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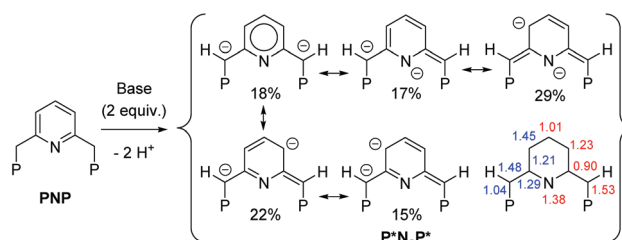
## Direct synthesis of doubly deprotonated, dearomatised lutidine PNP Cr and Zr pincer complexes based on isolated K and Li ligand transfer reagents†

Thomas Simler,<sup>a</sup> Gilles Frison,<sup>b</sup> Pierre Braunstein<sup>\*a</sup> and Andreas A. Danopoulos<sup>\*a,c</sup>

Double deprotonation of 2,6-bis-(di-*tert*-butylphosphinomethyl)-pyridine (<sup>t</sup>BuPN<sup>t</sup>BuP), with KCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> afforded K<sub>2</sub>(<sup>t</sup>BuP<sup>-</sup>N<sup>-</sup><sup>t</sup>BuP<sup>-</sup>), N<sub>a</sub> = anionic amido N, <sup>t</sup>BuP\* = di-*tert*-butyl vinylic P donor. The analogous [Li<sub>2</sub>(<sup>t</sup>BuP<sup>-</sup>N<sup>-</sup><sup>t</sup>BuP<sup>-</sup>)]<sub>2</sub> (1) was reacted with [CrCl<sub>2</sub>(THF)<sub>2</sub>] and [ZrCl<sub>4</sub>(THT)<sub>2</sub>] to give the helical [Cr{Cr(<sup>t</sup>BuP<sup>-</sup>N<sup>-</sup><sup>t</sup>BuP<sup>-</sup>)Cl<sub>2</sub>}]<sub>2</sub> (2) and [Zr(<sup>t</sup>BuP<sup>-</sup>N<sup>-</sup><sup>t</sup>BuP<sup>-</sup>)Cl<sub>2</sub>] (3), respectively. DFT calculations support dearomatisation of P<sup>-</sup>N<sub>a</sub>P<sup>-</sup> and its high donor ability.

'Pincer' ligands attract continuing interest due to the formation of stable, well-defined and finely-tunable complexes.<sup>1</sup> From the large diversity currently available, designs bearing diphosphines attached to the monoanionic *m*-( $\alpha,\alpha'$ -xylylenyl-, (<sup>R</sup>PC<sup>R</sup>P), and the neutral 2,6-lutidine-backbones (<sup>R</sup>PN<sup>R</sup>P),<sup>2</sup> R = carbon substituent at P (Scheme 1), have found wider application in catalysis, materials and biomedicine, in particular with late transition metals.<sup>3</sup> In comparison, examples of <sup>R</sup>PN<sup>R</sup>P ligands coordinated to early and/or electropositive metals are rare (e.g. Cr,<sup>4</sup> Mo<sup>5</sup> and W<sup>6</sup>). Catalytic applications with 3d-transition metal <sup>R</sup>PN<sup>R</sup>P complexes have also emerged.<sup>4,7</sup> Recent reaction mechanisms for the activation of small molecules by <sup>R</sup>PN<sup>R</sup>P complexes involve as key catalytic steps protonation-monodeprotonation at one  $\alpha$ -methylene arm, accompanied by aromatisation-dearomatisation of the lutidine ring, in support of metal-ligand cooperation in <sup>R</sup>PN<sub>a</sub><sup>R</sup>P\* (N<sub>a</sub> = anionic amido N donor, P\* = vinylic P donor)<sup>8</sup> systems.<sup>3c,9</sup>

However, reports on complexes with two mono-deprotonated  $\alpha$ -methylene arms of PCP and PNP skeletons are scarce,<sup>10</sup> probably due to the high reactivity of the resulting products and the lack of general synthetic access. To the best



**Scheme 1** Double deprotonation of <sup>R</sup>PN<sup>R</sup>P and relevant resonance structures of <sup>R</sup>P<sup>-</sup>N<sub>a</sub><sup>-</sup>P<sup>-</sup>. NBO weight of the resonance structures, electronic  $\pi$ -populations (in red) and Wiberg bond indexes (in blue) calculated for R = Me at the M06-2X/6-31++G(d,p) level of theory.

of our knowledge, there is only one report of structurally characterised <sup>R</sup>P<sup>-</sup>N<sub>a</sub><sup>-</sup>P<sup>-</sup> complexes, obtained from coordinated PNP on a Ni<sup>II</sup> centre.<sup>10d</sup> Occasionally 'sluggish' (using KN-(SiMe<sub>3</sub>)<sub>2</sub>) or requiring large excess of base (with MeLi),<sup>10c</sup> and lacking generality,<sup>10e</sup> abstractions of both the  $\alpha$ - and  $\alpha'$ -CH<sub>2</sub><sup>R</sup>P of coordinated <sup>R</sup>PN<sup>R</sup>P (leading to dianionic <sup>R</sup>P<sup>-</sup>N<sub>a</sub><sup>-</sup>P<sup>-</sup>) have resulted in Pd<sup>II</sup>, Pt<sup>II</sup>,<sup>10c,f</sup> and recently Re<sup>IV</sup> (R = *t*Bu) complexes,<sup>10e</sup> 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.<sup>11</sup>

While <sup>R</sup>P<sup>-</sup>N<sub>a</sub><sup>-</sup>P<sup>-</sup> complexes are usually accessed by deprotonation with bulky external amide bases (pK<sub>a</sub>  $\approx$  26–37 in THF)<sup>12</sup> of one  $\alpha$ -CH<sub>2</sub><sup>R</sup>P in preformed <sup>R</sup>PN<sup>R</sup>P complexes, this method has limited applicability to the deprotonation of both the  $\alpha$ - and  $\alpha'$ -CH<sub>2</sub><sup>R</sup>P. Alternatively, organolithium bases (pK<sub>a</sub>  $\approx$  40–56)<sup>13</sup> have been used for the *in situ* formation of <sup>R</sup>P<sup>-</sup>C<sup>R</sup>P<sup>-</sup>-Pt<sup>II</sup> and <sup>R</sup>P<sup>-</sup>N<sub>a</sub><sup>-</sup>P<sup>-</sup>-Rh<sup>I</sup> complexes (R = Ph), that were further quenched with electrophiles (*vide supra*).<sup>10a,b</sup> 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 <sup>R</sup>P<sup>-</sup>N<sub>a</sub><sup>-</sup>P<sup>-</sup> have not been reported and may overcome the aforementioned synthetic difficulties.

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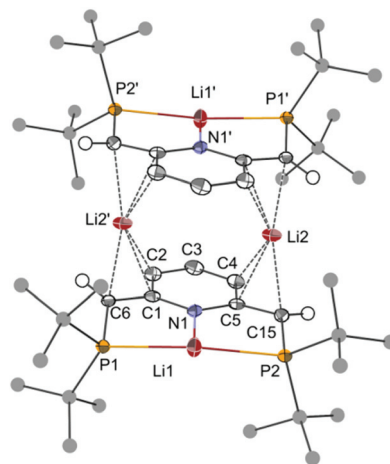
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Herein, we disclose K and Li complexes of  ${}^R\text{P}^*\text{N}_a{}^R\text{P}^*$ , as new reagents that allow the preparation of unprecedented metal complexes. The structural diversity of the latter illustrates the versatility of  ${}^R\text{P}^*\text{N}_a{}^R\text{P}^*$  arising from its extended electronic delocalisation, also studied by DFT methods (Scheme 1).

Complete conversion of  ${}^t\text{BuPN}{}^t\text{BuP}$  to the doubly deprotonated  ${}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*$  succeeded with the potent benzyl potassium (KBn,  $\text{p}K_a = ca. 42$  in polar aprotic solvents).<sup>14</sup> Thus, monitoring by  ${}^1\text{H-NMR}$  the reaction of 2 equiv. KBn with a THF or toluene solution of  ${}^t\text{BuPN}{}^t\text{BuP}$  at  $-78\text{ }^\circ\text{C}$  revealed the formation of a new species ( $\delta$  6.38 (1H), 4.99 (2H) and 3.00 (2H) in  $\text{C}_6\text{D}_6$ ); in addition, a broad  ${}^{31}\text{P}\{^1\text{H}\}$ -NMR singlet at  $\delta$  13.1 (*cf.*  $\delta$  35.2 for  ${}^t\text{BuPN}{}^t\text{BuP}$ ) 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  ${}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*$  (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  $\text{D}_2\text{O}$  and the resulting isotopomer  $\alpha,\alpha'\text{-d}_2\text{-}{}^t\text{BuPN}{}^t\text{BuP}$  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  $\text{K}_2({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)$  due to rotation about the  $\text{PC}\cdots\text{C}$  bonds (see section I.3.2 in ESI†).

More detailed characterisation of the dianion  ${}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*$  succeeded by using organolithium bases. Thus, reaction of two equiv.  $\text{LiCH}_2\text{SiMe}_3$  with  ${}^t\text{BuPN}{}^t\text{BuP}$  in  $\text{C}_6\text{D}_6$  led to the slow formation of  $[\text{Li}_2({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)]_2$  (**1**) with NMR data supporting the presence of a symmetrical doubly deprotonated species. A more useful protocol to access  $[\text{Li}_2({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)]_2$  was developed by using  ${}^t\text{BuLi}$ .<sup>15</sup> 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  $\text{D}_2\text{O}$  (section I.4 in ESI†). The structure of **1** was determined from a yellow crystal formed during the reaction of a  $\text{C}_6\text{D}_6$  solution of  ${}^t\text{BuPN}{}^t\text{BuP}$  with excess  $\text{LiCH}_2\text{SiMe}_3$  (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  $\text{P}^*$  and the  $\text{N}_a$ ) ( $\text{P-Li-P} = 167.6^\circ$ ). Two additional Li atoms bridge these two subunits through two  $\eta^3$ -allylic-type interactions involving the  $\text{CH}_{\alpha\text{-P}}$ ,  $\text{C}_{\alpha\text{-N}}$  and  $\text{C}_{\beta\text{-N}}$  atoms of the heterocycle (crystallographic C6–C1–C2 and C15–C5–C4). A relevant  $\eta^3$ -allylic interaction with  $\text{Li}^+$  has been described in the ion pair  $[\text{Li}(\text{ether})_2][\text{Ni}^{\text{II}}({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)\text{Me}]$ .<sup>10d</sup> It is plausible that the P-atom adjacent to the deprotonated site in the 2,6-lutidine backbone contributes to the stabilisation of the dianion in **1**.<sup>16</sup> DFT calculations on the model ligands  ${}^{\text{Me}}\text{PN}{}^{\text{Me}}\text{P}$ ,  ${}^{\text{Me}}\text{PN}_a{}^{\text{Me}}\text{P}^*$  (for comparison) and  ${}^{\text{Me}}\text{P}^*\text{N}_a{}^{\text{Me}}\text{P}^*$  shed light on their electronic structures. They show extensive delocalisation of the 6, 8 and 10  $\pi$ -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



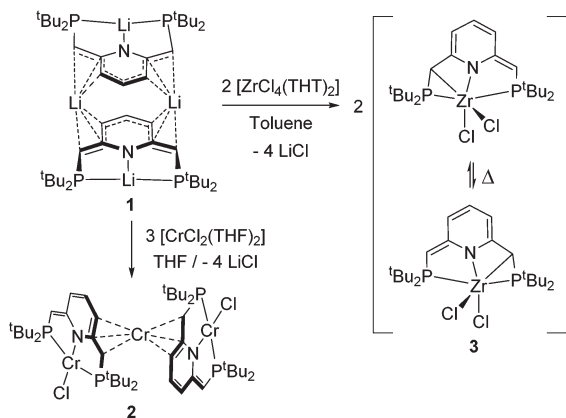
**Fig. 1** The centrosymmetric structure of **1** with ellipsoids at 40% probability except the  ${}^t\text{Bu}$  atoms that are depicted as spheres. H atoms are omitted except for the  $\alpha$ -CHP.

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  ${}^{\text{Me}}\text{P}^*\text{N}_a{}^{\text{Me}}\text{P}^*$  (Scheme 1). Delocalisation is also reflected by the number and nature of significant resonance structures, determined by the natural resonance theory (NRT),<sup>17</sup> which show that the anionic sites are delocalised over N,  $\text{C}_{\beta\text{-N}}$  and  $\text{C}_{\alpha\text{-P}}$  (Scheme 1 and ESI†). The six-membered ring of  ${}^{\text{Me}}\text{P}^*\text{N}_a{}^{\text{Me}}\text{P}^*$  is populated by 6.65  $\pi$ -electrons, indicating a charge transfer of *ca.* 0.3 e from each  $\text{C}_{\alpha\text{-P}}$  deprotonated site. Its smaller value compared to the charge transfer from  $\text{C}_{\alpha\text{-P}}$  in  ${}^{\text{Me}}\text{PN}_a{}^{\text{Me}}\text{P}^*$  (0.5 e) is presumably due to competition between the two anionic sites.

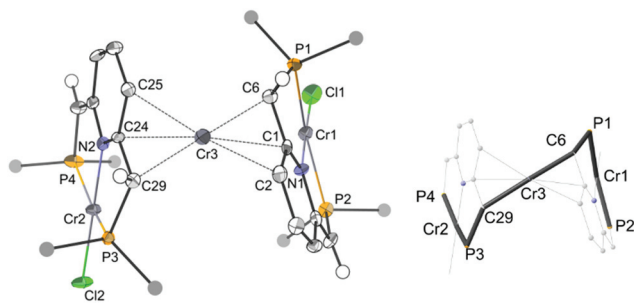
Consequently, the  $\pi$ -population at  $\text{C}_{\alpha\text{-P}}$  is higher in  ${}^{\text{Me}}\text{P}^*\text{N}_a{}^{\text{Me}}\text{P}^*$  than in  ${}^{\text{Me}}\text{PN}_a{}^{\text{Me}}\text{P}^*$  (1.53 e *vs.* 1.42 e), which also induces larger stabilisation of the anionic site by hyperconjugation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

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

This unusual complex is paramagnetic, with  $\mu_{\text{eff}} = 8.50\mu_{\text{B}}$  (Evans' method in THF, see ESI†), a value consistent with three uncoupled  $\text{Cr}(\text{II})$  ( $d^4$ ,  $S = 2$ ) centres giving rise to a spin-only moment of  $8.48\mu_{\text{B}}$ . The trinuclear structure of **2** (Fig. 2) features two terminal subunits, each comprising one 12 electron Cr centre coordinated to a ( $\kappa\text{P}, \kappa\text{N}_a, \kappa\text{P}$ ) 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  $\eta^3$ -allylic-type interactions, through their  $\text{CH}_{\alpha\text{-P}}$ ,  $\text{C}_{\alpha\text{-N}}$  and



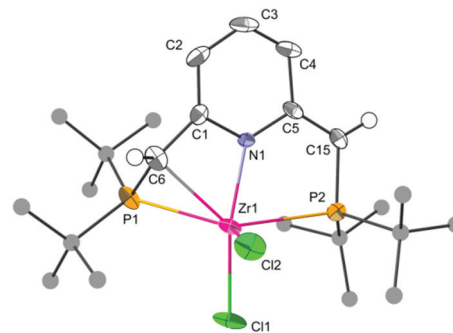
**Scheme 2** Synthesis of  $[\text{Cr}(\text{Cr}(\text{tBuP}^*\text{N}_a^{\text{tBuP}^*})\text{Cl}_2)]$  (**2**) and  $[\text{Zr}(\text{tBuP}^*\text{N}_a^{\text{tBuP}^*})\text{Cl}_2]$  (**3**) by transmetalation from **1**.



**Fig. 2** The structure of  $[\text{Cr}(\text{Cr}(\text{tBuP}^*\text{N}_a^{\text{tBuP}^*})\text{Cl}_2)]$  (**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  $\alpha\text{-CH}$ . Stick representation of the helical chirality (right).

$\text{C}_{\beta\text{-N}}$  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  $[\text{Cr}(\text{allyl})_2]$  (allyl = bulky 1,3-bis(trimethylsilyl)allyl), the molecular symmetry is  $C_{2h}$  and the conformation 'staggered'.<sup>18</sup> The Cr–N bond lengths (2.052(6) and 2.058(6) Å) are in the high range of anionic Cr–N<sub>a</sub><sup>19</sup> but shorter than the Cr–N<sub>pyridine</sub> in  $[\text{Cr}(\text{PhPN}^{\text{Ph}}\text{P})\text{Cl}_2]$  (2.164(2) Å).<sup>4</sup> 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<sub>allyl</sub> bonds show also 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.  $[\text{Li}(\text{THF})_x][\text{Cr}^{\text{II}}(\text{tBuP}^*\text{N}_a^{\text{tBuP}^*})\text{Cl}]$ ,<sup>10d</sup> that subsequently react with  $[\text{CrCl}_2(\text{THF})_2]$  to form **2**. Alternative bonding modes of the  $\text{tBuP}^*\text{N}_a^{\text{tBuP}^*}$ , in particular on a single (electropositive,  $d^0$ , large size) metal ion are conceivable, and shown with  $[\text{Zr}(\text{tBuP}^*\text{N}_a^{\text{tBuP}^*})\text{Cl}_2]$  (**3**), obtained as dark-green crystals by reaction of **1** with  $[\text{ZrCl}_4(\text{THT})_2]$ , THT = tetrahydrothiophene, in toluene at  $-78^\circ\text{C}$  (Scheme 2). Its structure (Fig. 3) reveals an unexpected coordination mode of the  $\text{tBuP}^*\text{N}_a^{\text{tBuP}^*}$  ligand,



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

featuring anionic phosphinoalkanide functionality (*cf.* phosphino-methanides),<sup>20</sup> tethered to the anionic heterocycle. Comparison of the metrical data in **3** (short Zr–P and Zr–C <sub>$\alpha$</sub> -P bonds) supports an  $\eta^2\text{-}(\text{P}-\text{C})$  coordination (up to 10 e<sup>−</sup> donor, 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 dearomatized. 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–N<sub>amido</sub> bond (mean Zr–N<sub>amido</sub> 2.12(9) Å).<sup>19</sup>

The unsymmetrical arrangement seen in the solid state is retained in  $\text{C}_6\text{D}_6$  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  $70^\circ\text{C}$ , 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  $-40^\circ\text{C}$  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) ( $\Delta G^\ddagger = 62 \pm 2 \text{ kJ mol}^{-1}$ ). This assumption has been confirmed by DFT calculations which allow locating a symmetric transition state situated 63  $\text{kJ mol}^{-1}$  above  $[\text{Zr}(\text{Me}^e\text{P}^*\text{N}_a^{\text{Me}^e\text{P}^*})\text{Cl}_2]$  (**3'**, as model for **3**). Furthermore, an energy decomposition analysis combined with the natural orbitals for chemical valence scheme (ETS-NOCV)<sup>21</sup> was conducted on **3'**. The total  $\text{Me}^e\text{P}^*\text{N}_a^{\text{Me}^e\text{P}^*}\text{-ZrCl}_2$  interaction energy is estimated at  $-2801 \text{ kJ mol}^{-1}$ . Due to the dicationic and dianionic nature of the interacting fragments, electrostatic interactions contribute significantly ( $-2270 \text{ kJ mol}^{-1}$ , *i.e.* 61%) to the attractive interactions, the remaining 39% ( $-1462 \text{ kJ mol}^{-1}$ ) being due to covalent bonding, whereas the Pauli repulsion term amounts to  $931 \text{ kJ mol}^{-1}$ . 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  $\Delta E$ .

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



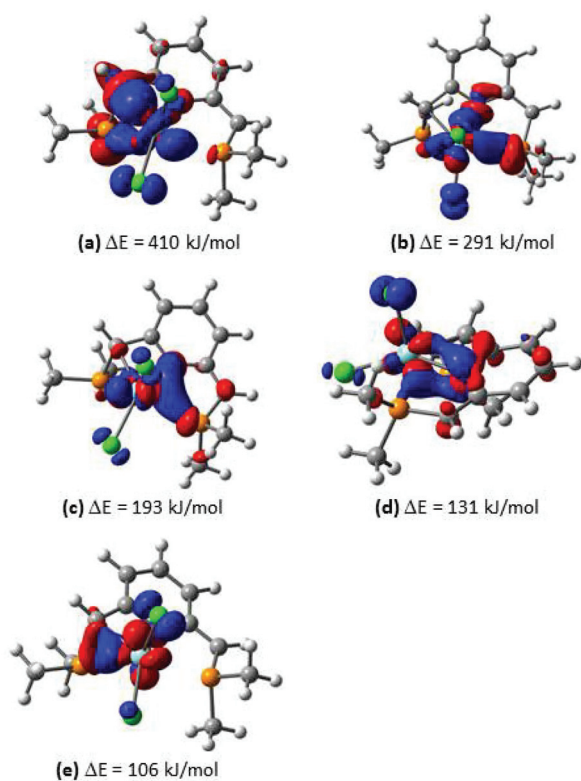


Fig. 4 Deformation densities associated with the orbital interactions in  $[\text{Zr}(\text{MeP}^*\text{N}_a\text{MeP}^*)\text{Cl}_2]$ . The charge flow of the electronic density is red  $\rightarrow$  blue.

the two lone pairs at P1 and C6 (Fig. 3) to the metal, the former being the dominant term of the orbital interaction. Similar  $\sigma$ -donation type deformation densities are observed from the two  $\sigma$  lone pairs at N1 and P2 (Fig. 4b and c). The deformation density in Fig. 4d displays the weak charge flow that originates from the  $\pi$ -interaction between the six-membered ring and the metal. This decomposition confirms the very high donor ability of  $\text{P}^*\text{N}_a\text{P}^*$ .

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  ${}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*$  ligand and  $[\text{Li}_2({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)]_2$  was structurally characterised. They provide a new and efficient route to access doubly deprotonated and dearomatised transition metal complexes with unprecedented structures by transmetallation reactions, as illustrated with  $\text{Cr}^{\text{II}}$  and  $\text{Zr}^{\text{IV}}$ . This versatile procedure extends the scope of the  $\text{R}^*\text{P}^*\text{N}_a\text{R}^*$  ligand to early transition metal centres. Considering the high and increasing importance of (doubly) deprotonated and dearomatised pincer complexes in catalysis, such systems are good candidates for metal–ligand cooperativity.<sup>9c</sup>

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