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Formation of a chiral NPPN ligand *via* metallation of acyclic NPNCN systems

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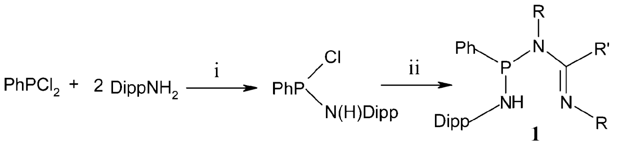
A new type of bidentate *N*,*N′*-chelating ligand containing a chiral phosphorus centre has been synthesized *via* the metallation of an acyclic NPNCN species. The zwitterionic ligand backbone contains a phosphenium centre stabilised by an imido phosphine fragment.

Interest in the coordination chemistry of β-diketiminato ligands has been increasing significantly over the past few years.[1,2] These versatile ligands, using bulky *N*-substituents, are effective in stabilizing low-coordinate complexes for both main group[3,4] and transition metal elements.[5] The steric demands of the ligand can be tuned with relative ease, by changing the organic substituents on the nitrogen atoms. In comparison, relatively little work has been done on the electronic influence engendered at the metal centre by variation of the elements in the ligand backbone. Recent studies from the groups of Stephan[6] and Piers[7] have focused on the inclusion of phosphinimine donors in the ligand framework. We report here investigations of the reactivity of novel, acyclic NP(III)NCN systems which, unexpectedly, give rise to chelating NPPN ligands containing a chiral phosphorus centre upon metallation with Bu^nLi or Me_3Al.

Synthesis of neutral acyclic compounds of the type DippN(H)-PhPNRCR′NR (Dipp = 2,6-$Pr^i C_6H_3$) (**1**) was achieved in good yield according to Scheme 1. Derivatives **1a** and **1b** have been characterised by elemental analyses, multinuclear NMR (^1H, ^{13}C and ^{31}P) and X-ray crystallography.†

Deprotonation reactions of **1a** using one equivalent of Bu^nLi gave an unexpected ^{31}P NMR spectrum. Instead of a single resonance corresponding to the expected lithium complex, two mutually coupled doublets are observed at δ = 26.9 and 59.8 ($^1J_{P-P}$ = 298 Hz) suggesting the formation of a complex containing two inequivalent phosphorus centres bonded together. Analysis by X-ray crystallography showed the product to be Li[DippNPhP–P(Bu^n)PhNDipp]·OEt_2 (**2**) (Fig. 1). A similar aluminium-containing complex, $Al(Me)_2$[DippNPhP–P(Me)PhNDipp] (**3**), was isolated from the reaction of **1b** with equimolar amounts of Me_3Al (Fig. 2). Complexes **2** and **3** have isostructural DippNPhP–P(R)PhNDipp ligand backbones *N*,*N′*-chelated to the metal centre. Nucleophilic attack by the respective metallating reagents has occurred to create a four-coordinate, chiral P2 centre bonded to an *n*-butyl group in **2** and a methyl group in **3**. As illustrated in Scheme 2, the new complexes **2** and **3** can be viewed in terms of two resonance structures: a phosphine(P1)–phosphonium(P2) complex **2a** or a phosphine-stabilised phosphenium cation **2b**. The P–P bond lengths of *ca.* 2.24 Å are at the upper limit of the range of values reported for phosphine–phosphenium cation complexes.[8] In both complexes, the P–N bond from the four-coordinate phosphorus centre (P2–N2) is *ca.* 0.05 Å shorter than P1–N1, which involves the three-coordinate phosphorus. This shortened bond length suggests a larger degree of ionicity on the P2–N2 side of the ligand and hence that resonance form **2a** contributes significantly to the structure. Consistently, the metal centre in both **2** and **3** is also more strongly coordinated to N1 than to N2. The geometry at P2 is distorted tetrahedral with bond angles in the range 103.4–114.5° (**2**) and 101.5–115.7° (**3**), while P1 adopts a pyramidal geometry reflecting the presence of a lone pair. A similar aluminium complex, which contains an intramolecular P–P coordination, has been reported by Burford *et al.*[9] In that case however, the two phosphorus centres are bridged by an $NSiMe_3$ group to form a three-membered aza-diphosphiridene ring.[9]



Scheme 1 *Reagents and conditions*: i Et_2O, −78 °C, ii Li[CR′(NR)$_2$] in hexane, −78 °C (**1a**, R = Bu^t, R′ = Bu^n; **1b**, R = Cy, R′ = Bu^t).

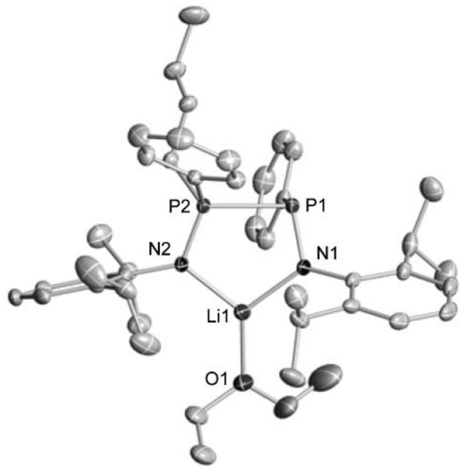


Fig. 1 Thermal ellipsoid plot of Li[DippNPhP–P(Bu^n)PhNDipp]·OEt_2 (**2**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.6522(15), P(2)–N(2) 1.6065(15), P(1)–P(2) 2.2436(7), N(1)–Li(1) 1.939(3), N(2)–Li(1) 1.965(4), N(1)–P(1)–C(1) 108.90(8), N(1)–P(1)–P(2) 97.83(6), C(1)–P(1)–P(2) 93.04(6).

The ^{31}P NMR spectra of complexes **2** and **3** provide some insight

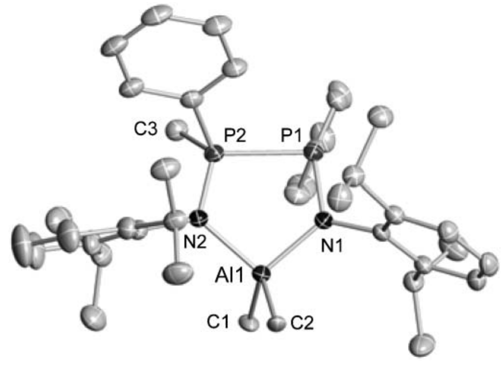


Fig. 2 Thermal ellipsoid plot of $Al(Me)_2$[DippNPhP–P(Me)PhNDipp] (**3**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.673(2), P(2)–N(2) 1.634(2), P(1)–P(2) 2.2367(11), N(1)–Al(1) 1.892(2), N(2)–Al(1) 1.929(2), N(1)–P(1)–C(4) 108.05(12), N(1)–P(1)–P(2) 95.36(8), C(4)–P(1)–P(2) 98.37(9).

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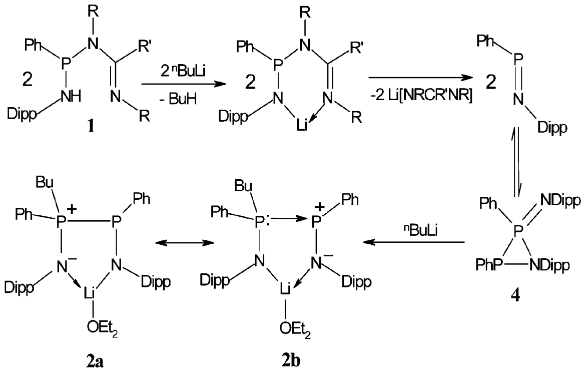

Scheme 2 Proposed route of formation of **2**.

into the nature of the bonding in the two complexes. The $^1J_{\mathrm{P-P}}$ couplings of 298 and 264 Hz, respectively, are consistent with a phosphine–phosphenium interaction,[8] however the coordination of the ligand to two different metal centres markedly changes the phosphorus chemical shifts. The two, well-separated, equal intensity doublets at 59.8 and 26.9 ppm observed for complex **2** indicate two distinctly different chemical environments for the phosphorus centres. However for complex **3**, a second-order AB type pattern is observed with chemical shifts of 45.9 and 40.2 ppm, arising from two phosphorus centres which are in a more comparable chemical environment.

Stabilised phosphenium ions were first reported over thirty years ago and advances in this area were reviewed extensively by Cowley *et al.* in 1985.[10] A recent structurally characterised example of an amidophosphenium ion is the complex [{N(Dipp)CH_2CH_2N(Dipp)}P–PMe_3]OTf[11] in which the cation is stabilised by a classical phosphine donor. Complexes **2** and **3** can be viewed as examples of zwitterionic imido phosphenium species; stabilisation by a diorganophosphorus imido moiety results in monoanionic ligands that chelate to the metal. A dianionic NPPN ligand involving two chemically equivalent, three-coordinate phosphorus centres has been characterized by spectroscopic methods in a PhB complex.[12]

Formation of **2** and **3** from the metallation reactions of **1a** and **1b** must involve the elimination of the corresponding metal amidinate (Scheme 2). This is supported by the isolation of crystalline $(Me)_2$Al[CyNCBu^{t}NCy] from the reaction of **1b** with Me_3Al.[13] The loss of amidinate will be accompanied by the formation of an iminophosphane RP=NR′ which are known to form readily by thermal elimination of lithium salts at low temperatures.[14] Iminophosphanes undergo cyclodimerization which, in the case of P-aryl and -alkyl derivatives, involves a reversible [2 + 1] cycloaddition to give the corresponding λ^3,λ^5-azadiphosphiridine (**4**) (Scheme 2).[14,15] In such examples, [2 + 2] cycloaddition to give the symmetric dimer is not observed.[15] While this cannot be completely ruled out for the iminophosphane DippN=PPh, a [2 + 1] cycloaddition would account for the observed P–P bond formation. Nucleophilic attack of a further equivalent of Bu^{n}Li on the exocyclic P=N bond of **4** would then afford **2**. When the reaction is carried out using a 3 : 2 stoichiometry (Bu^{n}Li : **1a**), as required by Scheme 2, complex **2** is produced quantitatively by ^{31}P NMR spectroscopy.

Iminophosphanes are known to form readily by LiX elimination (X = halide),[14] suggesting the possibility of a more direct route to the novel ligand in **2**. Preliminary investigations have shown that the reactions of PhP(Cl)NHDipp with RLi reagents (R = Bu^n, Me) in the ratio 2 : 3 afford **2** and the related *P*-methylated derivative in *ca.* 60% isolated yields. Details of this straightforward, general synthesis together with the characterization of the protonated NP(III)NCN reagents **1** will be given in a full account of this work.

In summary, metallation reactions of NP(III)NCN systems have uncovered a synthetic route to a new type of bidentate *N*,*N*′ ligand containing a phosphine–phosphenium bond and a chiral phosphorus centre. The presence of a phosphenium centre in **2** and **3** affords the intriguing possibility of additional metal coordination *via* this Lewis basic site.

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Notes and references

† Synthesis of **2**: ^{n}BuLi (0.8 mL, 2.5 M solution in hexane, 2 mmol) was added dropwise to a solution of DippN(H)PhPNBu^{t}CBu^{n}NBu^t (**1a**) (0.99 g, 2 mmol) in *n*-hexane (20 mL) at −78 °C producing a clear yellow solution. The solution was warmed to 25 °C and stirred for 1 h. The volume was reduced *in vacuo* to approximately 10 mL and diethyl ether (5 mL) was added to give a clear yellow solution. Concentration of the reaction mixture to *ca.* 5 mL, and storage at 25 °C for 24 h, yielded colourless crystalline blocks (0.17 g, 24% yield). Synthesis of **3**: Me_3Al (1 mL, 2.0 M solution in heptane, 2 mmol) was added dropwise to a stirred solution of DippN(H)PhPNCyCBu^{t}NCy (**1b**) (1.094 g, 2 mmol) in *n*-hexane (30 mL) at −78 °C resulting in a pale yellow solution. The solution was stirred for 2 h at 25 °C. The volume of solvent was reduced to approximately 10 mL and the solution was stored at −15 °C for 24 h. This yielded colourless crystalline blocks which were identified as $Al(Me)_2$[CyNCBu^{t}NCy] by ^{1}H NMR spectroscopy and elemental analysis (0.19 g, 30% yield). The yellow solution was decanted and further reduced in volume to a yellow oil. Storage at −15 °C for 24 h yielded colourless crystalline blocks (0.23 g, 48% yield). Crystal data for **2**: M = 704.84, monoclinic, $P2_1/c$, a = 11.712(2), b = 19.656(3), c = 18.528(2) Å, β = 97.821(10)°, V = 4225.7(11) Å^3, Z = 4, T = 173(2) K, D = 1.108 g cm^{-3}, μ(Mo–Kα) = 0.136 mm^{-1}, R = 0.0493 and wR = 0.1452 (all data). CCDC 247957. Anal calcd. for $C_{44}H_{63}LiN_2OP_2$: C 74.97, H 9.01, N 3.97; found C 74.67, H 9.15, N 4.28. Selected NMR data: ^{31}P{^{1}H} (C_6D_6, 25 °C, 161.821 MHz): δ = 59.8 (d, $^1J_{\mathrm{P-P}}$ = 298 Hz), 26.9 (d, $^1J_{\mathrm{P-P}}$ = 298 Hz); ^{7}Li (C_6D_6, 25 °C, 155.459 MHz): δ = 2.17 (s). Crystal data for **3**: M = 638.75, orthorhombic, $P2_12_12_1$, a = 9.5496(19), b = 13.510(3) c = 29.730(6) Å, V = 3835.5(13) Å^3, Z = 4, T = 173(2) K, D = 1.106 g cm^{-3}, μ(Mo–Kα) = 0.164 mm^{-1}, R = 0.0515 and wR = 0.1359 (all data). CCDC 247958. Anal calcd. for $C_{39}H_{53}AlN_2P_2$: C 73.33, H 8.36, N 4.39; found C 73.15 H 8.60, N 4.22. Selected NMR data: ^{31}P{^{1}H} (C_6D_6, 25 °C, 161.821 MHz): δ = 45.9 (d, $^1J_{\mathrm{P-P}}$ = 264 Hz), 40.2 (d, $^1J_{\mathrm{P-P}}$ = 264 Hz). See http://www.rsc.org/suppdata/cc/b4/b413137a/ for crystallographic data in .cif or other electronic format.

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