

Site-selective coordination behaviour of the Py_2P^- -anion: the N–C–P-allylic system as σ - and π -donor in $[(\text{PMDETA})\text{Cs}\{(\mu\text{-PPy})\text{Py}\}]_2$ and as a μ_2 - σ -phosphorus-donor in $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{(\mu\text{-P})\text{Py}_2\}][\text{BMe}_4]^\ddagger$

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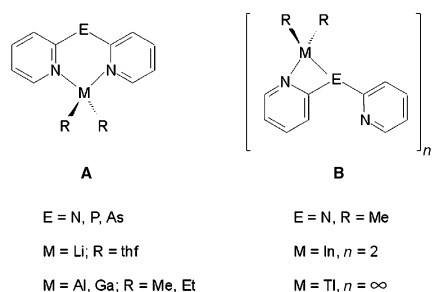
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The coordination flexibility of the ambidentate Py_2P^- -anion (Py = 2-pyridyl) spans the wide range from σ -all-nitrogen chelation to hard organometallic moieties, σ -phosphorus μ_2 -bridging in dinuclear iron complexes to π -N,C,P heteroallylic coordination to the soft caesium.

Primary and secondary alkali metal phosphides MPR_2 and MPHR are key transfer reagents in organophosphorus synthesis and in the introduction of phosphide ligands to catalytically active transition metal fragments.¹ The structural topology of these species has been reviewed recently² and is mainly determined by the donor base, *e.g.* in the $[(\text{donor})\text{LiPPH}_2]$ complexes,³ by the radius and polarisability of the alkali metal⁴ and the size of the substituents.⁵ In general, bulky groups (*e.g.* 2,4,6-(F_3C) $_3\text{C}_6\text{H}_2$ ^{5a} or terphenyl^{5b-d}) and heavier alkali metals prompt M–aryl π interactions in addition to M–P σ bonds.^{2b} Rather than varying the bulk of the aryl substituent we incorporate donor centres in group 14 and 15 element bonded rings such as di(2-pyridyl)-amides, -phosphides and -arsenides Py_2E^- (Py = 2-pyridyl, E = N, P, As) to modulate the coordination behaviour.⁶ In the Py_2P^- anion both ring nitrogen atoms chelate the metal to leave the phosphorus divalent.⁷ The alkali metal coordination in the substituent periphery opens up the door to unique reactivity in these complexes, *e.g.* the reduction of the iminophosphorane $\text{Py}_3\text{P}=\text{NSiMe}_3$ to chiral phosphane amines $\text{RPyPN}(\text{H})\text{SiMe}_3$ *via* lithium organics involving the cleavage of two P–C Py bonds in a single step.⁸ The adaptability of these pyridyl substituted ligands is exemplified by the flexible coordination behaviour towards various metal centres. Thus, the pyridyl nitrogen atoms may be involved in coordination exclusively (Scheme 1, **A**)^{6,7} or in conjunction with the bridging heteroatom (Scheme 1, **B**).⁹

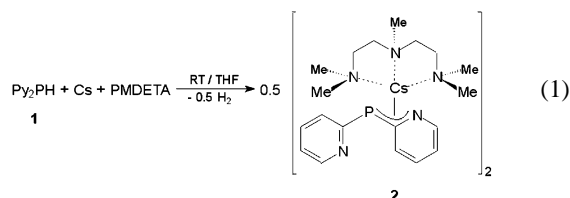
Although it is anticipated that in species **A**, the central atom E can further function either as a 2e or 4e donor to form heterometallic derivatives, recent theoretical calculations, supported by experiments, have shown that while in the amides (E



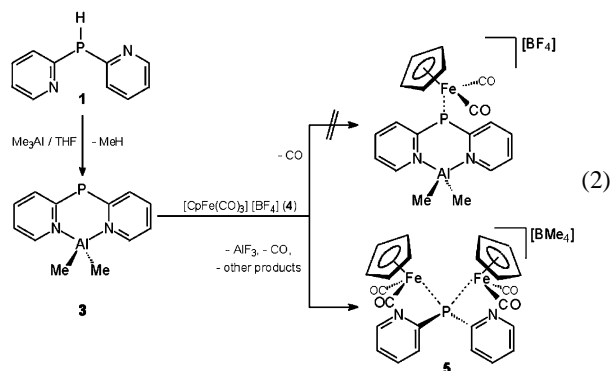
Scheme 1

[†] Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday.

= N) the amido nitrogen does function as a typical Lewis base,⁹ the situation in the corresponding phosphides (E = P) is different.¹⁰ In the latter, nearly all the charge density couples into the pyridyl rings, leaving the central phosphorus atom only attractive for soft metals in the form of a π -acid type of coordinating centre. In order to test the coordination abilities further, we reacted the pyridyl phosphides with two contrasting type of metals *viz.*, Cs(I) and Fe(II). Towards the soft caesium metal in the complex $[(\text{PMDETA})\text{Cs}\{(\mu\text{-PPy})\text{Py}\}]_2$ **2** [PMDETA = $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$] an unprecedented coordination behaviour of the di(2-pyridyl)phosphide ligand is observed. In this complex the ligand is involved *simultaneously* in a σ (through P and N) as well as a π (through the P–C–N segment) interaction with the caesium ions. This hetero aza allylic coordination represents an entirely new facet of coordination capability of the pyridyl phosphide ligands. In the iron complex $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{(\mu\text{-P})\text{Py}_2\}][\text{BMe}_4]$ **5** the phosphorus atom of the ligand bridges two Fe(II) centres without any further Fe–N contacts. The reaction of di(2-pyridyl)phosphane, Py_2PH ⁷ **1** with caesium metal in the presence of PMDETA afforded the dimeric complex **2** [eqn. (1)].[‡] In an attempt to prepare



heterobimetallic compounds we have reacted the aluminium derivative $[\text{Me}_2\text{Al}(\text{Py}_2\text{P})]$ **3**⁷ with $[\text{CpFe}(\text{CO})_3][\text{BF}_4]$ **4**¹¹ where in general a carbonyl group can easily be replaced by a phosphane.¹² We aimed to utilise the vacant phosphorus site for coordination with Fe(II) while retaining the Al–N bonds. However, the Al–N bonds in the complex are cleaved presumably by the formation of the thermodynamically favourable AlF_3 accompanied by the alkylation of the tetrafluoroborate anion. This leads to the formation of $[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\{(\mu\text{-P})\text{Py}_2\}][\text{BMe}_4]$ **5** [eqn. (2)].[‡]



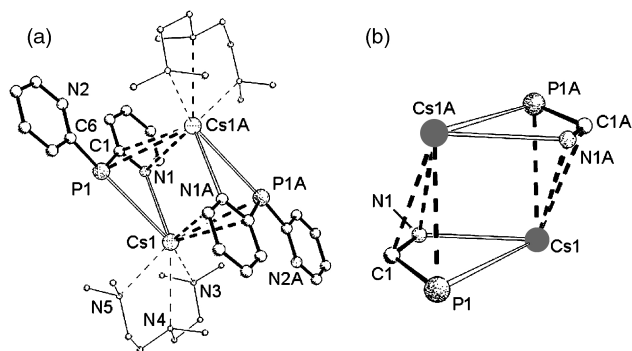


Fig. 1 Solid-state structure of **2**. Selected bond distances (pm) and angles ($^{\circ}$): P1–C1 179.4(4), P1–C6 179.8(4), P1–Cs1 365.2(2), P1–Cs1A 369.3(2), N1–Cs1 321.2(4), N1–Cs1A 337.3(4), C1–Cs1A 334.6(4); C1–P1–C6 108.67(18), P1–C1–N1 111.3(3), P1–C6–N2 126.2(3).

Both [(PMDETA)Cs $\{\mu$ -PPy)Py] $\}_2$ **2** and [{Cp(CO) $_2$ -Fe] $_2$ { μ -P)Py $_2$ }] [BMe $_4$] **5**, were structurally investigated, allowing the ambidentate coordination flexibility of the Py $_2$ P $^-$ anion toward soft metals to be probed. The dimeric structure of **2** comprises of two distinct modes of bonding of the Py $_2$ P $^-$ ligand [Fig. 1(a)].

The atoms P1 and N1 are involved in a σ -type of interaction with Cs1. At the same time the hetero aza allylic P1–C1–N1 moiety is η^3 -coordinated through a π -type of interaction with the second caesium ion Cs1A of the dimeric complex [Fig. 1(b)]. One pyridyl nitrogen on each of the Py $_2$ P $^-$ ligands remains non-coordinated. The P–C bond lengths in the anion are not affected by the metal coordination and are identical within esds [179.4(4), π -coordinated and 179.8(4) pm, non-coordinated] and as long as in other metal di(2-pyridyl)phosphides.⁷ Even the P–Cs distances are only marginally different [365.2(2), σ -coordinated and 369.3(2) pm, π -coordinated] and are similar to other caesium phosphides.⁵ It is only in the N–Cs distances where the different bonding mode is mirrored in different lengths [321.2(4), σ -coordinated and 337.3(4) pm, π -coordinated]. The different coordination of the ring nitrogen atoms gives rise to two different signals in the 15 N MAS NMR spectrum (δ –68.2 and –71.7) although these environments equilibrate in solution. The Cs1–C1 bond of 334.6(4) pm is as short as found in Cs– η^6 -carbon coordination^{1b} and considerably shorter than to terphenyl substituted phosphides.⁵ Hence the P,C,N–Cs π bonding has to be considered a hetero aza allyl coordination with the negative charge not only delocalized to the coordinated ring but also to the other. This clearly proves the anticipated ability of the phosphorus centre in the Py $_2$ P $^-$ anion to coordinate soft metals. This is further substantiated in the structure of [{Cp(CO) $_2$ Fe] $_2$ { μ -P)Py $_2$ }] [BMe $_4$] **5**. Two soft Lewis acidic metal fragments [CpFe(CO) $_2$] $^+$ are bridged by the phosphorus atom of a single di(2-pyridyl)phosphide ligand to give the [{Cp(CO) $_2$ Fe] $_2$ { μ -P)Py $_2$ }] $^+$ cation (Fig. 2).

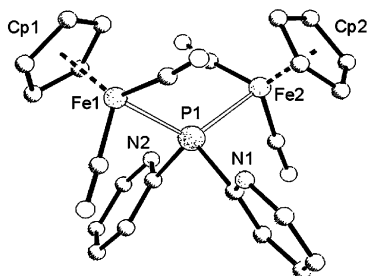


Fig. 2 Solid state structure of the [{Cp(CO) $_2$ Fe] $_2$ { μ -P)Py $_2$ }] $^+$ cation in **5**. Selected bond distances (pm) and angles ($^{\circ}$): P1–C1 184.9(5), P1–C6 184.4(5), P1–Fe1 226.4(2), P1–Fe2 226.5(2), Fe1...Cp1(centre) 172.7, Fe2...Cp2(centre) 171.5, Fe–CO 176.1(7)–176.9(7), C–O 113.7(7)–115.1(7); C1–P1–C6 101.7(3), Fe1–P1–Fe2 120.49(7).

In conclusion the di(2-pyridyl)phosphide ligand shows a metal-dependant coordination response and is involved in a highly unusual σ/π interaction with caesium ion. The latter is clearly reminiscent of the coordination of an allylic type of ligand. On the other hand the phosphorus atom in the Py $_2$ P $^-$ anion is Lewis basic enough to bridge two soft iron metal centres. Yet again the structure determining influence of different metals is obvious.⁴

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Notes and references

‡ Preparation of **2**: to a suspension of caesium (1.00 g; 7.52 mmol) in 10 ml thf a solution of Py $_2$ PH (1.62 g; 8.77 mmol) in 10 ml thf was added. The deep red reaction mixture was stirred for 12 h at room temperature. It was gently warmed and filtered through Celite. The clear filtrate was treated with PMDETA (1.34 ml; 6.39 mmol) and stirred for 24 h at room temperature. The reaction mixture was kept at –38 $^{\circ}$ C. Red crystals of compound **2** were isolated. Yield (3.11 g; 72%). Mp: 49 $^{\circ}$ C. Satisfactory elemental analysis.

§ Crystal data for **2**: C $_{19}$ H $_{31}$ CsN $_5$ P, M = 493.37, triclinic, space group $P\bar{1}$, a = 935.6(3), b = 1076.6(3), c = 1277.5(4) pm, α = 71.29(3), β = 72.89(3), γ = 83.82(2) $^{\circ}$, U = 1.165(1) nm 3 , T = 173(2) K, Z = 2, D_c = 1.273 g cm $^{-3}$, μ (Mo–K α , λ = 71.073 pm) = 1.670 mm $^{-1}$. $R1[F > 4\sigma(F)]$ = 0.027 and $wR2$ = 0.066 (all data). For **5**: C $_{28}$ H $_{30}$ BF $_2$ N $_2$ O $_4$ P, M = 493.37, monoclinic, space group $P2_1/c$, a = 1310.7(6), b = 840.3(2), c = 2600.5(10) pm, β = 96.37(2) $^{\circ}$, U = 2.846(2) nm 3 , T = 193(2) K, Z = 4, D_c = 1.428 g cm $^{-3}$, μ (Mo–K α , λ = 71.073 pm) = 1.111 mm $^{-1}$. $R1[F > 4\sigma(F)]$ = 0.051 and $wR2$ = 0.113 (all data); (G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467; G. M. Sheldrick, SHELXL-96, program for crystal structure refinement, 1996, Göttingen). CCDC 152867 and 152868. See <http://www.rsc.org/suppdata/cc/b0/b008662m/> for crystallographic data in .cif or other electronic format.

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