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An *N*,*P*-disubstituted-2-aminophosphaalkene and lithium and potassium complexes of the deprotonated "phosphaamidinate" anion†

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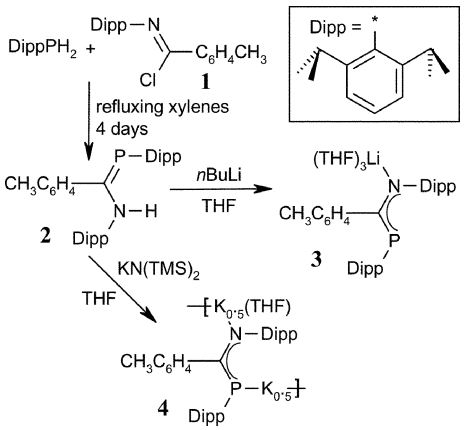
The reaction of $DippPH_2$ (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) with DippN=C(*p*-$CH_3C_6H_4$)Cl in refluxing xylenes affords DippP=C(*p*-$CH_3C_6H_4$)N(H)Dipp; deprotonation with alkali metal reagents produces unique lithium and potassium complexes with the ligand in a different geometry to that of the free phosphaamidine.

Amidines with super-bulky substituents are of considerable current interest as precursors to metal 1,3-diazaallyl anions (amidinates).[1] Yttrium and aluminium complexes of very bulky amidinates are active catalysts for ring opening polymerization of cyclic esters and olefin polymerization,[2] and reflect the current search for soluble "non-metallocene" polymerization catalysts.[3] Related ligands have been explored where the core atoms of the allylic unit are CCN, CNC, CCO, NCS, and CCP.[4] An η^1-Li bound 1,3-diphosphaallyl has recently been reported (PCP).[5] Several examples of the NCP unit, *i.e.* 1,3-azaphosphaallyls of Mg, Ca, Sr, Ba, Li and Sn have been prepared.[6] These anions were prepared *in situ* by the addition of an R′N(SiR$_3$)M moiety to a nitrile lacking a β-H atom, resulting necessarily in an R$_3$Si substituent on N. Amidinates, by contrast, can be tuned with a wide variety of substituents R, R′ and R″ in the RN(CR′)NR″ positions, and can be made by many routes, of which the deprotonation of RN(CR′)NHR″ is the most common and the most versatile.[7] It seems likely that the development of 1,3-azaphosphaallyl chemistry has been hindered by the lack of analogous starting materials.

Our contribution to this area was the development of super-amidines bearing the bulky 2,6-diisopropylphenyl (Dipp) group on N.[8] Our "stepwise" synthetic route to these amidines was designed from the outset to allow the preparation of heavier group 15 analogues. Herein we report the first such result from the thermal reaction of $DippPH_2$,[9] a new bulky primary phosphine, with **1**[8] to yield the stable aminophosphaalkene **2** (Scheme 1).¶ It has long been accepted that 2-amino substitution electronically stabilizes the P=C bond, although low steric-demand substituents lead to dimerization.[10] More recently it has been recognized that the presence of one, and especially two, amino groups on the C atom of a P=C bond induces a reversal of polarity with significant negative charge accumulation at phosphorus.[11]

The molecular structure of **2** in the solid state obtained *via* X-ray crystallography (Fig. 1)‖ has a (*Z*)-*anti*(P=C) configuration (Scheme 2) which is highly reminiscent of the *N*,*N* analogue.**[8] This is the first *N*,*P*-disubstituted aminophosphaalkene to have been structurally characterized. The closest analogous structure to be reported is that of the *P*-monosubstituted species



Scheme 1

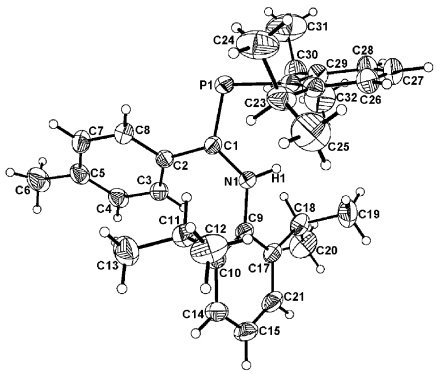
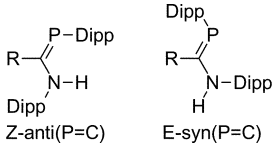


Fig. 1 ORTEP drawing of **2** (25% probability except H). P1–C1 1.709(2), C1–N1 1.367(2), C1–C2 1.488(3) Å; C1–P1–C21 101.86(9), P1–C1–N1 123.37(16), P1–C1–C2 116.34(13), N1–C1–C2 120.02(17)°.

MesP=C(Ph)NH$_2$.[6g] Metric parameters for **2** are consistent with this and other, trisubstituted, aminophosphaalkenes.[11]

Deprotonation of **2** with *n*BuLi in THF solution produces a single product (NMR in d_8-THF)¶ which can be crystallized from THF at 0 °C to afford **3** (Fig. 2).‖ The lithium ion is coordinated to the nitrogen atom of **2** and is found in the plane of the N–C–P unit. Elongation of the formal P=C and shortening of the N–C bonds occurs, as is consistent with charge delocalization in a "phosphaamidinate" anion. The ligand adopts the (*E*)-*syn* geometry, formally derived from the (*E*)-*syn*(P=C) tautomer which



Scheme 2

† Electronic supplementary information (ESI) available: experimental procedures, NMR, IR, UV, MS and elemental analyses, crystal structure diagrams and refinement details. See http://www.rsc.org/suppdata/cc/b4/b408994d/

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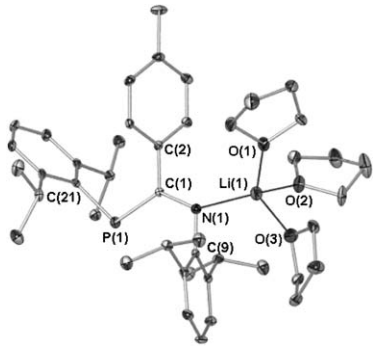

Fig. 2 ORTEP drawing of **3** (40% probability). All hydrogen atoms omitted for clarity. Li–N1 2.060(5), Li–O1 1.941(4), Li–O2 2.011(4), Li–O3 2.046(5), P1–C1 1.766(2), C1–N1 1.343(3), C1–C2 1.493(3) Å; Li–N1–C1 142.2(2), Li–N1–C9 103.6(2), C1–P1–C21 103.1(1), P1–C1–N1 122.5(2), P1–C1–C2 122.6(2)°.

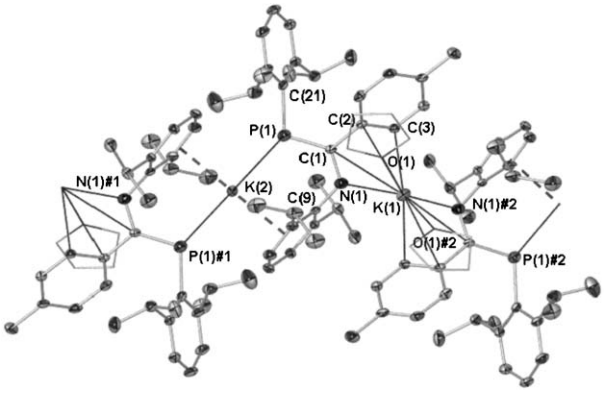

Fig. 3 ORTEP drawing of **4** (40% probability). All hydrogen atoms and lattice solvent omitted for clarity; coordinated THF depicted as wire frame. K1–N1 2.845(3), K2–P1 3.196(2), K2–centroid 2.993(9), P1–C1 1.767(4), C1–N1 1.324(4), C1–C2 1.501(5) Å; P1#–K–P1 180.0(1), K2–P1–C1 115.7(1), P1–C1–N1 123.2(3), K1–N1–C1 109.7(2), N1–C1–C2 112.4(3)°.

by NMR in THF is present in **2** in equilibrium with the (*Z*)-*anti*(P=C) tautomer in a ~40 : 60 ratio (Scheme 2). The coordination environment of the Li ion is completed by three THF molecules forming a close to tetrahedral coordination environment at Li. The solvated complexes are isolated in the crystal lattice, unlike previously reported lithium salts of azaphosphaallyl anions where intermolecular contacts dominate.[6]

In contrast to the result with lithium, deprotonation using potassium hexamethyldisilylamide yields the infinite chain complex **4** (Fig. 3),‖ which contains two distinct types of K ions in the solid-state lattice occupying Wyckoff sites 4*b* and 4*e*, respectively, in a *C*2/*c* unit cell. The 4*e* K ions are coordinated by η^4–NCCC units from *two* ligands and by *two* THF molecules, related to each other by two-fold rotation. The K ion is distinctively out of the N–C–P plane, possibly a result of the large size of the cation. The 4*b* ions are coordinated to phosphorus atoms of two centrosymmetrically related ligands in the N–C–P plane as well as by two η^6 interactions with the aromatic carbon atoms of the Dipp rings attached to N. Similar K coordination by electron-rich aromatic rings has been noted previously.[1a] The result is an infinite zigzag chain in the basal *bc* plane which is repeated, offset by ½ in *b*, at $a = ½$. Additional THF of crystallization is found between the ribbons formed by the infinite stacks of these chains. The ligand geometry is again (*E*)-*syn* and the same delocalization of charge is observed in the P–C and N–C bond distances as for **3**. The K(2)–P(1) distance of 3.196(2) Å is one of the shortest on record. Of 29 structures in the CCDC database (Release 5.25, Nov 2003), only the cluster bis((η^3-2,6-dimesitylphenylphosphido)-(η^2-2,6-dimesitylphen-ylphosphido)-dipotassium) has shorter K–P bonds (3.048, 3.162 and 3.189 Å).[12] The average K–P distance in the database is 3.34(11) Å.

In conclusion, we have developed a large-scale synthetic route that affords for the first time robust, high-purity *N*,*P*-disubstituted-2-aminophosphaalkenes as ideal precursors for 1,3-azaphosphaallyls. Protolysis leads to Li^+ and K^+ adducts with unique structures that confirm the utility of our route into the anion chemistry.

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Notes and references

¶ All compounds have satisfactory combustion analyses and are fully characterized by NMR, IR, and mass spectroscopy, and crystallography. See ESI†

‖ *Crystal data* (Mo Kα, $\lambda = 0.71073$ Å) for **2**: $C_{32}H_{42}NP$, $M = 471.64$, monoclinic, space group $P2_1/c$, $a = 18.2910(17)$, $b = 10.0442(5)$, $c = 18.1511(16)$, $\beta = 117.179(10)$, $U = 2966.5(4)$ Å^3, $Z = 4$, $D_c = 1.056$ Mg m^{-3}, $\mu = 0.111$ mm^{-1}, $T = 293$ K, $R(F^2 > 2\sigma) = 0.0460$, R_w (F^2, all data) = 0.1217, goodness-of-fit = 0.814 for all 5528 unique data (24466 measured), $R_{int} = 0.0717$, and 316 parameters. CCDC 210233. **3**: $C_{44}H_{65}LiNO_3P$, $M = 693.88$, monoclinic, space group $P2_1/c$, $a = 10.988(2)$, $b = 17.609(4)$, $c = 21.417(4)$, $\beta = 91.28(3)$, $U = 4143(1)$ Å^3, $Z = 4$, $D_c = 1.113$ Mg m^{-3}, $\mu = 0.104$ mm^{-1}, $T = 123(2)$ K, $R(F^2 > 2\sigma) = 0.061$, R_w (F^2, all data) = 0.1425, goodness-of-fit 0.967 for all 9781 unique data (40101 measured), $R_{int} = 0.1370$, and 460 parameters. CCDC 242544. **4**: $C_{40}H_{57}KNO_2P$, $M = 653.94$, monoclinic, space group $C2/c$, $a = 35.698(7)$, $b = 12.253(3)$, $c = 24.118(5)$, $\beta = 131.31(3)$, $U = 7928(3)$ Å^3, $Z = 8$, $D_c = 1.096$ Mg m^{-3}, $\mu = 0.206$ mm^{-1}, $T = 223(2)$ K, $R(F^2 > 2\sigma) = 0.0892$, R_w (F^2, all data) = 0.2221, goodness-of-fit 0.975 for all 9326 unique data (43557 measured), $R_{int} = 0.2154$, and 418 parameters. The lattice THF molecule (not shown in Fig. 3) is disordered. CCDC 242545. See http://www.rsc.org/suppdata/cc/b4/b408994d/ for crystallographic data in .cif or other electronic format.

** Nomenclature based on the CIP sequence rules as used by G. Häfelinger and K.H. Kuske, in *The chemistry of the amidines and imidates*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, 1991, vol. 2, ch. 7, pp. 1–100 for *N*,*N*′-disubstituted amidines, with addition of (P=C) for aminophosphaalkene or (N=C) for phosphinoimine tautomers.

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