(000) = 1280$, $\mu = 5.888$ mm^{-1} (Mo Kα, $\lambda = 0.71070$ Å), $T = 113(2)$ K, 6625 unique reflections (34 036 measured, $R_{int} = 0.0583$), $R_1 = 0.0335$ [$I > 2\sigma(I)$], w$R_2 = 0.0704$ (all data).

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