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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†

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Double deprotonation of 2,6-bis-(di-*tert*-butylphosphinomethyl)-pyridine (${}^t\text{BuPN}{}^t\text{BuP}$), with $\text{KCH}_2\text{C}_6\text{H}_5$ afforded $\text{K}_2({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)$, N_a = anionic amido N, ${}^t\text{BuP}^*$ = di-*tert*-butyl vinylic P donor. The analogous $[\text{Li}_2({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)]_2$ (1) was reacted with $[\text{CrCl}_2(\text{THF})_2]$ and $[\text{ZrCl}_4(\text{THT})_2]$ to give the helical $[\text{Cr}(\text{Cr}({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)\text{Cl})_2]$ (2) and $[\text{Zr}({}^t\text{BuP}^*\text{N}_a{}^t\text{BuP}^*)\text{Cl}_2]$ (3), respectively. DFT calculations support dearomatisation of $\text{P}^*\text{N}_a\text{P}^*$ 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-, (${}^{\text{R}}\text{PC}^{\text{R}}\text{P}$), and the neutral 2,6-lutidine-backbones (${}^{\text{R}}\text{PN}^{\text{R}}\text{P}$),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 ${}^{\text{R}}\text{PN}^{\text{R}}\text{P}$ ligands coordinated to early and/or electropositive metals are rare (e.g. Cr,⁴ Mo⁵ and W⁶). Catalytic applications with 3d-transition metal ${}^{\text{R}}\text{PN}^{\text{R}}\text{P}$ complexes have also emerged.^{4,7} Recent reaction mechanisms for the activation of small molecules by ${}^{\text{R}}\text{PN}^{\text{R}}\text{P}$ complexes involve as key catalytic steps protonation-monodeprotonation at one α -methylene arm, accompanied by aromatisation-dearomatisation of the lutidine ring, in support of metal-ligand cooperation in ${}^{\text{R}}\text{PN}_a{}^{\text{R}}\text{P}^*$ (N_a = anionic amido N donor, P^* = vinylic P donor)⁸ 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

Scheme 1 Double deprotonation of ${}^{\text{R}}\text{PN}^{\text{R}}\text{P}$ and relevant resonance structures of ${}^{\text{R}}\text{PN}_a{}^{\text{R}}\text{P}^*$. NBO weight of the resonance structures, electronic π -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 ${}^{\text{R}}\text{PN}_a{}^{\text{R}}\text{P}^*$ complexes, obtained from coordinated PNP on a Ni^{II} centre.^{10d} Occasionally 'sluggish' (using $\text{KN}(\text{SiMe}_3)_2$) or requiring large excess of base (with MeLi),^{10c} and lacking generality,^{10e} abstractions of both the α - and α' - CH_2 RP of coordinated ${}^{\text{R}}\text{PN}^{\text{R}}\text{P}$ (leading to dianionic ${}^{\text{R}}\text{PN}_a{}^{\text{R}}\text{P}^*$) have resulted in Pd^{II} , Pt^{II} ,^{10cf} and recently Re^{IV} (R = *t*Bu) complexes,^{10e} which were characterised only *in situ* by NMR techniques. Relevant deprotonation at both $-\text{NH}-$ linkers of a cobalt bis(aminophosphine) PNP analogue has been postulated in the generation of catalytic species.¹¹

While ${}^{\text{R}}\text{PN}_a{}^{\text{R}}\text{P}^*$ complexes are usually accessed by deprotonation with bulky external amide bases ($\text{p}K_a \approx 26\text{--}37$ in THF)¹² of one $\alpha\text{-CH}_2$ RP in preformed ${}^{\text{R}}\text{PN}^{\text{R}}\text{P}$ complexes, this method has limited applicability to the deprotonation of both the α - and α' - CH_2 RP. Alternatively, organolithium bases ($\text{p}K_a \approx 40\text{--}56$)¹³ have been used for the *in situ* formation of ${}^{\text{R}}\text{P}^*\text{C}^{\text{R}}\text{P}^*\text{-Pt}^{\text{II}}$ and ${}^{\text{R}}\text{P}^*\text{N}_a{}^{\text{R}}\text{P}^*\text{-Rh}^{\text{I}}$ 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 ${}^{\text{R}}\text{PN}_a{}^{\text{R}}\text{P}^*$ have not been reported and may overcome the aforementioned synthetic difficulties.

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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, $\text{p}K_a = \text{ca. } 42$ in polar aprotic solvents).¹⁴ Thus, monitoring by ^1H -NMR the reaction of 2 equiv. KBN with a THF or toluene solution of $^t\text{BuPN}^t\text{BuP}$ at -78°C revealed the formation of a new species (δ 6.38 (1H), 4.99 (2H) and 3.00 (2H) in C_6D_6); in addition, a broad $^{31}\text{P}\{^1\text{H}\}$ -NMR singlet at δ 13.1 (*cf.* δ 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 D_2O 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 C_6D_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 $^t\text{BuLi}$.¹⁵ 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_2O (section I.4 in ESI†). The structure of **1** was determined from a yellow crystal formed during the reaction of a C_6D_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 P^* and the N_a) ($\text{P-Li-P} = 167.6^\circ$). Two additional Li atoms bridge these two subunits through two η^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 η^3 -allylic interaction with Li^+ has been described in the ion pair $[\text{Li}(\text{ether})_2][\text{Ni}^\text{II}(^t\text{BuP}^*\text{N}_a^t\text{BuP}^*)\text{Me}]$.^{10d} 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**.¹⁶ 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 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

Fig. 1 The centrosymmetric structure of **1** with ellipsoids at 40% probability except the ^tBu atoms that are depicted as spheres. H atoms are omitted except for the α -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),¹⁷ 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 π -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 π -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 σ^* P-C_{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 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 Cr^II and Zr^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 η^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 ^tBu carbon is shown as a sphere and H-atoms are omitted, except for the α -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'.¹⁸ The Cr–N bond lengths (2.052(6) and 2.058(6) Å) are in the high range of anionic Cr–N_a¹⁹ but shorter than the Cr–N_{pyridine} in $[\text{Cr}(\text{PhPN}^{\text{Ph}}\text{P})\text{Cl}_2]$ (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 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. $[\text{Li}(\text{THF})_x][\text{Cr}^{\text{II}}(\text{tBuP}^*\text{N}_a\text{tBuP}^*)\text{Cl}]$,^{10d} 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°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 ^tBu atoms that are depicted as spheres. H-atoms are omitted, except for the α -CHP (see ESI† for the second independent molecule of **3**).

featuring anionic phosphinoalkenide functionality (*cf.* phosphino-methanides),²⁰ tethered to the anionic heterocycle. Comparison of the metrical data in **3** (short Zr–P and Zr–C _{α} -P bonds) supports an η^2 -(P–C) coordination (up to 10 e[−] 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 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–N_{amido} bond (mean Zr–N_{amido} 2.12(9) Å).¹⁹

The unsymmetrical arrangement seen in the solid state is retained in C_6D_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 δ 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 δ 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 ^1H -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 kJ mol^{-1} above $[\text{Zr}(\text{MeP}^*\text{N}_a\text{MeP}^*)\text{Cl}_2]$ (**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 $\text{MeP}^*\text{N}_a\text{MeP}^*\text{--ZrCl}_2$ 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 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 ΔE .

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

Fig. 4 Deformation densities associated with the orbital interactions in $[\text{Zr}(\text{MeP}^*\text{Na}^*\text{MeP}^*)\text{Cl}_2]$. 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 σ -donation type deformation densities are observed from the two σ 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 π -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 $^t\text{BuP}^*\text{N}_a^*\text{P}^*$ ligand and $[\text{Li}_2(^t\text{BuP}^*\text{N}_a^*\text{P}^*)]_2$ 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 Cr^{II} and Zr^{IV} . This versatile procedure extends the scope of the $\text{P}^*\text{N}_a^*\text{P}^*$ 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.^{9c}

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