Direct synthesis of doubly deprotonated, dearomatised lutidine PNP Cr and Zr pincer complexes based on isolated K and Li ligand transfer reagents†

Thomas Simler,a Gilles Frison,b Pierre Braunstein*a and Andreas A. Danopoulos*a,c

Double deprotonation of 2,6-bis-(di-tert-butylphosphinomethyl)-pyridine (RP*PNRP), with KCH$_2$C$_6$H$_5$ afforded K$_2$(tBuP*Na$^-$)(tBuP*), N$_a$ = anionic amido N, tBuP* = di-tert-butyl vinylic P donor. The analogous [Li$_2$(tBuP*Na$^-$)]$_2$ (1) was reacted with [CrCl$_2$(THF)$_2$] and [ZrCl$_2$(THF)$_2$] to give the helical [Cr(CrCl(tBuP*Na$^-$)(tBuP*))Cl$_2$] (2) and [Zr(tBuP*Na$^-$)(tBuP*)Cl] (3), respectively. DFT calculations support dearomatisation of PNP*P* and its high donor ability.

‘Pincer’ ligands attract continuing interest due to the formation of stable, well-defined and finely-tunable complexes.1 From the large diversity currently available, designs bearing diphosphines attached to the monoanionic m-(α,α’)-xylylenyl, (8PC$_2$P), and the neutral 2,6-lutidine-backbones (8PN$_2$P).2 R = carbon substituent at P (Scheme 1), have found wider application in catalysis, materials and biomedicine, in particular with late transition metals.3 In comparison, examples of 8PN$_2$P ligands coordinated to early and/or electropositive metals are rare (e.g. Cr,4 Mo$_5$ and W$_6$). Catalytic applications with 3d-transition metal 8PN$_2$P complexes have also emerged.4,7 Recent reaction mechanisms for the activation of small molecules by 8PN$_2$P complexes involve as key catalytic steps protonation-mondeprotonation at one α-methylene arm, accompanied by aromatisation-dearomatisation of the lutidine ring, in support of metal–ligand cooperation in 8PN$_2$P*P* (N$_a$ = anionic amido N donor, P* = vinylic P donor)§ systems.3c,9

However, reports on complexes with two mono-deprotonated α-methylene arms of PCP and PNP skeletons are scarce,10 probably due to the high reactivity of the resulting products and the lack of general synthetic access. To the best of our knowledge, there is only one report of structurally characterised 8P*Na$_2$P* complexes, obtained from coordinated PNP on a Ni$^0$ centre.10d Occasionally ‘sluggish’ (using KN-(SiMe$_3$)$_2$) or requiring large excess of base (with MeLi),10c and lacking generality,10b abstractions of both the α- and α’-CH$_2$P of coordinated 8PN$_2$P (leading to diionic 8PN$_2$P*) have resulted in Pd$^0$, Pt$^I$,10c,f and recently Re$^IV$ (R = Bu) complexes,10e which were characterised only in situ by NMR techniques. Relevant deprotonation at both –NH – linkers of a cobalt bis(aminophosphine) PNP analogue has been postulated in the generation of catalytic species.11

While 8PN$_2$P*P* complexes are usually accessed by deprotonation with bulky external amide bases (pK$_a$ ≈ 26–37 in THF)12 of one α-CH$_2$P in preformed 8PN$_2$P complexes, this method has limited applicability to the deprotonation of both the α- and α’-CH$_2$P. Alternatively, organolithium bases (pK$_a$ ≈ 40–56)11 have been used for the in situ formation of R$^+$P–P*–Pt$^III$ and R$^+$P$^-$Na$^-$R$^+$–Rh$I$ complexes (R = Ph), that were further quenched with electrophiles (vide supra).10a,b Stronger, more aggressive bases may lead to undesirable side reactions, limiting the scope of the approach. In contrast, transfer reagents (e.g. based on alkali metals) allowing direct complexation of 8P*Na$_2$P* have not been reported and may overcome the aforementioned synthetic difficulties.
Herein, we disclose K and Li complexes of $^8\text{P}^*\text{Na}^*\text{P}^*$, as new reagents that allow the preparation of unprecedented metal complexes. The structural diversity of the latter illustrates the versatility of $^8\text{P}^*\text{Na}^*\text{P}^*$ arising from its extended electronic delocalisation, also studied by DFT methods (Scheme 1).

Complete conversion of $^6\text{BuP}^*\text{N}^*\text{BuP}^*$ to the doubly deprotonated $^6\text{BuP}^*\text{Na}^*\text{BuP}^*$ succeeded with the potent benzylic potassium (KBN, $pK_a = \text{ca. } 42$ in polar aprotic solvents). Thus, monitoring by $^1\text{H}$-NMR the reaction of 2 equiv. KBN with a THF or toluene solution of $^6\text{BuP}^*\text{N}^*\text{BuP}^*$ at $-78\,^\circ\text{C}$ revealed the formation of a new species ($\delta = 6.38$ (1H), 4.99 (2H) and 3.00 (2H) in C$_6$D$_6$); in addition, a broad $^{31}\text{P}[^1\text{H} ]$-NMR singlet at $\delta = 13.1$ (cf. $\delta = 35.2$ for $^6\text{BuP}^*\text{N}^*\text{BuP}^*$) was observed, all these data being consistent with a symmetrical species in solution (for more details see section I.3.1 in ESI†). It was tentatively assigned to the symmetrical dianion $^6\text{BuP}^*\text{N}^*\text{BuP}^*$ (Scheme 1). Although single crystals suitable for X-ray diffraction could not be obtained, evidence for the double deprotonation was obtained by the reaction with D$_2$O and the resulting isotopomer $^6\text{BuP}^*\text{N}^*\text{BuD}^*$ was characterised by NMR spectroscopy (section I.4 in ESI†). Moreover, a NOESY experiment in THF established the presence of an equilibrium between different geometric isomers of $K_2[ ^6\text{BuP}^*\text{N}^*\text{BuP}^*]$ due to rotation about the PC$_3$C$_3$ bonds (see section I.3.2 in ESI†).

More detailed characterisation of the dianion $^6\text{BuP}^*\text{N}^*\text{BuP}^*$ succeeded by using organolithium bases. Thus, reaction of two equiv. LiCH$_2$SiMe$_3$ with $^6\text{BuP}^*\text{N}^*\text{BuP}^*$ in C$_6$D$_6$ led to the slow formation of $[\text{Li}[^6\text{BuP}^*\text{N}^*\text{BuP}^*]]_2$ (1) with NMR data supporting the presence of a symmetrical doubly deprotonated species. A more useful protocol to access $[\text{Li}[^6\text{BuP}^*\text{N}^*\text{BuP}^*]]_2$ was developed by using $^1\text{BuLi}$. The reaction proceeded fast at r.t. in pentane, from which 1 conveniently precipitated and was isolated by filtration as a yellow, extremely air-sensitive solid (up to 2 g scale, 75%). Evidence for the double deprotonation was again obtained by the reaction of 1 with D$_2$O (section I.4 in ESI†). The structure of 1 was determined from a yellow crystal formed during the reaction of a C$_6$D$_6$ solution of $^6\text{BuP}^*\text{N}^*\text{BuP}^*$ with excess LiCH$_2$SiMe$_3$ (see above). The structure reveals a centrosymmetric dimeric aggregate with the two heterocyclic rings being 4.090 Å apart (Fig. 1). In each constitutive planar subunit, one Li atom is in a T-shaped environment (two P* and the N$_a$) (P-Li-P = 167.6°). Two additional Li atoms bridge these two subunits through two η^1-allylic-type interactions involving the CH$_{\alpha}$-P, C$_\beta$-N and C$_\beta$-N atoms of the heterocycle (crystallographic C6-C1-C2 and C15-C5-C4). A relevant η^1-allylic interaction with Li* has been described in the ion pair [Li(ether)$_2$].[Ni($^6\text{BuP}^*\text{N}^*\text{BuP}^*$)Me]$^{10\text{d}}$ It is plausible that the P-atom adjacent to the deprotonated site in the 2,6-hutidine backbone contributes to the stabilisation of the dianion in 1. DFT calculations on the model ligands $^{13}\text{P}^*\text{Na}^*\text{P}^*$, $^{13}\text{P}^*\text{Na}^*\text{Me}^*$ (for comparison) and $\text{MP}^*\text{Na}^*\text{Me}^*$ shed light on their electronic structures. They show extensive delocalisation of the 6, 8 and 10 π-electrons, respectively, as illustrated (see ESI†) by the delocalised molecular orbitals, the CC and CN bond distances that are intermediate between a single (1.54 and 1.47 Å) and a double bond (1.34 and 1.29 Å), respectively, as well as the Wiberg bond indexes for the CC and CN bonds, which range from 1.21 to 1.48 for $^{13}\text{P}^*\text{Na}^*\text{Me}^*$ (Scheme 1). Delocalisation is also reflected by the number and nature of significant resonance structures, determined by the natural resonance theory (NRT), which show that the anionic sites are delocalised over N, C$_\beta$-N and C$_\alpha$-P (Scheme 1 and ESI†). The six-membered ring of MeP*Na$^*$ is populated by 6.65 π-electrons, indicating a charge transfer from ν each C$_\alpha$-P deprotonated site. Its smaller value compared to the charge transfer from C$_\alpha$-P in $^{13}\text{P}^*\text{Na}^*\text{Me}^*$ (0.5 e) is presumably due to competition between the two anionic sites.

Consequently, the π-population at C$_\alpha$-P is higher in $^{13}\text{P}^*\text{Na}^*\text{Me}^*$ than in $^{13}\text{P}^*\text{Na}^*\text{Me}^*$ (1.53 e vs. 1.42 e), which also induces larger stabilisation of the anionic site by hyperconjugation with the σ* P-C$_\text{Me}$ bond, as revealed by the shorter P-C bond length (1.774 vs. 1.790 Å) and the larger lone pair → σ* second-order interaction energy (95 vs. 73 kJ mol$^{-1}$) (from NBO analysis). Lastly, as for $^{13}\text{P}^*\text{Na}^*\text{Me}^*$, NICS(0) value: +1.6), $^{13}\text{P}^*\text{Na}^*\text{Me}^*$ shows deamalisation of the pyridine ring (NICS(0) value: +1.0) relative to the neutral $^{13}\text{P}^*\text{Na}^*\text{Me}^*$ (NICS(0) value: -6.2).

The utility and potential of 1 as transmetallation reagent was demonstrated by the synthesis of Cr$^{II}$ and Zr$^{IV}$ complexes. Yellow 1 reacted with [CrCl$_3$(THF)$_2$] at low temperatures to give the trinuclear complex [Cr[($^6\text{BuP}^*\text{N}^*\text{BuP}^*$)Cl]$_2$] (2), isolated as red air sensitive crystals from pentane (Scheme 2).

This unusual complex is paramagnetic, with $\mu_{eff} = 8.50\mu_B$ (Evans’ method in THF, see ESI†), a value consistent with three uncoupled Cr(III) ($d^4$, S = 2) centres giving rise to a spin-only moment of 8.48µB. The trinuclear structure of 2 (Fig. 2) features two terminal subunits, each comprising one 12 electron Cr centre coordinated to a [κP$_2$NX$_2$K] donor set in a distorted square planar environment completed by a Cl ligand, and one internal 12 electron Cr linking the two subunits via two η^1-allicyclic-type interactions, through their CH$_{\alpha}$-P, C$_\beta$-N and C$_\alpha$-P.

---

**Fig. 1** The centrosymmetric structure of 1 with ellipsoids at 40% probability except the $\text{^1Bu}$ atoms that are depicted as spheres. H atoms are omitted except for the α-CHP.
reaction of \( \text{Li(THF)} \) with \( \text{Zr(2.164(2) Å)} \). The C\(_{1,3}\)-bis(trimethylsilyl)allyl, the molecular symmetry is staggered whereas in the known \( \text{[Cr(allyl)\text{2}]} \) (allyl = bulky dianionic ligand). Overall, the coordination geometry at Zr can be described as distorted octahedral. Interestingly, the ligand departs from planarity (cf. 2) and the heterocyclic ring remains dearomatised. The Zr-P bond distances are different (2.643(2) Å and 2.811(2) Å) and the Zr-N bond distance (2.120(4) Å) is typical for a Zr-Namide bond (mean Zr-Namide 2.12(9) Å).

The unsymmetrical arrangement seen in the solid state is retained in C\(_6\)D\(_6\) solution at room temperature: in the \(^{31}\text{P}\{^1\text{H}\}\)-NMR spectrum two closely spaced, broad singlets can be assigned to the inequivalent P arms (at \( \delta 56.0 \) and 55.2); the appearance of the spectrum is field-independent, and upon heating to 70 °C, it coalesced to one singlet at \( \delta 56.5, \) indicating non-rigidity. In pentane, two broad singlets were observed also at r.t., which upon cooling to \(-40 \) °C split into two weakly coupled doublets. The \(^1\text{H}\)-NMR data are consistent with an oscillation of the Zr centre within the ligand pocket (section I.6 in ESI† and Scheme 2) (\( \Delta G^\ddagger = 62 \pm 2 \) kJ mol\(^{-1}\)). This assumption has been confirmed by DFT calculations which allow locating a symmetric transition state situated 63 kJ mol\(^{-1}\) above \([\text{Zr(MF\(_3\)P\(_{\text{N}}\text{MeP}\_\text{P})\text{Cl}_2}] \) (3, as model for 3). Furthermore, an energy decomposition analysis combined with the natural orbitals for chemical valence scheme (ETS-NOCV)\(^{21}\) was conducted on 3. The total \( \text{MeP\_\text{N}MeP\_\text{ZrCl}_2} \) interaction energy is estimated at \(-2801 \) kJ mol\(^{-1}\). Due to the dicatonic and dianionic nature of the interacting fragments, electrostatic interactions contribute significantly (\(-2270 \) kJ mol\(^{-1}\), \( i.e. \) 61%) to the attractive interactions, the remaining 39% (\(-1462 \) kJ mol\(^{-1}\)) being due to covalent bonding, whereas the Pauli repulsion term amounts to 931 kJ mol\(^{-1}\). The orbital interactions can be further decomposed into contributions related to the deformation density due to the bonding. Fig. 4 shows the deformation densities corresponding to the five most important orbital interactions as well as their calculated strength \( \Delta \varepsilon \).

The deformation densities in Fig. 4a and e illustrate the \( \sigma \)-donation of the out-of-phase and in-phase combinations of

**Scheme 2** Synthesis of \([\text{Cr(Cr}^{\text{BuP\_N}}\text{BuP\_P})\text{Cl}_2] \) (2) and \([\text{Cr}^{\text{BuP\_P}}\_\text{N}^{\text{BuP\_P}}\text{Cl}_2] \) (3) by transmetallation from 1.

**Fig. 2** The structure of \([\text{Cr(Cr}^{\text{BuP\_N}}\text{BuP\_P})\text{Cl}_2] \) (2) with ellipsoids at 30% probability (left). Only one \( \text{tBu} \) carbon is shown as a sphere and H-atoms are omitted, except for the \( \text{tBu} \) atoms that are depicted as spheres. H-atoms are omitted, except for the \( \alpha\text{-CH} \) Stick representation of the helical chirality (right).

**Fig. 3** The molecular structure of one of the two \([\text{Zr}^{\text{BuP\_N}^{\text{BuP\_P}}\text{Cl}_2}] \) (3) units with ellipsoids at 30% except the \( \text{tBu} \) atoms that are depicted as spheres. H-atoms are omitted, except for the \( \alpha\text{-CH} \) (see ESI† for the second independent molecule of 3).

C\(_{p-N}\) backbone atoms. The overall approximate molecular symmetry of helical 2 is \( C_2 \) (chiral space group \( P2_12_12_1 \), Flack parameter = 0.002(18)). The allylic moieties are in an ‘eclipsed-like’ arrangement whereas in the known \([\text{Cr(allyl)}]_2 \) (allyl = 1,3-bis(trimethylsilyl)allyl), the molecular symmetry is \( C_{3v} \) and the conformation ‘staggered’.\(^{18}\) The Cr-N bond lengths (2.052(6) and 2.058(6) Å) are in the high range of anionic \( \text{Cr-N} \),\(^{19}\) but shorter than the \( \text{Cr-Npyridine} \) in \([\text{Cr}^{\text{BuP\_N}^{\text{BuP\_P}}\text{Cl}_2}] \) (2.164(2) Å).\(^4\) The C-C distances within the allylic units are unequal (1.408(10), 1.442(10) Å and 1.389(10), 1.449(10) Å, respectively) and the six Cr-C\(_{allyl} \) bonds show substantial variation (2.175(8)–2.393(8) Å).

No intermediate was isolated in the formation of 2, but it is reasonable to assume that the two pincer units are initially formed leading to ‘ate’ type Cr-Li complexes, or ion pairs e.g. \([\text{Li(THF)}]_2[\text{Cr}^{\text{BuP\_N}^{\text{BuP\_P}}\text{Cl}_2}]^{\text{ff}} \) that subsequently react with \([\text{CrCl}_2(\text{THF})]_2 \) to form 2. Alternative bonding modes of the \( \text{BuP\_N}^{\text{BuP\_P}} \), in particular on a single (electropositive, \( d^0 \), large size) metal ion are conceivable, and shown with \([\text{Zr}^{\text{BuP\_N}^{\text{BuP\_P}}\text{Cl}_2}] \) (3), obtained as dark-green crystals by reaction of 1 with \([\text{ZrCl}_2(\text{THF})]_2 \), \( \text{THT} = \text{tetrahydrothiophene} \), in toluene at \(-78 \) °C (Scheme 2). Its structure (Fig. 3) reveals an unexpected coordination mode of the \( \text{BuP\_N}^{\text{BuP\_P}} \) ligand,
very high donor ability of $P^*Na^*P^*$.

This decomposition confirms the $\pi$ interaction that originates from the two lone pairs at P1 and C6 (Fig. 3) to the metal. The deformation density in Fig. 4d displays the weak charge flow from the two lone pairs at N1 and P2 (Fig. 4b and c). The charge in on N (see Scheme 1).

In conclusion, the choice of strong bases and conditions has allowed the first isolation of the pure K and Li salts of the dearomatised, doubly deprotonated $tBuP^*Na^*P^*$ ligand and $[Li(tBuP^*Na^*P^*)]^-$, was structurally characterised. They provide a new and efficient route to access doubly deprotonated and dearomatised transition metal complexes with unprecedented ligand cooperativity. The notations $^8P^*N^*P^*$ and $^8P^*N^*P^*$ designate structures corresponding to resonance forms where the anionic charge in on N (see Scheme 1).

The USIAS, CNRS, Unistra, Région Alsace and Communauté Urbaine de Strasbourg are acknowledged for the award of fellowships and a Gutenberg Excellence Chair (2010-11) to AAD. We thank the CNRS and the MESR (Paris) for funding and for a PhD grant to TS. We are grateful to Dr L. Karmazin (Service de Radiocristallographie, Unistra) for solving the crystal structures and Dr B. Vincent (Service de Résonance Magnétique Nucléaire, Unistra) for the VT analysis. Calculations were performed using HPC resources from GENCI-IDRIS (Grant 2015-086894). GF thanks C. Clavaguera for technical support for the NRT calculations.

References


4 A. Alzamly, S. Gambarotta and I. Korobkov, Organometalics, 2013, 32, 7204.


8 The notations $^8PN^*P^*$ and $^8P^*N^*P^*$ designate structures corresponding to resonance forms where the anionic charge in on N (see Scheme 1).


Fig. 4 Deformation densities associated with the orbital interactions in $[Zr(tBuP^*Na^*P^*)Cl_2]^{-}$. The charge flow of the electronic density is red $\rightarrow$ blue.