The $P(bth)_2^-$ anion as a *Janus head* staple between lithium and manganese (bth = benzothiazol-2-yl, C_7H_4NS)

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Deprotonation of $HP(bth)_2$ (1) affords the lithium phosphanide $[(Et_2O)_2Li(bth)_2P]$, (2) with both nitrogen atoms coordinated to the lithium atom while in the heterobimetallic complex $[Li(bth)_2P\{Mn(CO)_2Cp\}_2]_n$ (3) additionally the phosphorus atom μ-bridges two $Mn(CO)_2Cp$ residues.

Our principal strategy in ligand design is to include the substituent periphery of phosphanides and phosphoranates in metal coordination.[1] Rather than providing merely bulk or stereo information like in classical phosphane ligands to d-block metal centres the heteroaromatic substituted *Janus head* ligands supply a second or third coordination site, apart from the divalent P(III) atom. Originally synthesised as diacyl-[2] or diguanidinephosphanide ligands,[3] low coordinated phosphorus species[4] attract more and more interest, remarkably even as 1,3-diphosphaallyl complexes.[5]

The enhanced site selectivity of the *Janus head* ligands presented in this paper might serve as anionic staples in mixed metal complexes employed in homogeneous catalysis.[6] Recent charge density studies revealed the presence of two lone pairs at the central phosphorus atom in $[Me_2Al(\mu\text{-}py)_2P]$ containing a divalent P(III) atom (py = pyrid-2-yl). The *sec.* phosphane $HPpy_2$ can be employed in unusual μ-bridging to two $W(CO)_5$ moieties in an unsupported dinuclear complex $[\{(OC)_5W\}_2(\mu\text{-}P)py_2(H)]$ mimicking a 4-electron donor.[7]

Interestingly, in the secondary phosphane $HP(bth)_2$ (**1**) the hydrogen atom is not bonded to the central phosphorus atom like in $HPpy_2$[8] but to one ring nitrogen atom, leaving the P(III) atom divalent. This is reminiscent of the diacylphosphanes[2] which show keto-enol tautomerism in solution. The question occurs whether such an unusual divalent P(III) atom should be regarded a potential 2-electron- or 4-electron-donor (Scheme 1).

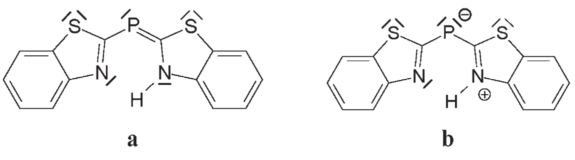
Although for R_2P^- phosphanides the μ-bridging is most common it was only recently that this coordination mode was brought to light for phosphanes.[9] Various computational studies suggested that the divalent P(III) atom as a bridgehead between two heteroaromatic rings is electronically depleted and would be a poor Lewis base to any metal centre[10] but the py_2P^- anion exhibits a μ-bridging complexation in $[\{Cp(CO)_2Fe\}_2\{(\mu\text{-}P)py_2\}]^+$ and a σ- and π-donating P atom in dimeric $[(PMDETA)Cs\{(\mu\text{-}Ppy)py\}]_2$, suggesting some charge density accumulated at the phosphorus atom.[11]

To elucidate the bonding and to explore the non-bonding regions it is essential to quantify the valence shell charge concentrations (VSCCs) at the phosphorus atom. The maxima in the VSCC are the (3,−3) critical points in the negative Laplacian, *i.e.* local charge concentrations. They are not only regarded as physical basis of the VSEPR model within Bader's QTAIM, moreover, there is a *one-to-one mapping of the electron pairs of the Lewis model* onto these VSCC.[12]

The inspection of the Laplacian distribution in $P(bth)_2H$ (**1**) from DFT based geometry optimizations† shows four (3, −3) critical points around the phosphorus atom. These prove the presence of four VSCCs. Within the QTAIM theory, these are the physical expression for Lewis electron pairs, no matter whether they are bonding or non bonding. Therefore, the phosphorus centre has to be regarded as sp^3 hybridised with two 2e2c bonds and two lone pairs (Fig. 1).

Deprotonation of $P(bth)_2H$ (**1**) with ^{n}BuLi affords the lithium phosphanide $[(Et_2O)_2Li(bth)_2P]$ (**2**, Fig. 2).‡ As expected, the hydrogen atom is replaced by the lithium and the metal is coordinated to both nitrogen atoms of the ligand. The coordination sphere of the lithium atom is completed by two diethyl ether molecules. The phosphorus atom remains two-coordinated.§

The connectivity is virtually identical to that in $[(thf)_2Li(py)_2P]$.[8] However, the P–C bonds in **2** are marginally shorter (178.0(2) *vs* 180.0(5) pm) while the Li–N bonds are longer (203.0(3) *vs* 197.0(7) pm). The coordinated five-membered rings in **2** permit a considerably smaller C–P–C angle than in the latter (104 *vs* 110°). The distance between the two nitrogen atoms (308.5 pm) is



Scheme 1 Two canonical forms of $P(bth)_2H$ (**1**).

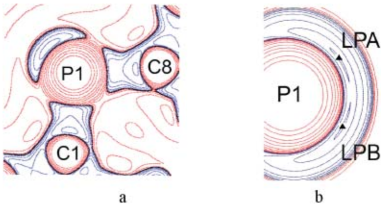


Fig. 1 Contour plot of the theoretically obtained Laplacian function of **1** in the plain (a) and orthogonal to the mean plane (b) of the phosphane, calculated with AIM2000.[13] Charge concentrations (blue lines) refer to negative values of $\nabla^2\rho(\mathbf{r})$, charge depletions (red lines) to positive values of $\nabla^2\rho(\mathbf{r})$.

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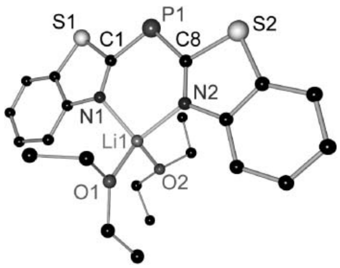
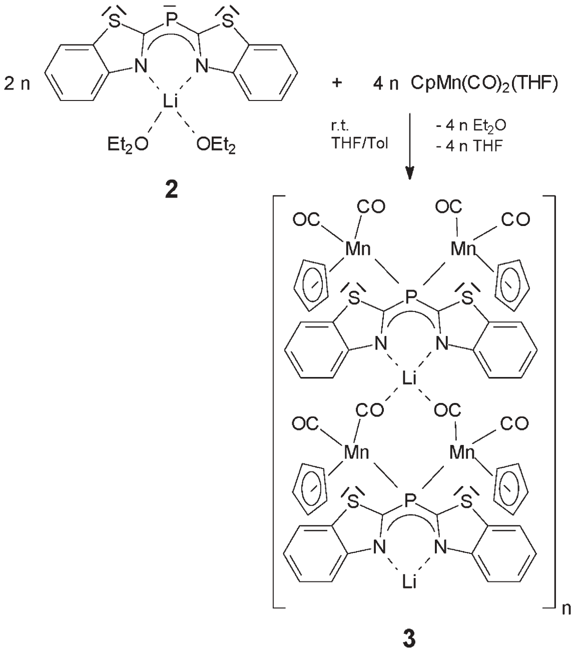


Fig. 2 Crystal structure of [$(Et_2O)_2Li(bth)_2P$] (**2**). For reasons of clarity only one site of the disordered ether molecule around O2 is dipicted. Selected bond lengths [pm] and angles [°]: P1–C1 177.9(2), P1–C8 177.9(2), N1–Li1 202.4(3), N2–Li1 203.7(3), N1···N2 308.7(2); C1–P1–C8 104.2(1), N–Li–N 99.0(1), O1–Li–O2 106.2(2), planes (bth)···(bth′) 9.9.

considerably longer compared to the N···N distance in (**1**) (262.2 pm).

To examine the Lewis basicity of **2** we tried the synthesis of a dinuclear organometallic complex to employ the lone pair density at the phosphorus atom (Scheme 2). We selected [$CpMn(CO)_2(THF)$] as the appropriate starting material because the THF molecule can easily be replaced by other Lewis bases and the remaining $CpMn(CO)_2$ moiety should be soft enough to suit the soft lithium phosphane.†

As intended, the lithium di(benzothiazol-2-yl)phosphanide (**2**) coordinates the manganese metal, replacing the THF molecule in the transition metal complex and gives the coordination polymer [$Li(bth)_2P\{Mn(CO)_2Cp\}_2]_n$ (**3**).‡ Each phosphorus atom in the product is bridging two $CpMn(CO)_2$ moieties akin to the cationic metal fragment [$\{Cp(CO)_2Fe\}_2\{(\mu\text{-}P)py_2\}]^+$.[11] The nitrogen face of the *Janus head* ligand coordinates the lithium atom like in the starting material **2**. The diethyl ether molecules of the phosphanide are replaced by two bridging carbon monoxide molecules. This leads to infinite strands, generated by the 2_1 screw axes parallel to *b*. The P–C bond distances in **3** (Fig. 3) are the longest ever observed in related species as they are 185.2(4) pm for the P1–C1 bond and 185.5(4) pm for the P1–C8 bond. These values match those of standard P–C single bonds.[14] Employing the phosphorus atom as a Lewis base in metal μ-coordination leads to long P–C bond distances.[7] Apparently, there is enough electron density left at the phosphorus atom to be attractive to the organometallic residue. With the manganese centres bridged, the electron density at the phosphorus centre that usually couples into the heteroaromatic ring systems is needed for the coordination of the metal atoms. The phosphorus centre in **3** mimics a four electron donor as it formally donates two electrons to each of the two manganese centres. The manganese atoms are located almost in the position where the lone pairs of a sp^3 hybridised phosphorus atom are anticipated. This hybridisation is in accordance with the results of the theoretical calculations discussed earlier.



Scheme 2 Synthesis of [$Li(bth)_2P\{Mn(CO)_2Cp\}_2]_n$ (**3**).

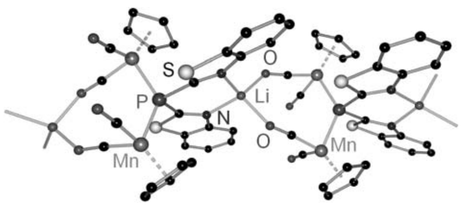


Fig. 3 Crystal structure of [$Li(bth)_2P\{Mn(CO)_2Cp\}_2]_n$ (**3**). The 2.5 non-coordinating disordered toluene lattice solvent molecules are not depicted. Selected bond lengths [pm] and angles [°]: P1–C1 185.2(4), P1–C8 185.5(4), N1–Li1A 199.0(7), N2–Li1A 199.5(7), P–Mn1C 229.2(1), P–Mn2 229.6(1), O2–Li1 194.8(7), O4–Li1 192.6(7); C1–P1–C8 102.7(2), planes (bth)/(bth′) 24.7.

Each manganese atom is coordinated by two carbon monoxide donor molecules, one of which is C/O bridging the manganese and lithium atoms. Thus, the electron density in the bridging carbonyls has to be shared between two metals and is reduced in comparison to the non-bridging carbonyl ligands. This electronic depletion is partly compensated by an emphasised back bonding from the metal atom, resulting in shorter Mn–CO bond distances (173.7(4) and 174.1(4) pm compared to 178.5(4) and 176.5(4) pm). C/O bridging of carbonyl donors is not without precedence but relatively rare.[15]

In conclusion, the di(benzothiazol-2-yl)phosphanide is a site-selective *Janus head* ligand that coordinates the lithium cation *via* the hard N-site and μ-bridges two soft unsupported $CpMn(CO)_2$-residues with the central P-atom, mimicking a 4-electron donor. This is an experimental evidence for the theoretically derived two lone pairs (non-bonding VSCCs) present at the phosphorus atom in the secondary phosphane.

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Notes and references

† full B3LYP[16]/6-311++G** gas phase optimization without symmetry restrictions performed with Gaussian98.[17]

‡ **Synthesis of [$(Et_2O)_2Li(bth)_2P$] (2)** 3.33 ml (3.33 mmol) of *n*-BuLi (1 molar in diethylether) was added in a period of 25 min to a suspension of 1.00 g (3.33 mmol) **1** in 40 ml diethylether at −78 °C. The suspension turned the color from bright yellow to intense red. Solvent was evaporated *in vacuo*

after stirring the contents for 12 h. The orange residue was washed three times with 10 ml *n*-hexane and then dissolved in 30 ml THF. Keeping the solution at −35 °C gave (**2**) (1.15 g, 76%) as orange crystals. mp 42 °C (dec.). ^{1}H ($CDCl_3$) δ 1.12 (t, $^3J_{H–H}$ = 6.85 Hz, 12 H, $O(CH_2C\mathit{H}_3)_2$), 3.39 (q $^3J_{H–H}$ = 6.86 Hz, 8 H, $O(C\mathit{H}_2CH_3)_2$) and 6.93–8.08 (m, 8 H, bth). ^{13}C ($CDCl_3$) *δ* 16.14 (s, 4 C, $O(CH_2\mathit{C}H_3)_2$), 66.78 (s, 4 C, $O(\mathit{C}H_2CH_3)_2$), 122.68 (s, 2 C, C3, C10), 123.28 (s, 2 C, C6, C13), 126.54 (s, 2 C, C4, C11), 127.11 (s, 2 C, C5, C12), 138.60 (s, 2 C, C2, C9), 155.35 (s, 2 C, C7, C14) and 157.17 (s, 2 C, C1, C8). ^{31}P ($CDCl_3$) *δ* −4.55 (s, 1 P). **[Li(bth)$_2$P{Mn(CO)$_2$Cp}$_2$] + 2.5toluene (3)** A 20 ml THF solution of 1.20 g (2.64 mmol) of **2** was added to a 200 ml THF solution of 0.90 g (2.90 mmol) $[(Cp)_2Mn(CO)_2(THF)]$ at room temperature. The mixture was stirred, followed by evaporation of the solvent under reduced pressure. Subsequently, toluene was added to the grey residue, which gave a deep red suspension. The insoluble components were filtered off employing celite. The filtrate was stored at −35 °C for 3 weeks to give red crystals of **3**. (yield 1.33 g, 64%). ν_{max}(film/cm^{-1}) 1954, 1932, 1919, 1909, 1891 and 1855. ^{1}H ($CDCl_3$) *δ* 4.17 (s, 20 H, Cp), 7.12 (dd, $^3J_{H3–H4}$ = 6.11 Hz, $^3J_{H5–H4}$ = 7.44 Hz, 2 H, H4, H11), 7.19 (dd, $^3J_{H4–H5}$ = 7.44 Hz, $^3J_{H6–H5}$ = 7.18 Hz, 2 H, H5, H12) and 7.94–7.97 (m, 4 H, H6, H13, H3, H10). ^{13}C ($CDCl_3$) *δ* 84.10 (s, 10 C, Cp), 121.99 (s, 2 C, C3, C10), 122.51 (s, 2 C, C6, C13), 125.18 (s, 2 C C4, C11), 126.22 (s, 2 C, C5, C12), 137.74 (s, 2 C, C2, C9), 153.95 (s, 2 C, C7, C14), 154.00 (s, 2 C, C1, C8) and 234.93 (s, 4 C, CO). ^{31}P ($CDCl_3$) *δ* 103.3 (s, 1 P).

§ Crystal data for **2**: $C_{22}H_{28}LiN_2O_2PS_2$, M = 454.49, orthorhombic, space group $Pca2_1$, a = 1444.94(8), b = 922.34(5), c = 1777.95(10) pm, V = 2.3695(2) nm^3, T = 100(2) K, Z = 4, D_c = 1.274 g cm^{-3}, μ (Mo Kα, λ = 71.073) = 0.312 mm^{-1}. $R1(F > 4(F))$ = 0.030 and $wR2$ = 0.071 (all data). Crystal data for **3**: $C_{28}H_{18}LiMn_2N_2O_4PS_2$, M = 888.69, monoclinic, space group $C2/c$, a = 2795.7(12), b = 1639.7(7), c = 2161.2(9) pm, β = 120.372(8)°, V = 8.547(6) nm^3, T = 173(2) K, Z = 8, D_c = 1.381 g cm^{-3}, μ (Mo Kα, λ = 71.073) = 0.771 mm^{-1}. $R1(F > 4(F))$ = 0.062 and $wR2$ = 0.175 (all data); (Sheldrick, G. M. *Acta Crystallogr., Sect. A*, 1990, **46**, 467; and Sheldrick, G. M. SHELXL-96, program for crystal structure refinement, 1996, Göttingen). CCDC 618733 for **2** and 618735 for **3**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612247g

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