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N-Heterocyclic carbene-phosphino-picolines as precursors of anionic 'pincer' ligands with dearomatised pyridine backbones; transmetallation from potassium to chromium^{†‡}

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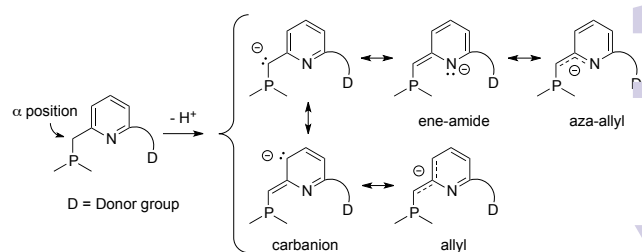
Thomas Simler,^a Andreas A. Danopoulos,^{*a, b} and Pierre Braunstein^{*a}

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Deprotonation of the α -picolinyl-CH₂ in the hybrid ligands R₂P-NC_{NHC} (-N = substituted 2-picoline, R = Cy, *t*-Bu; C_{NHC} = *N*-heterocyclic carbene) (L^R) with KN(SiMe₃)₂ in ether gave [KL_H^{Cy}(ether)]₂ featuring a dearomatised picoline backbone. Assisted by 18-crown-6, K⁺ dissociation afforded the *Z*- and *E*-isomers of [L_H^R]. Transmetallation of L_H^R from KL_H^R led to [CrCl(L_H^{*t*-Bu})].

A landmark in the use of the topical¹ P-N-P 'pincer' ligands in catalysis, P = phosphine donor, -N- = α , α' -disubstituted lutidine donor, was the recognition of the participation of the acidic α -CH₂ lutidine protons of the coordinated ligand in elementary catalytic steps, eventuating remarkable catalytic transformations, in particular with late transition metals.² This form of ligand non-innocence^{1a} leading to metal-ligand cooperativity³ stems from the proton responsiveness⁴ of the pincer ligand. In this context, the crucial role of the central lutidine (-N-) donor was highlighted by its dearomatisation after α -CH₂ deprotonation in the coordinated ligand.⁴⁻⁵ Recently, proton responsiveness of the less common trifunctional pincers, *i.e.* P-N-N' (N' = N(C₂H₅)₂) or P-NN'' (-N = α -substituted 2-picoline, N'' = pyridine) has been reported,⁶ as well as rare studies of 3d metal complexes (Fe, Co, Ni, Cu) with a dearomatised pincer P-N-P.^{6a, 7} In all cases where isolation of complexes with dearomatised ligands has been described, deprotonation took place by the reaction of bases (*e.g.* KN(SiMe₃)₂, KO^{*t*}-Bu, Li-alkyl) on the pre-coordinated ligand.

α -Deprotonation of 2-picoline by organo-lithium and -potassium reagents has been studied in detail to elucidate the carbanionic, enamido, or aza-allylic contribution to the description of the resulting anionic species (Scheme 1).⁸ However, an analogous approach, *i.e.* the α -deprotonation of



Scheme 1 Important resonance contributions to the electronic structure of deprotonated 2-picoline-based pincers.

P-N-P and related ligands by external organometallic bases, to access well defined dearomatised 'pincer' ligand transfer reagents has not been explored. It is plausible that the anionic species formed by the α -deprotonation of a pincer may similarly exhibit carbanionic, eneamido or aza-allylic character (Scheme 1), the respective contributions being modulated by the presence of the vicinal and/or distal donors and the detailed electronic properties of the 'pincer'.

Herein, we describe preliminary results aimed at characterising the primary deprotonation products from the reaction of KN(SiMe₃)₂ with pincer ligand precursors. Based on the 'phosphine mimicry' of NHCs, we envisaged that a hybrid P-NC_{NHC} ligand (L^R, R = Cy, *t*-Bu), formally derived by replacing one PR₂ or NHC in the symmetrical P-N-P or C_{NHC}NC_{NHC} with NHC or PR₂, respectively (Scheme 2), may lend itself to the study of α -deprotonation and present more diverse coordination properties than the parent P-N-P and C_{NHC}NC_{NHC} ligands as well as extend the range and potential of P and NHC pincers. Furthermore, proton-responsiveness is plausible at the CH₂ linker of the substituted picoline.

The synthetic approach to the pro-ligand L^R-2HBr (Scheme 3) is modular, amenable to scaling-up and convenient, since L^R-2HBr is air stable. The crystal structure of L^{Cy}-2HBr is shown in Fig. 1 (details in the ESI). The use of the di-cationic pro-ligands for the direct synthesis of metal complexes is under investigation.⁹

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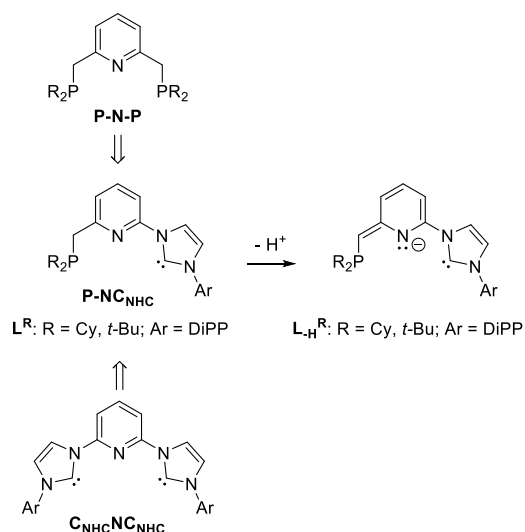
[†] Dedicated to Malcolm Chisholm on the occasion of his 70th birthday, with our most sincere congratulations for his outstanding contributions to chemistry and best wishes.

[‡] Electronic Supplementary Information (ESI) available: Experimental procedures, characterisation data and X-ray crystallographic data. CCDC 1057714-1057716 for L^{Cy}-2HBr, [KL_H^{Cy}-Et₂O]₂ and [CrCl(L_H^{*t*-Bu})]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

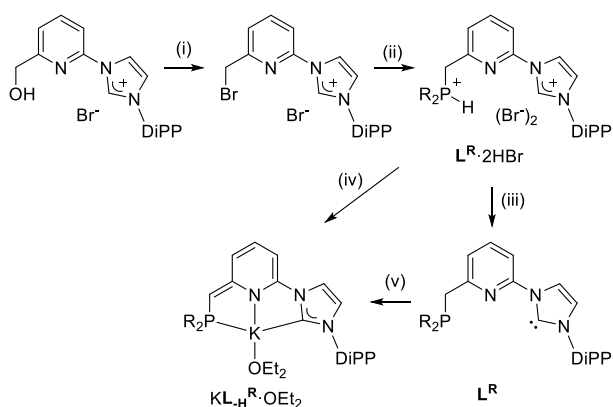
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Deprotonation of $L^R \cdot 2HBr$ with 2 equiv. of $KN(SiMe_3)_2$ in THF afforded the neutral L^R in high yield as colourless solids,



Scheme 2 Hybrid donor ligand L^R , its symmetrical P-N-P and C^NHCNC^NHC analogues and its deprotonated, dearomatised form $L-H^R$. DiPP = 2,6-di-isopropylphenyl.



Scheme 3 Synthesis of the precursors of L^R , and their deprotonation (R = Cy, *t*-Bu).† (i) PBr_3 , CH_2Cl_2 , 0 °C to r.t., 2 h (98%); (ii) HPR_2 (R = Cy, *t*-Bu), MeCN/THF 5:1, r.t., 2 d (79-87%); (iii) 2 equiv. of $KN(SiMe_3)_2$, THF, -78 °C to r.t., 1 h (80-90%); (iv) 3 equiv. of $KN(SiMe_3)_2$, Et_2O , -78 °C to r.t., 1 h (80-90%); (v) 1 equiv. of $KN(SiMe_3)_2$, Et_2O , -78 °C to r.t., 1 h (>90%).

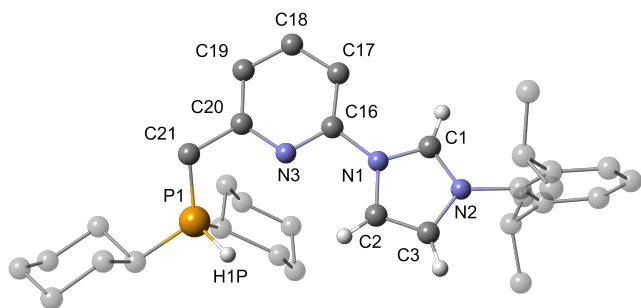


Fig. 1 The structure of the dication in $[L^{Cy} \cdot 2HBr] \cdot CH_2Cl_2$. For clarity, only one disordered cyclohexyl group is displayed. Crystallisation solvent and hydrogen atoms have been omitted except for H1P and the imidazolium protons. Metrical data are given in the ESI.

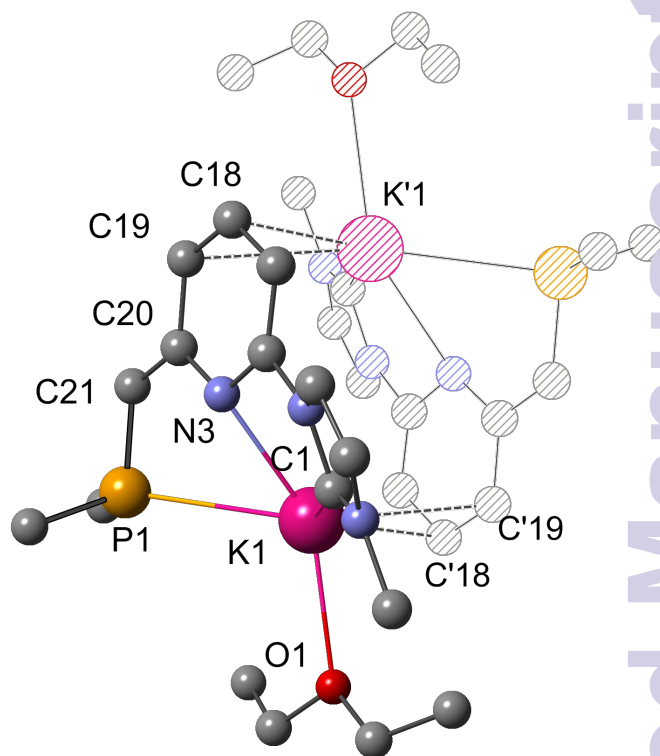
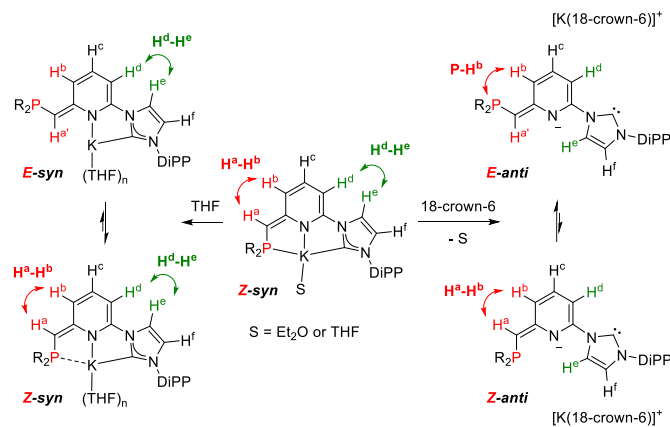


Fig. 2 View of one of the dimers present in the structure of $[KL-H^{Cy} \cdot OEt_2]_2$. For clarity, only one carbon of the DiPP group and one of the disordered cyclohexyl groups are displayed.†

that were crystallised from pentane/ether mixtures.† Spectroscopically, L^R are easily differentiated from the precursors by the absence of the $C_{imidazol-H}$ and the appearance of C_{NHC} in the 1H - and ^{13}C -NMR spectra, respectively. Reaction of $L^R \cdot 2HBr$ with 3 equiv. of $KN(SiMe_3)_2$ in ether afforded the new species $KL-H^R$ by deprotonation at the α - CH_2 of the picoline. Single crystals of the etherate of $KL-H^{Cy}$ were obtained and characterised crystallographically.† The crystal structure comprises two different types of dimers, in which the monomeric $KL-H^{Cy} \cdot OEt_2$ building blocks show very similar metrical data. In the first type (Fig. 2), the dimer formation is through the interaction of K^+ with the π -electrons at the 3- and 4-positions of the six-membered heterocycle; in the second (Fig. S12), the dimer formation is through the interaction of the K^+ with the π -electron density at the α -CH, C_{ipso} and C_3 position; these positions correspond to areas of high electron density, consistent with the canonical resonance forms (Scheme 1).

The striking structural feature of the $KL-H^{Cy} \cdot OEt_2$ unit is the deprotonation of the picoline backbone at the α -carbon to give the anionic $L-H^{Cy}$ bound to K. The 'pincer-like' (*i.e.* kP, kN, kC, \dots) arrangement creates a lacuna that accommodates the potassium cation; one ether molecule is also incorporated into the primary coordination sphere. Remarkably, perusal of the bond distances within the heterocycle clearly reveals alternation, in support of its dearomatisation. Finally, the distance of the *ipso*-C to the α -CH is in the range of double bonds, with *Z*-configuration. The NHC and the dearomatised pyridine planes form an angle of *ca.* 35-36°.

The structure of KL_H^{Cy} in solution was probed by multinuclear 1D- and 2D-NMR spectroscopies. Thus, in C_6D_6 , highly diagnostic spectral features include: (i) in the ^{31}P -NMR spectrum, an upfield shifted signal at δ -15.5 compared to L^{Cy} (δ 3.3); (ii) in the 1H -NMR spectrum, a downfield shifted signal (δ 3.54, $^2J_{PH} = 6.9$ Hz), assignable to the α -CH (*cf.* δ 2.98 for L^{Cy}) and a group of signals at δ 6.73 (p - $C_{pyridine}$ -H), 6.48 and 5.43 (m - $C_{pyridine}$ -H) that support the dearomatisation of the pyridine



Scheme 4 Isomerisation of KL_H^R in solution with or without addition of crown-ether. The 1H - 1H and 1H - ^{31}P correlations established by NOESY/HOESY experiments that were used to determine the solution structures have been highlighted.

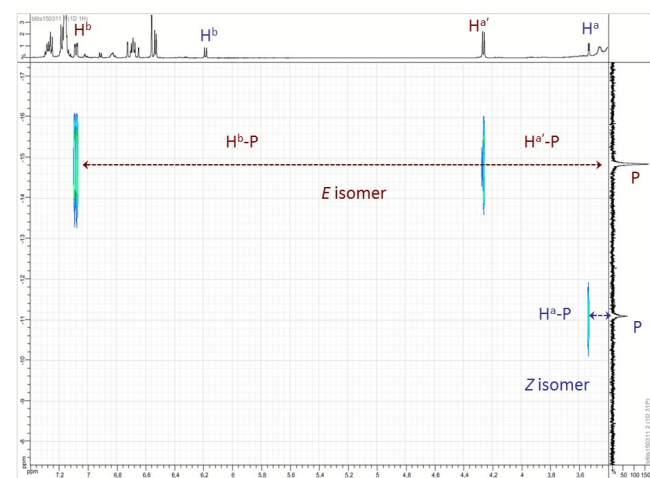


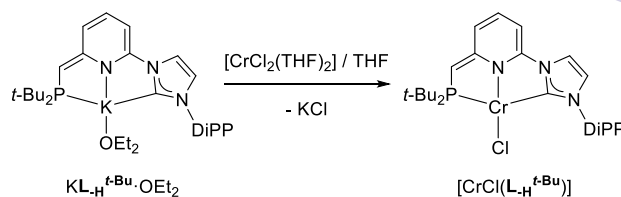
Fig. 3 Representative ^{31}P - 1H HOESY spectrum of KL_H^{Cy} in C_6D_6 in the presence of 18-crown-6. Through-space H^b -P and H^a' -P correlation peaks are present for both isomers but only the H^b -P correlation peak exists for the *E* isomer.

ring. Similar spectroscopic features were observed for the *tert*-butyl derivatives L^{t-Bu} and KL_H^{t-Bu} .

NOESY spectroscopy in C_6D_6 solution provided convincing evidence that the predominant isomer is *Z-syn* (Scheme 4, middle), *i.e.* the configuration at the exocyclic double bond of KL_H^{Cy} is *Z*, (as in the crystal), and the conformation of the NHC ring orients the C_{NHC} towards the lacuna. This was established from the correlations of H^a/H^b and H^d/H^e , respectively.[†] Therefore, it is plausible that the dearomatised ligand adopts a *Z*-enamido, KP,KN,KC_{NHC} 'pincer'-like form under these

conditions. Interestingly, addition of 18-crown-6 (*ca.* 1 equiv.) to the C_6D_6 solution of KL_H^{Cy} resulted in rapid disappearance of the latter and the formation of two new species. Based on comparative analysis of the 1D-NMR and 2D-NMR spectra (NOESY[†] and ^{31}P - 1H HOESY, Fig. 3) of the solution, these are formulated as the *Z*- and *E*-geometrical isomers with respect to the exocyclic C=C double bond (Scheme 4, right). These isomers are in slow exchange, as shown by phase-sensitive NOESY (protons H^a and H^a'). The binding of the potassium cation to the 18-crown-6 and the 'unlocking' of the 'pincer-type' geometry facilitates conversion to a thermodynamic equilibrium mixture of *E*- and *Z*-isomers of the uncoordinated anion (possibly as a constituent of a loose solvent-separated ion-pair¹⁰) and also leads to a re-orientation of the C_{NHC} group (from 1D-NMR and 2D-NMR data), away from the enamido N atom (*E*-/*Z*-anti, Scheme 4, right).

In THF- d_8 , decoordination of the phosphorus donor concomitant *Z* \rightarrow *E* isomerisation also occur but are much slower. However, the nature of the *E*-isomer in this case is different from that in the *E*-/*Z*-anti mixture obtained in the presence of 18-crown-6 (Scheme 4, left); it appears (NOESY) that K^+ maintains coordination to the enamido N and the C_{NHC} donors (KN,KC_{NHC} , *E-syn*). As mentioned above, the well-defined, pre-formed KL_H^R complex may provide new synthetic tools to expand the scope of dearomatised pyridine coordination chemistry across the transition metals by ligand transfer reactions rather than by the more conventional approach of pre-coordinating the ligand followed by deprotonation. In order to probe this potential with a metal relevant to ethylene oligomerisation catalysis, 1 equiv. of KL_H^{t-Bu} was added to a cold solution $[CrCl_2(THF)_2]$ in THF. After work-up, red purple crystals of $[CrCl(L_H^{t-Bu})]$ were obtained which were characterised crystallographically (Scheme 5 and Fig. 4).



Scheme 5 Synthesis of $[CrCl(L_H^{t-Bu})]$ by transmetalation from the dearomatised KL_H^{t-Bu} .

The metal centre in $[CrCl(L_H^{t-Bu})]$ adopts a distorted square planar geometry, where the anionic pincer ligand occupies three coordination sites (KP,KN,KC_{NHC} mode); the plane of the ligand forms an angle of *ca.* 6.5° with the metal coordination plane. The Cr-N bond (2.047(2) Å) falls into the long end of the range for anionic amido ligands.¹¹ To the best of our knowledge $[CrCl(L_H^{t-Bu})]$ constitutes the first Cr complex with a dearomatised pyridine-type pincer. P-N-P¹² and $C_{NHC}NC_{NHC}$ ¹³ complexes of Cr^{II} and Cr^{III} have been described and studied as oligomerisation and polymerisation catalyst. Interestingly, one Cr/Al hetero-bimetallic species supported by the P-N-P has been obtained by the interaction of $[Cr(P-I-P)Cl_3]$ with an Al activator, resulting in α -CH metalation of the

Cr($\kappa P, \kappa N, \kappa P$) moiety by the activator.¹² The full characterisation of the metalated and dearomatised tridentate ligand in $[\text{CrCl}(\text{L}_H^{\text{t-Bu}})]$ suggests that related transformations may occur upon ligand metalation.

In conclusion, we have demonstrated that the novel P-NC_{NHC} ligand **L**^R is easily deprotonated to Z-enamido anionic species, with a dearomatised pyridine backbone. Computational studies of the P-N-N' dearomatisation showed higher stability of the $\alpha\text{-CHPR}_2$ vs. the $\alpha\text{-CHNR}_2$ isomer, presumably due to inductive effects;¹⁴ the rationalisation of the stability of KL_H^{R} may need invoking inductive effects and additional electronic factors. The diverse solution speciation of KL_H^{R} will have implications in its behaviour as transfer reagent and its considerable potential in coordination chemistry.

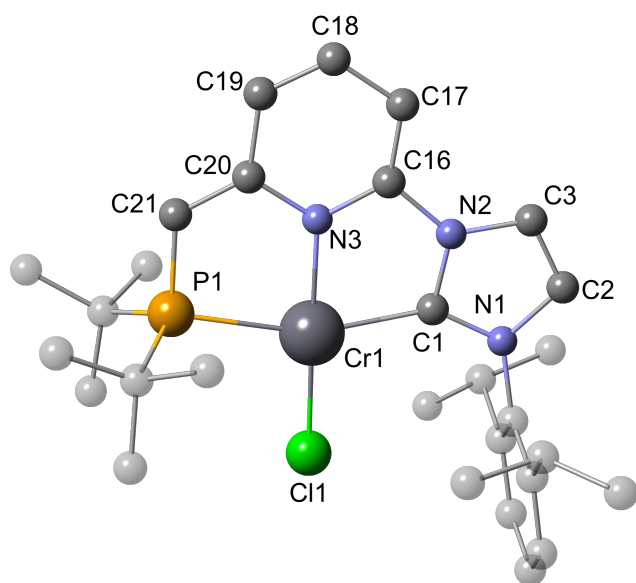


Fig. 4 Structure of $[\text{CrCl}(\text{L}_H^{\text{t-Bu}})]$. Selected bond distances (Å) and angles [°]: C18-C19 1.336(5), C19-C20 1.439(4), C20-C21 1.370(4), C1-Cr1 2.093(3), N3-Cr1 2.047(2), Cr1-Cl1 2.287(1), Cr1-P1 2.462(1); N1-C1-N2 104.2(2), C20-C21-P1 118.8(3), C1-Cr1-Cl1 101.15(9), Cl1-Cr1-P1 101.00(4), C1-Cr1-N3 77.5(1), N3-Cr1-P1 80.60(8).

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