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## A readily accessible PNP pincer ligand with a pyrrole backbone and its $Ni^{I/II}$ chemistry<sup>†</sup>:

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The novel chelating PNP pincer ligand 2,5-bis((diphenylphosphino)methyl)-1*H*-pyrrole (1) was prepared and its nickel coordination chemistry explored. The reaction with Ni(COD)<sub>2</sub> led to a diamagnetic dinuclear nickel(1) complex (4) which was also obtained by the reaction of the square planar Ni<sup>II</sup> complexes [(PNP-Ph<sub>2</sub>)NiX] (X = Cl (2), X = I (3)) with Li(Et<sub>3</sub>BH).

Hybrid ligands containing both soft and hard donors have been extensively studied in recent years and their metal complexes are used in a wide range of stoichiometric and catalytic reactions.<sup>1–7</sup> These include the amidophosphine ligands containing  $SiMe_2CH_2$  backbones studied by Fryzuk and co-workers which have given rise to remarkable patterns of reactivity with metals across the periodic table.<sup>8–11</sup>

The first monoanionic PNP pincer ligand was prepared in the late sixties by Sacconi and co-workers.<sup>12,13</sup> In recent years this ligand and its complexes with late transition metals have received increasing attention.<sup>14–17</sup> A more robust and rigid system was first reported by Liang and co-workers and also studied by Ozerov *et al.*<sup>18–22</sup> Cui, Hou and co-workers have synthesized a monoanionic PNP ligand with a large bite angle based on a carbazole framework.<sup>23</sup>

Here we report the synthesis of a novel monoanionic PNP pincer ligand HPNP-Ph<sub>2</sub> (1) containing a pyrrole backbone and two diphenylphosphinomethyl "arms". The protio-ligand is obtained by the reaction of 2,5-bis[(trimethylammonio)-methyl]-pyrrole diiodide<sup>24,25</sup> with potassium diphenylphosphide which was generated *in situ* and **1** has been characterized by NMR, mass spectrometry and elemental analysis (Scheme 1).

Given the suitability for coordination of this ligand in square planar complexes, we investigated its coordination chemistry with nickel. The square-planar complex [(PNP-Ph<sub>2</sub>)NiCl] (2) was prepared by salt metathesis of [(PNP-Ph<sub>2</sub>)Li] with NiCl<sub>2</sub>DME at -78 °C and subsequent warming to ambient temperature, giving the reaction product in 77% yield (Scheme 2),

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Scheme 1 Ligand synthesis.



Scheme 2 Complex synthesis.

and halide exchange with sodium iodide readily afforded  $[(PNP-Ph_2)NiI]$  (3). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 2 and 3 display one singlet at 30.6 ppm (2) and at 42.5 ppm (3) for the two equivalent P atoms  $[\delta(^{31}P) = -16.5 \text{ ppm for the protioligand}]$ . A single crystal X-ray structure analysis of 3 established the structural details associated with the coordination of the new PNP pincer ligand.§ The structure of 3 is depicted in Fig. 1. Ligand 1 was designed to chelate metals in a tridentate motif with P(1), N and P(2) spanning a common plane with the aromatic backbone, and the structure confirms that the ligand is bound to nickel in a tridentate geometry. The coordination geometry of 3 is approximately square planar. The two Ni–P bond

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<sup>†</sup>Dedicated to Professor Mary McPartlin on the occasion of her 80th birthday.

<sup>‡</sup> Electronic supplementary information (ESI) available: Characterisation data for **1–4** and crystallographic data for **3** and **4**. CCDC 901720 and 901721. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32199h



Fig. 1 Molecular structure of **3** (thermal ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ni–P(1) 2.195(1), Ni–P(2) 2.208(1), Ni–N 1.860(2), Ni–I 2.481(1), P(1)–Ni–P(2) 166.52(3), N–Ni–I 174.75(6).

lengths of 2.1952(1) Å and 2.2084(1) Å and the Ni–N distance of 1.860(2) Å are in the range of literature values.<sup>26</sup> The P(1)–Ni–P(2) angle is 166.52(3)°, the deviation from the ideal value for square planar coordination being due to the steric constraints of the chelating ligand. The N–Ni–I angle is 174.75(6)° and thus close to 180°. The tridentate ligand adopts a slightly twisted conformation which makes the two methylene groups stick slightly out of the coordination plane. The distances between the plane spanned by the four donor atoms and the two methylene carbon atoms are 0.624 Å and 0.388 Å.

Previously, Liang, Ozerov and Kemp have shown with other monoanionic PNP ligands that [(PNP)NiH] complexes can be formed via oxidative addition of the N-H bond to Ni(0).<sup>19,22,27</sup> Remarkably, treatment of ligand 1 with Ni(COD)<sub>2</sub> gave the dinuclear nickel(I) complex 4 instead of the expected nickel(II) hydride complex without adding reducing agents (Scheme 2). Despite the fact that Ni<sup>I</sup> complexes play an important role in several chemically important processes, well defined Ni<sup>I</sup> complexes, generally prepared by reduction with magnesium or  $KC_8$ , are relatively rare due to the reactivity of these mostly radical species.<sup>28–31</sup> The <sup>1</sup>H NMR spectrum of the isolated compound **4** displayed only the signals corresponding to the ligand and no resonance for a hydride. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibited two doublets at 14.4 ppm and 25.2 ppm ( ${}^{2}J(P,P) = 21.9$  Hz). Both NMR spectra are consistent with an overall C2-symmetry of the dinuclear species in solution.

The dinuclear core structure of the molecule and the details of the ligand coordination are confirmed by the single crystal X-ray structure analysis of a toluene solvate (Fig. 2).§ The two d<sup>9</sup> metals are interacting strongly, forming a diamagnetic complex. The Ni–Ni distance of 2.3259(2) Å is in the range of metal– metal bond lengths found in other Ni–Ni complexes.<sup>26</sup> In complex **4** one phosphine of each PNP ligand is coordinated to a nickel atom with Ni–P bond lengths of 2.2333(3) Å and 2.2386(3) Å, respectively. The two other phosphine atoms are located at bridging positions between the two nickel atoms but the distances are asymmetric with two short bonds of 2.1240(3) Å and 2.1337(3) Å to the respective other Ni atom and two weaker interactions of 2.7805(3) Å and 2.6856(3) Å to the Ni atom bearing the ligand.<sup>32</sup> The angle between the two planes



**Fig. 2** Molecular structure of **4** (thermal ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity. Selected distances (Å): Ni(1)–Ni(2) 2.3259(2), Ni(1)–P(2) 2.1240(3), Ni(1)–P(3) 2.7805(3), Ni(1)–P(4) 2.2333(3), Ni(1)–N(3) 1.9194(8), Ni(2)–P(1) 2.2386(3), Ni(2)–P(2) 2.6856(3), Ni(2)–P(3) 2.1337(3), Ni(2)–N(2) 1.9273(8).

Ni(1)–P(2)–Ni(2) and Ni(1)–P(3)–Ni(2) is 117.05(1)°. There is precedent for a dinuclear Ni<sup>I</sup> complex with a monoanionic PNP pincer ligand synthesized by Mindiola.<sup>33,34</sup> However, that species contained the central amido nitrogen of the pincer ligand in the bridging position and the two phosphine donors coordinating to the two metal centres. The interatomic distance between the two nickel atoms in the dinuclear Ni<sup>I</sup> complex synthesized by Mindiola and co-workers is in the same range (2.3288(7) Å) as in **4**. However, the former shows paramagnetic behaviour and thus diradical character.

A structurally related complex with a cyclobutane-like Ni<sub>2</sub>N<sub>2</sub> core was described by Zargarian and co-workers.<sup>35,36</sup> They coordinated a POCN pincer type ligand in a dinuclear nickel(II) complex characterized by a Ni<sup>II</sup>–Ni<sup>II</sup> distance of about 2.51 Å which is larger than the Ni<sup>I</sup>–Ni<sup>I</sup> distance in complex **4**.

The formation of the Ni<sup>I</sup> complex 4 from the reaction of the protio-ligand 1 with Ni(COD)<sub>2</sub> raised the question of the reaction pathway involved. Liang et al. reported one case in which the targeted nickel hydride complex was not isolated but the product of COD insertion into a Ni-H bond instead.<sup>19</sup> A similar reaction could be involved in this case, and further studies to back up this hypothesis were carried out. Upon treating 1 with Ni(COD)<sub>2</sub> in an NMR tube no gas formation was observed and no signal attributable to molecular hydrogen was detected. However, the partially hydrogenated diolefin cyclooctene (COE) could be identified by NMR and GC-MS. Additionally, different COD isomers were identified by GC-MS. This indicates the possible formation of a nickel hydride complex followed by an insertion of COD into the Ni-H bond. The resulting complex may then react with a second nickel hydride complex leading to COE and complex 4. Alternatively β-hydrogen elimination would generate the different COD isomers observed. The detection of 1.3-cyclooctadiene is consistent with the reversibility of the insertion into the Ni-H bond. Addition of iodine to complex 4 led to [(PNP-Ph<sub>2</sub>)NiI] (3) by oxidative addition across the two metal sites.



Scheme 3 Following an alternative route starting from a nickel(II) complex gave complex 4 with 5 as an intermediate.

In an alternative approach for the synthesis of complex **4** (Scheme 3) Li(Et<sub>3</sub>BH) was added to a solution of complexes **2** or **3** in benzene-d<sub>6</sub>. In these cases evolution of a gas could be observed and the <sup>1</sup>H NMR spectrum showed a singlet at 4.47 ppm corresponding to the hydrogen molecule. Carrying out this reaction at low temperature ( $-40 \, ^{\circ}C$ ) a hydrido species [(PNP-Ph<sub>2</sub>)NiH] (**5**) was detected by NMR spectroscopy (Scheme 3). The <sup>1</sup>H NMR spectrum revealed a triplet at  $-16.72 \, \text{ppm}, \, ^{2}J(\text{P},\text{H}) = 56 \, \text{Hz}$ , the <sup>31</sup>P NMR spectrum a singlet at 52.0 ppm. Under these reaction conditions, a hydrido species is an intermediate in the formation of the dinuclear Ni<sup>1</sup> complex **4**.

In conclusion, a novel monoanionic PNP pincer type ligand based on a pyrrole backbone was synthesized and its nickel(1) and nickel(11) coordination chemistry was investigated. Interestingly, a diamagnetic dinuclear nickel(1) complex was directly formed without addition of reducing agents. Further studies into the coordination chemistry of this ligand are ongoing in our laboratory.

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## Notes and references

§ *Crystal data*: complex **3**: C<sub>30</sub>H<sub>26</sub>INNiP<sub>2</sub>, monoclinic, space group *P*<sub>21</sub>/ *c*, *a* = 14.291(9), *b* = 16.499(11), *c* = 11.466(6) Å, *β* = 107.243(9)°, *V* = 2582(3) Å<sup>3</sup>, *Z* = 4,  $\mu$  = 2.092 mm<sup>-1</sup>, *F*<sub>000</sub> = 1296, *T* = 100(2) K, *θ* range 1.5 to 32.2°. Index ranges *h*, *k*, *l* (indep. set): -21...20, 0...24, 0...17. Reflections measd: 53 737, indep.: 8602 [*R*<sub>int</sub> = 0.0493], obsvd [*I* > 2*σ*(*I*)]: 6783. Final *R* indices [*F*<sub>o</sub> > 4*σ*(*F*<sub>o</sub>)]: *R*(*F*) = 0.0329, w*R*(*F*<sup>2</sup>) = 0.0691, GooF = 1.059.

Complex 4·1.5 toluene:  $C_{70.5}H_{63.5}N_2Ni_2P_4$ , triclinic, space group  $P\overline{I}$ , a = 13.4842(2), b = 14.8729(2), c = 16.2602(3) Å,  $\alpha = 65.464(2), \beta =$   $81.949(1), \gamma = 72.130(1)^{\circ}, V = 2823.09(7)$  Å<sup>3</sup>,  $Z = 2, \mu = 0.827$  mm<sup>-1</sup>,  $F_{000} = 1233, T = 115(1)$  K,  $\theta$  range 3.2 to 32.4°. Index ranges h, k, l: -20...20, -22...22, -24...24. Reflections measd: 133 676, indep.: 19 493 [ $R_{int} = 0.0310$ ], obsvd [ $I > 2\sigma(I)$ ]: 17 569. Final R indices [ $F_0 > 4\sigma(F_0)$ ]:  $R(F) = 0.0260, wR(F^2) = 0.0652$ , GooF = 1.032.

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