## Dalton Transactions

## COMMUNICATION



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Published on 14 April 2014. Downloaded by Florida State University on 21/10/2014 22:20:24.

**Cite this:** *Dalton Trans.*, 2014, **43**, 8595 Received 3rd March 2014,

www.rsc.org/dalton

Accepted 11th April 2014

DOI: 10.1039/c4dt00639a

A new PC(sp<sup>3</sup>)P ligand and its coordination chemistry with low-valent iron, cobalt and nickel complexes<sup>†</sup>

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A new PC(sp<sup>3</sup>)P ligand *N,N'*-bis(diphenylphosphino)dipyrromethane [PCH<sub>2</sub>P] (1) was prepared and its iron, cobalt and nickel chemistry was explored. Two pincer-type complexes [PCHP]Fe(H)-(PMe<sub>3</sub>)<sub>2</sub> (2) and [PCHP]Co(PMe<sub>3</sub>)<sub>2</sub> (4) were synthesized in the reaction of 1 with Fe(PMe<sub>3</sub>)<sub>4</sub> and Co(Me)(PMe<sub>3</sub>)<sub>4</sub>. 1 reacted with Co-(PMe<sub>3</sub>)<sub>4</sub> and Ni(PMe<sub>3</sub>)<sub>4</sub> to afford Co(0) and Ni(0) complexes [PCH<sub>2</sub>P]Co(PMe<sub>3</sub>)<sub>2</sub> (3) and [PCH<sub>2</sub>P]Ni(PMe<sub>3</sub>)<sub>2</sub> (5). The structures of complexes 2–5 were determined by X-ray diffraction.

The "pincer era" began from the initial investigations of PCP ligands by Shaw<sup>1</sup> in the late 1970s. However, exploration of the PC(sp<sup>3</sup>)P ligands has been overshadowed for quite a long time by their aromatic counterparts.<sup>2</sup> This imbalance originated from not only the greater synthetic convenience for access to diverse ligands, but also the greater thermal and conformational stability of PC(sp<sup>2</sup>)P ligands compared to PC(sp<sup>3</sup>)P ligands.<sup>3</sup> Nevertheless, more recent work<sup>4</sup> has clearly demonstrated that the sp<sup>3</sup>-hybridized carbon coordinated to the metal centre highly influences the reactivity of the pincer complex and many interesting transformations have been spotted.<sup>5</sup> This makes the PC(sp<sup>3</sup>)P pincer system more and more attractive for further developments.

So far, the known PC(sp<sup>3</sup>)P ligands are relatively limited,<sup>5</sup> and research in this field has mainly been focused on platinum group metals<sup>6–10</sup> and nickel<sup>11</sup> chemistry. Due to our longstanding efforts in the chemistry of iron, cobalt and nickel,<sup>12</sup> we have set out to study the activation of the C(sp<sup>3</sup>)–H bond in pincer ligands by these metals. Several PC(sp<sup>3</sup>)P pincer complexes of iron and cobalt were reported in our previous work,<sup>12a</sup> but the examples of this type are still very limited. Among all the known PC(sp<sup>3</sup>)P ligands, a particular one based



on a dipyrromethane (DPM) scaffold pioneered by Ozerov and coworkers<sup>6b</sup> has caught attention for two reasons (Fig. 1). First, its construction is very straightforward, by taking advantage of the facile N–P bond formation. More importantly, the pyrrole ring as a rigid linker makes the communication between the metal centre and the  $C(sp^3)$ –H bond more efficient, which increases the chance for cyclometalation.<sup>6b,8b</sup> However, since the initial studies no further exploration has been made on this type of PC(sp<sup>3</sup>)P ligand because  $C(sp^3)$ –H cleavage is a challenge. Herein, we report a new DPM-based PC(sp<sup>3</sup>)P ligand and its first pincer complexes with iron and cobalt. We also describe the formation of its cobalt(0) and nickel(0) complexes where it was utilized as a bidentate ligand.

The new ligand *N*,*N'*-bis(diphenylphosphino)dipyrromethane [PCH<sub>2</sub>P] (**1**) was prepared according to a slightly modified procedure<sup>6b</sup> developed by Ozerov for the original ligand P<sub>2</sub>CH<sub>2</sub> (Scheme 1). Reaction of 2 equiv. of Ph<sub>2</sub>PCl with deprotonated dipyrromethane in THF afforded compound **1** which was isolated as a colourless viscous oil in 62% yield by column chromatography on silica gel under N<sub>2</sub>. **1** was characterized by <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR in solution. It displayed one



Scheme 1 Synthesis of the ligand [PCH<sub>2</sub>P].

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<sup>†</sup>Electronic supplementary information (ESI) available: Experimental details and characterization of all compounds; crystal structure data for **2**, **3**, **4** and **5**. CCDC 986904–986907. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00639a



Scheme 2 Preparation of complexes 2-5.

singlet resonance at  $\delta$  35.1 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The protons of the CH<sub>2</sub> linkage resonate at  $\delta$  4.81 ppm as a singlet in the <sup>1</sup>H NMR spectrum, and the carbon of the CH<sub>2</sub> linkage resonates at  $\delta$  25.4 ppm as a triplet with *J*<sub>CP</sub> = 18 Hz in the <sup>13</sup>C NMR spectrum.

We investigated its coordination chemistry with iron, cobalt and nickel (Scheme 2). When **1** was treated with 1 equiv. of Fe(PMe<sub>3</sub>)<sub>4</sub> in THF, the solution turned dark brown after 24 h. Complex [PCHP]Fe(H)(PMe<sub>3</sub>)<sub>2</sub> (2) was isolated as golden yellow needles from diethyl ether. A typical  $\nu$ (Fe–H) stretching band was found at 1922 cm<sup>-1</sup> in the IR spectrum. The characteristic hydride signal of **2** in the <sup>1</sup>H NMR spectrum (Fig. 2) as a tdd peak was found at –13.36 ppm with  $J_{PH}$  coupling constants of 71.1, 32.7 and 20.7 Hz. A single crystal X-ray structure analysis of **2** established the structural details associated with the coordination of the new PC(sp<sup>3</sup>)P ligand. In the molecular structure of **2** (Fig. 3), iron is centred in a distorted octahedral geometry. The axial angle P1–Fe1–P2 is 148.40(6)°, greatly deviating from 180°. [C29Fe1P3P4H1] are in the equatorial plane. The Fe1–C29 distance (2.166(5) Å) is within the range of



-13.00 -13.05 -13.10 -13.15 -13.20 -13.25 -13.30 -13.35 -13.40 -13.45 -13.50 -13.55 -13.60 -13.65 -13.70

Fig. 2 Hydride resonance of complex 2.



**Fig. 3** Molecular structure of complex **2**. The thermal ellipsoids are displayed at the 50% probability level, and hydrogen atoms except for Fe-H are omitted for clarity. Selected bond lengths (Å) and angles [°]: Fe1-H1 1.64(6), Fe1-C29 2.166(5), Fe1-P1 2.156(2), Fe1-P2 2.164(2), Fe1-P3 2.240(2), Fe1-P4 2.264(2); C29-Fe1-H1 92(2), C29-Fe1-P3 175.7(2), C29-Fe1-P4 91.3(2), P3-Fe1-H1 84(2), P1-Fe1-P2 148.40(6), P1-Fe1-P3 95.10(6), P1-Fe1-P4 105.65(6), P2-Fe1-P4 102.51(6), P3-Fe1-P4 92.89(6).

Fe–C(sp<sup>3</sup>) bonds.<sup>13</sup> Both Fe–P4 distance (2.264(2) Å) and Fe–P3 distance (2.240(2) Å) are longer than Fe1–P1 distance (2.156(2) Å) and Fe1–P2 distance (2.164(2) Å), presumably due to the strong *trans*-influence of the hydrido H and C(sp<sup>3</sup>) atoms being greater than that of the phosphorus atoms.

The reaction of **1** with Co(PMe<sub>3</sub>)<sub>4</sub> was different (Scheme 2). After stirring for 24 h in THF at 25 °C, complex [PCH<sub>2</sub>P]Co-(PMe<sub>3</sub>)<sub>2</sub> (3) was isolated as dark red blocks in the yield of 69%. Complex 3 is a paramagnetic species, and showed no  $\nu$ (Co–H) stretching bands in the IR spectrum, indicating that the cleavage of the C(sp<sup>3</sup>)–H had not happened. The structure of complex 3 was determined by X-ray diffraction analysis (Fig. 4).



Fig. 4 Molecular structure of complex 3. The thermal ellipsoids are displayed at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1–P1 2.208(1), Co1–P2 2.235(1), Co1–P3 2.136(1), Co1–P4 2.141(1); P1–Co1–P2 104.87(5), P1–Co1–P3 112.58(5), P1–Co1–P4 105.82(5), P2–Co1–P3 110.35(5), P2–Co1–P4 115.35(5), P3–Co1–P4 107.88(4).

The cobalt(0) centre is coordinated to two phosphorus atoms of the [PCH<sub>2</sub>P] ligand and two PMe<sub>3</sub> molecules. The environment of the cobalt centre is close to an idealized tetrahedral geometry. The Co1–C35 distance (*ca.* 3.34 Å) is much longer than those of the known Co–C(sp<sup>3</sup>) bonds (2.03–2.15 Å).<sup>14</sup> This suggests that no bond interaction exists between these two atoms, thus **1** [PCH<sub>2</sub>P] only served as a neutral bidentate ligand in this case.

A pincer complex of cobalt bearing this ligand was obtained in the following reaction (Scheme 2). Treatment of 1 with an equimolar amount of Co(Me)(PMe<sub>3</sub>)<sub>4</sub> in diethyl ether at 25 °C furnished complex  $[PCHP]Co(PMe_3)_2$  (4) in a yield of 84% as a red powder which can be crystallized in diethyl ether at 0 °C. The existence of the Co-CH moiety in 4 was evidenced by a doublet at  $\delta$  3.88 ppm in the <sup>1</sup>H NMR spectrum. A pair of doublets at  $\delta$  0.76 and 1.06 ppm in the <sup>1</sup>H NMR spectrum indicated that the PMe<sub>3</sub> ligands are not chemically identical. X-ray crystallography confirmed a slightly distorted trigonal bipyramidal structure of complex 4 (Fig. 5). C35 and P2 are transoriented in the axial positions and the C35-Co1-P2 angle is 176.65(7)°. Two five-membered metallacycles with remarkable ring bending (sum of the internal bond angles is 530.4° and 531.9° respectively) are formed through coordination of the two phosphine arms and the metalated  $C(sp^3)$  atom. The Co1– C35 distance of 2.140(3) Å is within the range of  $Co-C(sp^3)$ bonds (2.03-2.15 Å).<sup>14</sup>

The reaction of **1** with Ni(PMe<sub>3</sub>)<sub>4</sub> or Ni(Me)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> afforded the same product  $[PCH_2P]Ni(PMe_3)_2$  (5) (Scheme 2). Complex 5 was isolated as orange crystals in high yield in both reactions. The molecular configuration is depicted in Fig. 6. The nickel atom is situated in a distorted tetrahedral coordination sphere. The P1-Ni1-P2 (106.83(4)°), P1-Ni1-P3 (107.35(4)°), P1-Ni1-P4 (111.99(4)°), P2-Ni1-P3 (114.80(4)°), P2-Ni1-P4 (109.68(4)°) and P3-Ni1-P4 (111.99(4)°) angles are all close to 109.5°. The four Ni-P bond lengths of 2.1989(12) Å,





Fig. 6 Molecular structure of complex 5. The thermal ellipsoids are displayed at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Ni1–P1 2.199(1), Ni1–P2 2.217(1), Ni1–P3 2.149(1), Ni1–P4 2.141(1); P1–Ni1–P2 106.83(4), P1–Ni1–P3 107.35(4), P1–Ni1–P4 111.99(4), P2–Ni1–P3 114.80(4), P2–Ni1–P4 109.68(4), P3–Ni1–P4 111.99(4).

		1 - 2 mol% <b>2</b>	
PhCHO +	(EtO) <sub>3</sub> SiH	$\longrightarrow$	PhCH <sub>2</sub> OSi(OEt) <sub>3</sub>
	1.2 equiv.	THF, toluene or MeCN,	
		25 - 80 <sup>0</sup> C	

Scheme 3 Attempts on the hydrosilylation of benzaldehyde catalyzed by 2.

2.2167(11) Å, 2.1490(11) Å, and 2.1408(12) Å are comparable with literature values.<sup>12c</sup> Complex 5 can be viewed as a nickel version of Complex 2. It is noticeable that only a  $Fe(PMe_3)_4$  formed PC(sp<sup>3</sup>)P pincer-type complex with ligand 1 in these three zero valent species ( $Fe(PMe_3)_4$ ,  $Co(PMe_3)_4$ , and  $Ni(PMe_3)_4$ ).

Iron hydride complexes have been playing important roles in many catalytic systems.<sup>15</sup> Recently, several groups, including ours, have been interested in developing iron-catalysed hydrosilylation of aldehydes and ketones.<sup>12*c*,16</sup> Therefore, we also examined if complex 2 would catalyse similar reactions. Unfortunately, this proved to be unsuccessful although many attempts had been made (Scheme 3).

In conclusion, a new  $PC(sp^3)P$  pincer ligand based on a dipyrromethane backbone was synthesized and its coordination chemistry with iron, cobalt and nickel was investigated. The activation of the  $C(sp^3)$ -H bond is strongly metal-dependent. Further studies into the coordination chemistry of this ligand and the properties of its resulting complexes are ongoing in our laboratory.

We gratefully acknowledge the financial support by NSF China no. 21072113 and 21372143 and Shandong Province Natural Science Foundation ZR2010BZ002.

Fig. 5 Molecular structure of complex 4. The thermal ellipsoids are displayed at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1–C35 2.140(3), Co1–P1 2.2053(9), Co1–P2 2.2119(9), Co1–P3 2.1452(9), Co1–P4 2.1529(8); C35–Co1–P2 176.65(7), P1–Co1–P3 121.59(3), P1–Co1–P4 116.93(3), P3–Co1–P4 117.14(3), C34–C35–C36 109.1(2).

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