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# Structural diversity of 1,2,4-diazaphospholide complexes with alkali metals†‡

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**Treatment of H[3,5-$Ph_2$dp] (Hdp = 1*H*-1,2,4-diazaphosphole) with *n*BuLi or KH, or the reaction of K[3,5-*t*$Bu_2$dp] with an excess amount of $O_2$, afforded the dimeric species $[(\eta^2,\eta^1$-3,5-$Ph_2$dp)Li$(THF)_2]_2$ and the polymeric complexes $[(\eta^2:\eta^4$-3,5-$Ph_2$dp)K$(Et_2O)_2]_n$, and $[\{(\eta^2:\eta^5$-3,5-*t*$Bu_2$dp)K(THF)$\}\{\eta^2$(*N*,*N*)-$\eta^3$(*O*,*P*,*O*)-3,5-*t*$Bu_2$dp-(*O*,*O*)$O_2$K$\}]_n$, respectively.**

The investigation of alkali metal compounds with anions of five-membered aromatic ring systems has been a topic of considerable interest as they are important precursors in synthetic organometallic chemistry.[1–3] Deprotonated 1*H*-1,2,4-diazaphospholes with 6π electrons are mixed nitrogen–phosphorus ($\sigma^2\lambda^3$) heteroaromatic systems[4] and may be viewed as phospholyl analogues where two CH groups are replaced by two nitrogen atoms. They are expected to have versatile bonding ability towards metal centers, assembling complexes with rather intriguing structures.[4] It has been found that alkali metal derivatives of phospholides can adopt a half-sandwich structure in the presence of tetramethylethylenediamine,[3a] a double anionic sandwich structure,[3b] as well as a highly twisted conformation with σ–π coordination.[3b] However, only one structure of a lithium complex bearing an $\eta^1,\eta^1$-1,2,4-diazaphospholide ligand $[(\eta^1,\eta^1$-dp)(μ-Li)(DME)$]_2$ (DME = 1,2-dimethoxyethane) is known.[5] Recently, alkali metal complexes bearing bulky 1,2,4-diazaphospholides have served as excellent transfer reagents that allow access to the corresponding transition metal complexes.[6] Therefore, the investigation of structural conformation of the alkali metal complexes of 1,2,4-diazaphospholides is required for advances in this area. Herein, we report the preparation and structural investigation of several such complexes.

Reaction of 3,5-diphenyl-1,2,4-diazaphosphole H[3,5-$Ph_2$dp] (**1**)[7] with *n*BuLi in THF afforded compound $[(\eta^2,\eta^1$-3,5-$Ph_2$dp)Li$(THF)_2]_2$ (**2**).§ Structure elucidation of **2** evidenced a dimeric species with mixed *endo–exo*-multidentate bridging coordination sites (Fig. 1).¶ The two ligands are perfectly coplanar while two lithium atoms are respectively above and below the plane of ligands. No π-bonding between the metal and the 1,2,4-diazaphospholide is observed. The corresponding dihedral angle between the heterocycle and the Li1–N1–N2 ring is 146.4°. The difference of bond lengths between Li(1)–N(1) (2.053(6) Å) and Li(1)–N(2) (2.565(6) Å) is 0.512 Å, thus suggesting μ-$\eta^2$:$\eta^1$ bonding (slipped $\eta^2$).[8] The conformation observed in this case has not been reported before (*vs.* $[(\eta^1:\eta^1$-dp)(μ-Li)(DME)$]_2$[5]).

Reaction between **1** and KH in $Et_2O$ afforded complex $[(\eta^2:\eta^4$-3,5-$Ph_2$dp)K$(Et_2O)_2]_n$ (**3**).§ **3** is polymeric as established by X-ray crystallography (Fig. 2).¶ Each K is ten coordinate, being bound to two 1,2,4-diazaphospholides ($\eta^4$-(N1A, N2A, C1A, C2A) and $\eta^2$-(N1, N2)), to three carbon atoms of the phenyl group (π-interaction, $\eta^3$-(C11B, C12B, C13B)), and to one $Et_2O$ (O1) (Fig. 2a and b). The simplified representation clearly shows the head-to-tail arrangement of two 1,2,4-diazaphospholides (Fig. 2b) with a dihedral angle of 84.1° between the plane defined by the atoms N1A, N2A, K1 and the plane of the heterocyclic core (N1A, N2A, C1A, C2A, P1A). The potassium is located below the plane of the ligand with an $\eta^4$ interaction (slipped π-bonding), with a dihedral angle of 172.9° between the plane defined by the atoms N1, N2, K1 and the plane of the heterocyclic plane core (N1, N2, C1, C2, P1); the ion is set beside the N–N bond of the ligand, suggesting σ-donation of the in-plane nitrogen atom lone pairs to potassium. The perfect $\eta^2$-1,2,4-diazaphospholide interaction with potassium, with one potassium–nitrogen distance about 0.02 Å shorter than the other is indicated. However, K–C distances (K1–C1A 3.3700(17) Å, K1–C2A 3.4552(18) Å) are longer than those found in the

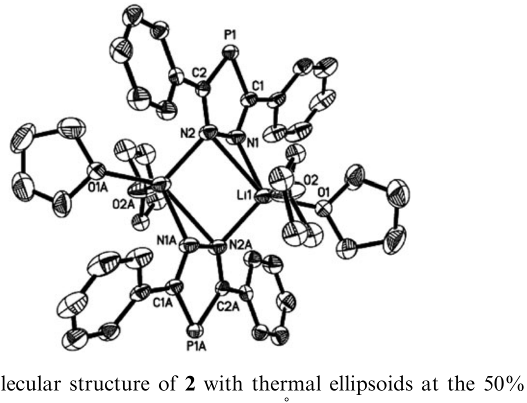

**Fig. 1** Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): O1–Li1 2.007(7), N1–Li1 2.053(6), N2–Li1 2.565(6); C1–P1–C2 85.88(14), N1–Li1–N2 31.92(12); Li1–N1–C1–P1 125.7(3). Symbol A ≡ the symmetry code (1 − *x*, 1 − *y*, 1 − *z*).

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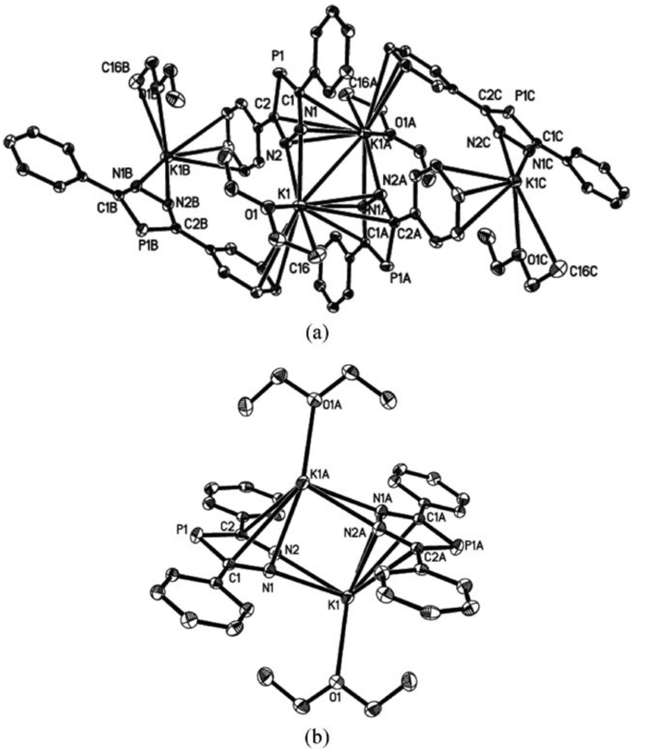
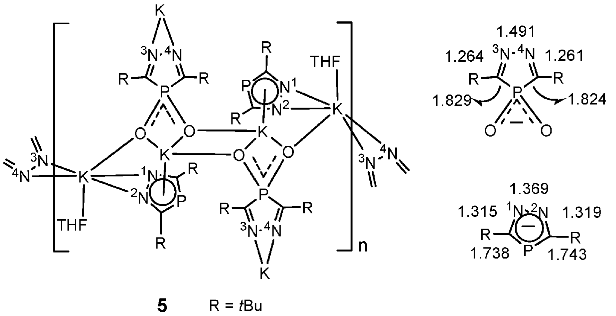


**Fig. 2** (a) Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): K1–O1 2.7430(14), K1–N1 2.7504(15), K1–N2 2.7348(16), K1–N1A 2.9653(16), K1–N2A 3.0220(17), K1–C1A 3.3700(17), K1–C2A 3.4552(18); N2–K1–O1 114.44(5), N2–K1–N1 28.78(4), N2–K1–N1A 81.79(4), N1–K1–N1A 81.79(4), N2–K1–N2A 88.12(5), N1–K1–N2A 80.51(4), N1A–K1–N2A 26.30(4). (b) Simplified representation of **3**. Symbol A ≡ the symmetry code (1/2 − *x*, 1/2 − *y*, −*z*).

double anionic sandwich bisphospholide potassium [K–C 3.16 Å (av.)][3b] and in $(C_5Me_5)K(Py)_2$(K–C 3.059(2)),[9] presumably reflecting the higher potassium coordination number. The K1–C11B (C12B, C13B) distances of the interaction with carbon atoms of the phenyl ring are between 3.3450(18)–3.4477(19) Å and they are comparable to those of K1–C1A (C2A), supporting the π-interaction. The K1–P1A distance of each $\eta^4$ interaction is 3.89(3) Å, which is about 0.80 Å longer than the sum of the covalent radii for potassium and phosphorus atoms. Therefore, any significant interaction between potassium and phosphorus atom can be neglected.

We were not able to obtain single crystals suitable for X-ray diffraction analysis of complex $[(3,5\text{-}t\mathrm{Bu}_2\mathrm{dp})\mathrm{K}]_n$ (**4**).[6] To gain a structural insight into the coordination of the ligand to potassium, the oxidation of **4** was carried out with $O_2$, S, and Se, respectively, in various mole ratios of reactants.§[10] After workup, an unusual complex of $\eta^2$:$\eta^5$-1,2,4-diazaphospholide-$\eta^2$:$\eta^3$-1,2,4-diazaphosphinato potassium $[\{(\eta^2\text{:}\eta^5\text{-}3,5\text{-}t\mathrm{Bu}_2\mathrm{dp})\mathrm{K(THF)}\}\{\eta^2(N,N)\text{-}\eta^3(O,P,O)\text{-}3,5\text{-}t\mathrm{Bu}_2\mathrm{dp}\text{-}(O,O)\text{-}\mathrm{O}_2\mathrm{K}\}]_n$ (**5**) was successfully isolated as colourless crystals.

X-Ray crystallography on **5** revealed a polymeric structure incorporating both 1,2,4-diazaphospholide and 1,2,4-diazaphosphinato ligands (Scheme 1, Fig. 3),¶ where one of two 1,2,4-diazaphospholides was formally oxidized at phosphorus ($\sigma^2\lambda^3$). One ion (K1) is six coordinate, being bound to 1,2,4-diazaphospholide *via* σ-donation of the in-plane nitrogen atom lone pairs ($\eta^2$(N1, N2)), with a dihedral angle of 176.8° between the heterocycle and the three-membered K1–N1–N2 ring (similar to that observed in **3**), THF(O1) and 1,2,4-diazaphosphinato (bridged *via* both O2 and $\eta^2$(N3, N4)) while the other (K2) is eight coordinate, being π-bonded by 1,2,4-diazaphospholide ($\eta^5$-slipped), phosphinato (O2–P2–O3), and bridged by an oxygen atom of the second phosphinato (O3A). The bond lengths of K1–N1 (2.792(2) Å), K2–N1 (2.794(2) Å), K1–N3(N4) (2.802(3), 2.881(3) Å) and K–C (K2–C5 3.129(3), K2–C6 3.280(3) Å) are shorter than those found in the $\eta^5$-complex $[\mathrm{Tp^{CF3,CH3}CuK(CO_3)KTp^{CF3,CH3}}]_2$ (K–N 3.277(2)–3.339(3) Å; K–C 3.339(3)–3.424(4) Å).[11] The K2–P1 distance (3.6310(16) Å) is 0.37 Å longer than that found in the double anionic phospholide potassium with kalocene structure (3.264(1) Å)[3b] and 0.26 Å shorter than that in **3** (3.89(3) Å) since the K2 ion is located directly above the N–N bonds of the 1,2,4-diazaphospholide ligand, where the plane defined by the atoms N1–N2–K2 ($\eta^5$ interaction) is virtually normal to the ring plane of 1,2,4-diazaphospholide ligands (87.4°). Interestingly, an elongated N3–N4 bond length (1.491(3) Å) in the 1,2,4-diazaphosphinato ligand relative to the N1–N2 distance (1.369(3) Å) in the 1,2,4-diazaphospholide ligand is found due to the destruction of aromaticity of the former (N3–N4 single bond *vs.* N1–N2 delocalized double bond) (Scheme 1).



**Scheme 1** Two different ligands in **5** (left); the bond lengths (Å) (right).

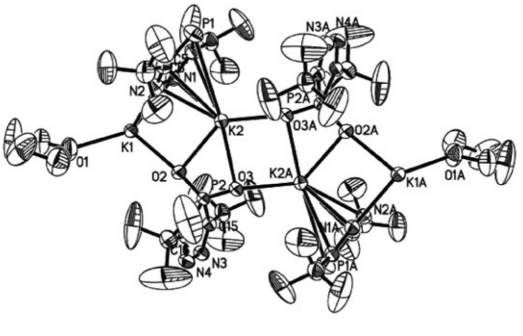


**Fig. 3** Part of the molecular structure of **5** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): N1–N2 1.369(3), N3–N4 1.491(3), K1–O2 2.637(2), K2–O2 2.876(2), K2–O3 2.778(2), K2–O3A 2.601(2), K2–P2 3.3067(13), K1–N1 2.792(2), K1–N2 2.735(3), K1–N3 2.802(3), K1–K2 4.0355(16), K2–K2A 4.0380(15), K2–N1 2.794(2), K2–N2 2.889(3), K2–C5 3.129(3), K2–C6 3.280(3), K2–P1 3.6310(16); O3–K2–O2 52.96(5), N2–K1–N1 28.66(7), N1–K2–N2 27.82(7). Symbol A ≡ the symmetry code (−*x*, 1 − *y*, 2 − *z*).

The $^1$H NMR ($CD_3CN$, 23 °C) spectrum of **5** displays two sets of resonances at $\delta$ = 1.27 (s), 1.36 (s) and 2.46 (br) (ratio: 18 : 12 : 6) for the *t*Bu groups. At 60 °C, two sharp resonances are observed at 1.30 (s), 1.41 (s) in a 1 : 1 ratio. The two downfield resonances are tentatively assigned to the three corresponding frozen non-equivalent methyl groups of the 1,2,4-diazaphosphinato observed below the temperature of coalescence and suggest that **5** is involved in dynamic processes in solution ($CD_3CN$) at 23 °C. Such dynamic behavior involving *t*Bu groups at variable temperatures has been previously observed in a solution of a polyhedron aluminum compound with an $Al_4C_4N_4$ framework.[12] The resonances of the $^{31}P\{^1H\}$ NMR ($CD_3CN$, 23 °C) spectrum are observed at +64.01 (s) for $P(\sigma^2\lambda^3)$ and +40.47 (d) ppm for $P(\sigma^4\lambda^5)$, and are comparable to those of the potassium salt **4** ($^{31}P$ $\delta$ = +50.65 ppm)[6] as well as of the palladium phosphinato in bimetallic complexes (Mn–Pd) ($^{31}P$ $\delta$ = +62.2–63.3 ppm for $P(\sigma^4\lambda^5)$).[13]

During the oxidation of **4** the phosphorus center changed from being nucleophilic to electrophilic. Notably, 3,5-di-*tert*-butyl-1,2,4-diazaphosphole is inert towards air and this may suggest that the potassium ion plays a key role in the oxidation of **4**.[14]

The complexes **2**, **3**, **4**, and **5** represent a new class of alkali metal 1,2,4-diazaphospholides that will thus provide support for the extension of the coordination chemistry with transition and main group metals.

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## Notes and references

§ Syntheses: **2**: to a solution of H[3,5-$Ph_2$dp] (2.38 g, 10 mmol)[7] in THF (20 mL) at 0 °C, *n*-BuLi (3.89 mL, 10 mmol) was added *via* syringe. After the solution was stirred for 15 h at room temperature the solvent was reduced to about 10 mL in high vacuum (0.01 mmHg). The solution was then kept at −20 °C to afford yellow crystals (2.08 g, 85%). Mp: >200 °C, dec. $^1$H NMR (DMSO-$d_6$, 23 °C): $\delta$ = 1.74, 3.60 (m, THF), 7.22, 7.36, 7.93 (m, 20 H, Ph ring); $^{13}C\{^1H\}$ NMR (DMSO-$d_6$, 23 °C): $\delta$ = 25.72, 67.62 (m, *C*(THF)), 126.30 (t, $^3J_{CP}$ = 12.50 Hz, *C*(Ph)), 127.00 (s, *C*(Ph)), 129.11 (s, *C*(Ph)), 139.09 (d, $^2J_{CP}$ = 27.5 Hz, $C_{ipso}$), 177.34 (d, $J_{CP}$ = 57.5 Hz, P*C*N); $^{31}P\{^1H\}$ NMR (DMSO-$d_6$, 23 °C): 68.01 (s); IR (KBr, Nujol mull, $cm^{-1}$): $\nu_{max}$ = 1463(s), 1377(s), 1255(w), 1168(w), 1071(s), 910(w), 748(s), 687(s); anal. calcd for $C_{44}H_{52}Li_2N_4O_4P_2$: C 68.04; H 6.75; N 7.21, found: C 67.65; H 6.83; N 7.30%.

**3**: To a mixture of H[3,5-$Ph_2$dp] (2.38 g, 10 mmol) and KH (0.06 g, 15 mmol), 20 mL ether was added *via* syringe at room temperature. After the evolution of gas ceased the solvent was filtered through Celite. The filtrate was reduced to about 10 mL in high vacuum (0.01 mmHg). The solution was then kept at room temperature to afford colourless crystals (2.18 g, 80.0%). Mp: >160 °C, dec. $^1$H NMR ($CD_3CN$, 23 °C): $\delta$ = 7.17, 7.29, 7.30, 8.01 (m, 20 H, Ph ring); $^{13}C\{^1H\}$ NMR ($CD_3CN$, 23 °C): $\delta$ = 118.32 (s), 126.80 (t, $^3J_{CP}$ = 13.80 Hz, *C*(Ph)), 129.14 (s), 141.60 (d, $J_{CP}$ = 22.50 Hz, $C_{ipso}$), 179.05 (d, $^1J_{CP}$ = 43.75 Hz, P*C*N); $^{31}P\{^1H\}$ NMR ($CD_3CN$, 23 °C): 65.15 (s); IR (KBr, Nujol mull, $cm^{-1}$): $\nu_{max}$ = 1460(s), 1377(s), 1300(w), 722(s); anal. calcd for $C_{36}H_{40}K_2N_4O_2P_2$: C 61.69; H 5.75; N 7.99, found: C 61.90; H 5.36; N 8.06%.

**5**: To K[3,5-*t*$Bu_2$dp] (**4**, 0.472g, 2.0 mmol)[6] in a 100 mL Schlenk flask, 20 mL THF was added *via* syringe at room temperature. A rubber septum was fixed on the flask and then a slight underpressure was kept inside the flask by applying a vacuum. 60 mL (2.68 mmol) dry $O_2$ was added by syringe. After the solution was stirred for three days, the solvent was reduced to about 10 mL in high vacuum (0.01 mmHg). The solution was then kept at room temperature to afford colourless crystals (0.31 g, 53.0%). Mp: 150 °C, dec. $^1$H NMR ($CD_3CN$, 23 °C): $\delta$ = 1.27 (s, 18 H, *t*Bu in 3,5-*t*$Bu_2$dp), 1.36 (s, 12 H, *t*Bu in 3,5-*t*$Bu_2$dp-(*O*,*O*)$O_2$K), 2.46 (br, 6 H, *t*Bu in 3,5-*t*$Bu_2$dp-(*O*,*O*)$O_2$K); $^{13}C\{^1H\}$ NMR ($CD_3CN$, 23 °C): $\delta$ = 28.48 (s, *C*$H_3$), 28.83 (s, *C*$H_3$), 32.16 (d, $^2J_{CP}$ = 21 Hz, *C*$CH_3$), 36.25 (d, $^2J_{CP}$ = 7.3 Hz, *C*$CH_3$), 174.5 (d, $^1J_{CP}$ = 28.0 Hz, P*C*N), 190.1 (br, P*C*N); $^{31}P\{^1H\}$ NMR ($CD_3CN$, 23 °C): 40.50 (d), 64.01 (s); IR (KBr, Nujol mull, $cm^{-1}$): $\nu_{max}$ = 1463(s), 1377(s), 1015(m), 723(m); anal. calcd for $C_{24}H_{44}K_2N_4$ $O_3P_2$: C 49.98; H 7.69; N 9.71, found: C 50.21; H 7.83; N 9.55%.

¶ Crystal data: **2**: $C_{44}H_{52}Li_2N_4O_4P_2$, $M_r$ = 776.72, monoclinic, space group *P*2(1)/*n*, *a* = 10.8365(18) Å, *b* = 13.267(2) Å, *c* = 14.755(2) Å, $\alpha = \gamma$ = 90.00°, $\beta$ = 93.300(4)°, *V* = 2117.8(6) Å$^3$, *Z* = 2, $\rho_{calcd}$ = 1.218 Mg $m^{-3}$, crystal size: 0.45 × 0.43 × 0.34 mm$^3$, *F*(000) = 824, $\mu$ ($Mo_{K\alpha}$) = 0.148 $mm^{-1}$, 3866 independent reflections ($R_{int}$ = 0.0528). Final *R* indices: $R_1$ = 0.0733 [$I > 2\sigma(I)$] and $wR_2$ = 0.1697 (all data), Minor THF disorder was found. **3**: $C_{36}H_{40}K_2N_4O_2P_2$, $M_r$ = 700.86, monoclinic, space group *C*2/*c*, *a* = 19.354(3) Å, *b* = 20.082(2) Å, *c* = 11.803(18) Å, $a = \gamma$ = 90.00°, $\beta$ = 127.450(2)°, *V* = 3641.1(9) Å$^3$, *Z* = 4, $\rho_{calcd}$ = 1.279 Mg $m^{-3}$, crystal size: 0.44 × 0.40 × 0.36 mm$^3$, *F*(000) = 1472, $\mu$ ($Mo_{K\alpha}$) = 0.385 $mm^{-1}$, 3326 independent reflections ($R_{int}$ = 0.0340). Final *R* indices were $R_1$ = 0.0378 [$I > 2\sigma(I)$] and $wR_2$ = 0.0815 (all data). **5**: $C_{24}H_{44}K_2N_4O_3P_2$, $M_r$ = 576.77, monoclinic, space group *P*2(1)/*c*, *a* = 11.350(4) Å, *b* = 14.531(5) Å, *c* = 20.237(7) Å, $a = \gamma$ = 90.00°, $\beta$ = 91.272(5)°, *V* = 3337(2) Å$^3$, *Z* = 4, $\rho_{calcd}$ = 1.148 Mg $m^{-3}$, crystal size: 0.20 × 0.18 × 0.15 mm$^3$, *F*(000) = 1232, $\mu(Mo_{K\alpha})$ = 0.644 $mm^{-1}$, 5864 independent reflections ($R_{int}$ = 0.0527). Final *R* indices were $R_1$ = 0.0473 [$I > 2\sigma(I)$] and $wR_2$ = 0.1351 (all data); Minor THF and *t*Bu-group disorder was found. CCDC-671979(**2**), -671980(**3**), -671981(**5**).‡

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