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A new PC(sp³)P ligand and its pincer complexes of Fe and Co are reported.
A new PC(sp³)P ligand and its coordination chemistry with low-valent iron, cobalt and nickel complexes†

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A new PC(sp³)P ligand \(N,N'-\text{bis(diphenylphosphino)dipyrromethane} \) \([\text{PCH}_2\text{P}] \) (1) was prepared and its iron, cobalt and nickel chemistry explored. Two pincer-type complexes \([\text{PCHP}]\text{Fe(H)(PMe}_3\text{)}_2 \) (2) and \([\text{PCHP}]\text{Co(PMe}_3\text{)}_2 \) (4) were synthesized in the reaction of 1 with \text{Fe(PMe}_3\text{)}_4 and \text{Co(Me)(PMe}_3\text{)}_4. 1 reacted with \text{Co(PMe}_3\text{)}_4 and \text{Ni(PMe}_3\text{)}_4 to afford \text{Co(0)} and \text{Ni(0)} complexes \([\text{PCH}_2\text{P}]\text{Co(PMe}_3\text{)}_2 \) (3) and \([\text{PCH}_2\text{P}]\text{Ni(PMe}_3\text{)}_2 \) (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\(^1\) in the late 1970s. However, exploration of the PC(sp³)P ligands has been overshadowed for quite a long time by their aromatic counterparts.\(^2\) 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(sp³)P ligands compared to PC(sp²)P ligands.\(^3\) Nevertheless, more recent work\(^4\) has clearly demonstrated that the sp²-hybridized carbon coordinated to the metal centre highly influences the reactivity of the pincer complex and many interesting transformations have been spotted.\(^5\) This makes the PC(sp³)P pincer system more and more attractive for further developments.

So far, the known PC(sp³)P ligands are relatively limited,\(^5\) and research in this field has mainly been focused on platinum group metals\(^6-10\) and nickel\(^11\) chemistry. Due to our long-standing efforts in the chemistry of iron, cobalt and nickel,\(^12\) we have set out to study the activation of C(sp³)-H bond in pincer ligands by these metals. Several PC(sp³)P pincer complexes of iron and cobalt were reported in our previous work,\(^12a\) but the examples of this type are still very limited. Among all the known PC(sp³)P ligands, a particular one based on a dipyrromethane (DPM) scaffold pioneered by Ozerov and coworkers\(^6\) has caught out interest for two reasons (Fig. 1).

First, its construction is very straightforward, by taking advantage of the facile N-P bond formation. More important, the pyrrole ring as a rigid linker makes the communication between the metal centre and the C(sp³)-H bond more efficient, which increases the chance for cyclometalation.\(^6b,8b\) However, since the initial studies no further exploration has been made to this type of PC(sp³)P ligand because C(sp³)-H cleavage is a challenge. Herein, we report a new DPM-based PC(sp³)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 \(N,N'-\text{bis(diphenylphosphino)dipyrromethane} \) \([\text{PCH}_2\text{P}] \) (1) was prepared according to a slightly modified procedure\(^6\) developed by Ozerov for the original ligand \(\text{P}_2\text{CH}_2\) (Scheme 1). Reaction of 2 equiv of \(\text{PH}_2\text{Cl} \) 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\(_2\). 1 was characterized by \(^1\)H, \(^31\)P, and \(^13\)C NMR in solution. It displayed one singlet
resonance at δ 35.1 ppm in the $^{31}$P{^1}H NMR spectrum. The protons of the CH$_2$ linkage resonate at δ 4.81 ppm as a singlet in the $^1$H NMR spectrum, and the carbon of the CH$_2$ linkage resonates at δ 25.4 ppm as a triplet with $J_{CP} = 18$ Hz in the $^{13}$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$_3$)$_4$ in THF, the solution turned dark brown after 24 h. Complex [PCHP]Fe(H)(PMe$_3$)$_2$ (2) was isolated as golden yellow needles from diethyl ether. A typical $\nu$(Fe-H) stretching band was found at 1922 cm$^{-1}$ in the IR spectrum. The characteristic hydride signal of 2 in the $^1$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$^3$)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 Fe-C(sp$^3$) bonds. 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 (2.164(2) Å), presumably due to the strong trans-influence of the hydrido H and C(sp$^3$) atom being greater than that of the phosphorus atoms.

The reaction of 1 with Co(PMe$_3$)$_4$ was different (Scheme 2). After stirring for 24 h in THF at 25 °C, complex [PCH$_2$P]Co(PMe$_3$)$_2$ (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 band in the IR spectrum, indicating the cleavage of the C(sp$^3$)-H had not happened. The structure of complex 3 was determined by X-ray diffraction analysis (Fig. 4). The cobalt(0) centre is coordinated to two phosphorus atoms of the [PCH$_2$P] ligand and two PMe$_3$ molecules. The environment about the cobalt centre is close to
bonds (2.03-2.15 Å).

between these two atoms, thus the bipyramidal structure of complex

the range of Co-C(sp³) bonds (2.03-2.15 Å).\textsuperscript{14}

The reaction of 1 with Ni(PMe₃)₄ or Ni(Me)(PMe₃)₃ afforded the same product [PCH₃]Ni(PMe₃)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 2.1898(12) Å, 2.2167(11) Å, 2.1490(11) Å, and 2.1408(12) Å are comparable with literature values.\textsuperscript{15} Complex 5 can be viewed as a nickel version of Complex 2. It is noticeable that only Fe(PMe₃)₃ formed PC(sp³)P pincer-type complex with ligand 1 in these three zero valent species (Fe(PMe₃)₃, Co(PMe₃)₃, Ni(PMe₃)₃).

Iron hydride complexes have been playing important roles in many catalytic systems.\textsuperscript{15} Recently, several groups, including ours, have been interested in developing iron-catalysed hydrosilylation of aldehydes and ketones.\textsuperscript{12c,16} 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).

\[
\text{PhCHO} + \text{(EO)₃SiH} \rightarrow \text{PhCH₂OSi(OEt)}₂
\]

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

In conclusion, a new PC(sp³)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(sp³)-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.s 21072113 and 21372143 and Shandong Province Natural Science Foundation ZR2010BZ002.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterization of all compounds; crystal structure data for 2, 3, 4 and 5. CCDC 986904-986907. See DOI:

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