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Di(benzothiazol-2-yl)phosphanide as a Janus-Head Ligand to Caesium

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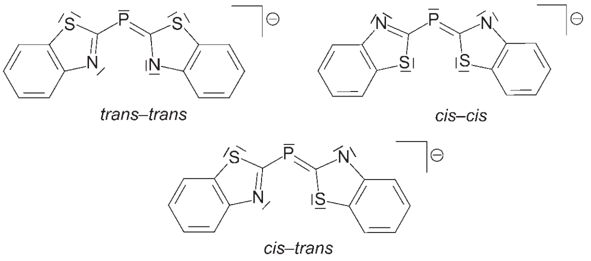
Abstract: Starting from tris(benzothiazol-2-yl)phosphane (**1**) an advanced Janus-head ligand, di(benzothiazol-2-yl)phosphane (**2**), was synthesised and structurally characterised. The heteroaryl substituents of this ligand provide both hard and soft donor sites. Surprisingly, the phosphorus atom in **2** is divalent and the hydrogen atom is directly bonded to one ring nitrogen atom and hydrogen bonded to the second. Compound **2** decomposes in any common solvent other than diethyl ether and a new preparation to improve the yields of **2** is presented. A coordination polymer, $[\{Cs(bth)_2P\}_8]$ (**3**) (bth = benzothiazol-2-yl), was obtained when the *sec*-phosphane **2** was allowed to react with elemental caesium in a 1:1 ratio in diethyl ether at −78 °C. In **3** each anion is coordinated to four caesium cations and vice versa. The central phosphorus atom is coordinated to two metal atoms above and below the mean plane of the anion in positions in which the two lone pairs of a four-electron donor are anticipated. Two additional cations μ-bridge both ring nitrogen atoms. Hence both faces of the Janus-head ligand are coordinated to the same number of metal cations but in a different way.

Keywords: alkali metals • caesium • N ligands • P ligands • phosphanes

Introduction

Pincer ligands with an active coordinating periphery[1] have attracted more and more attention during recent decades.[2] Over the last few years our group has concentrated on heteroaromatic-substituted chelating ligands.[3] These ligands do not only bear coordination sites for either hard or soft metal centres in terms of the hard–soft acid–base (HSAB) concept by Pearson,[4] but also for both. Depending on the metal fragment offered, the ligands act as a N,N-, P,N-chelating, or P-coordinating ligand.[5] Ligands of this type find many applications in alkane dehydrogenation,[6] cyclometalation,[7] cross-coupling,[8] organic transformation,[9] catalyst recovery,[10] antimicrobial agents,[11] light-emitting diodes (LEDs) and other electrophosphorescent devices.[12] To obtain heterobimetallic complexes it is useful to implement additional and qualitatively different coordination sites in the phosphane ligand periphery. This leads to the so-called "Janus-head" ligands. An advantage of these molecular staples is the combination of soft and hard coordination sites in the same molecule. In this sense we embarked on developing an enhanced Janus-head ligand system to investigate its reactivity as well as its coordination ability. Di(benzothiazol-2-yl)phosphane was chosen as a target because the benzothiazolyl substituent (bth = C_5H_4SN) features a sulfur atom and a nitrogen atom as potential donor centres. Thiazol is an electron-rich heteroaromatic ring in which the π electrons are mainly located on the nitrogen atom. Equipped with these substituents, a secondary phosphanide should provide rich coordination-site selectivity to various metal fragments.

Various possible conformations of the system (*trans–trans*, *cis–cis* and *cis–trans* (Scheme 1), not including the non-planar modifications) make this ligand more compatible



Scheme 1. Various different conformations of the planar di(benzothiazol-2-yl)phosphanide anion.

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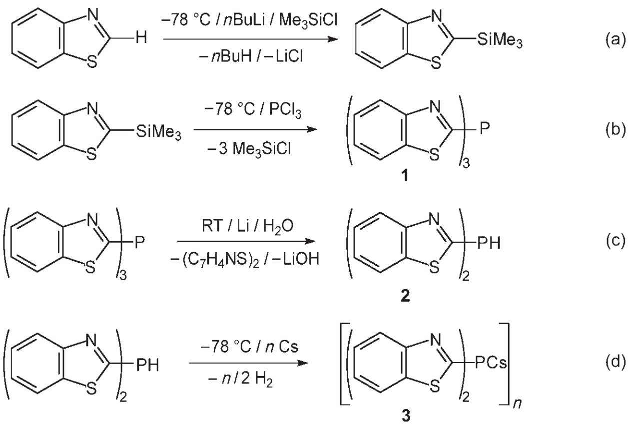
than homoatomic pincers or hemilabile ligands. Only a few benzothiazol-2-yl-substituted phosphanes have been structurally characterised, namely, 1,2-bis{di(benzothiazol-2-yl)-phosphanyl}ethane,[13] 1,1-bis{di(benzothiazol-2-yl)phosphanyl}methane[14] and tris(benzothiazol-2-yl)phosphane.[15] In some cases, such as the latter, the reaction of the lithiated benzothiazol-2-ide with phosphorus trichloride gives mainly the coupling product.[16] In this paper, we report on the synthesis, reactivity, X-ray structural and DFT computational characterisation of the new di(benzothiazol-2-yl)phosphane and the caesium phosphanide derivative.

Results and Discussion

Syntheses: Both the tris(benzothiazol-2-yl)phosphane, P(bth)$_3$ (**1**), and the di(benzothiazol-2-yl)phosphane, HP(bth)$_2$ (**2**), were prepared according to the method published by Moore and Whitesides.[15] First, benzothiazol was silylated (Scheme 2a) and reacted with phosphorus trichloride at $-78\,^{\circ}$C to give **1** (Scheme 2b). Phosphane **2** was obtained by reaction of **1** with elemental lithium in THF at room temperature followed by its subsequent hydrolysis with degassed water. As a major side product the substituent coupling product bisbenzothiazol ($(C_7H_4NS)_2$) was obtained (Scheme 2c).[17] Reacting the *sec*-phosphane **2** with elemental caesium at $-78\,^{\circ}$C (dry ice) gave the caesium phosphanide **3** (Scheme 2d).



Scheme 2. Syntheses of the *tert*-phosphane P(bth)$_3$ (**1**), the *sec*-phosphane HP(bth)$_2$ (**2**) and the caesium phosphanide $[\{CsP(bth)_2\}_n]$ (**3**).

Owing to the originally very poor yields obtained for **2** (about 10 % based on the employed benzothiazol), an innovative assembly was developed, which is based on the idea of a Soxhlet extractor. The use of this apparatus resulted in greatly improved yields of approximately 60 %. The hydrolisation mixture was added to the extraction flask with the extractor in the centre adapter (Figure 1). Diethyl ether was heated to reflux in the left flask and gaseous diethyl ether passed through the riser and condensed at the cooling unit. From there, the solvent dropped into the extractor, which is porous in order to force the solvent to interact with the mixture in the extraction flask. The diethyl ether containing the phosphane rose up the extraction flask to the overflow and ran back into the left flask after being dried over magnesium sulfate. The phosphane stayed in the left flask while the diethyl ether started the cycle again.

Abstract in German: *Ausgehend vom Tris(benzothiazol-2-yl)phosphane, P(bth)$_3$* (***1***) *(bth = benzothiazol-2-yl), wurde ein verbesserter Januskopfligand, das Di(benzothiazol-2-yl)-phosphan, HP(bth)$_2$* (***2***)*, synthetisiert und dessen Einkristallstruktur bestimmt. Die Heteroarylsubstituententen des Liganden stellen zusätzlich jeweils sowohl harte als auch weiche Koordinationsstellen zur Verfügung. Das Phosphoratom in* ***2*** *ist überraschenderweise nur zweibindig, da das Wasserstoffatom an ein Ringstickstoffatom gebunden ist und über eine intramolekulare Wasserstoffbrückenbindung vom zweiten Ring koordiniert wird. Da sich* ***2*** *in jedem anderen Lösungsmittel als Diethylether zersetzt wird hier eine verbesserte Darstellung mit höheren Ausbeuten beschrieben. In der Reaktion des sec. Phosphans* ***2*** *mit elementarem Cäsium im Molverhältnis 1:1 in Ether bei $-78\,^{\circ}$C wird $[\{Cs(bth)_2P\}_8]$* (***3***)*, erhalten. In diesem Koordinationspolymer ist jedes Phosphanid von vier Cäsiumkationen vice versa koordiniert. Das Brückenkopfatom ist von zwei Metallatomen ober- und unterhalb der Ligandebene in den Positionen der beiden freien Elektronenpaare eines 4-Elektronen-Donors koordiniert. Die übrigen beiden Kationen verbrücken jeweils die beiden Ringstickstoffatome. Beide Gesichter des Januskopfliganden sind von derselben Anzahl Metallatome koordiniert, jedoch in einer unterschiedlichen Art und Weise.*

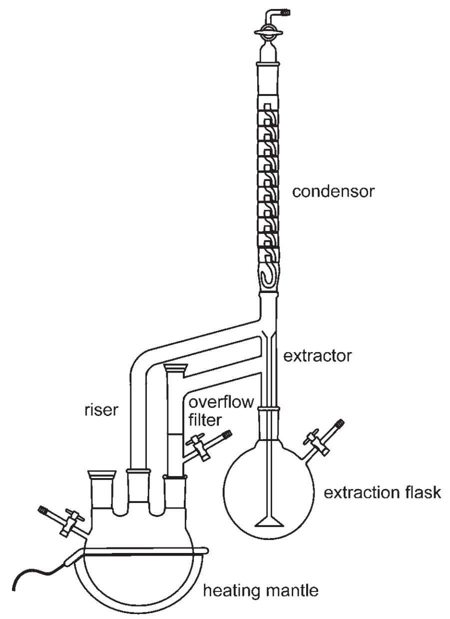
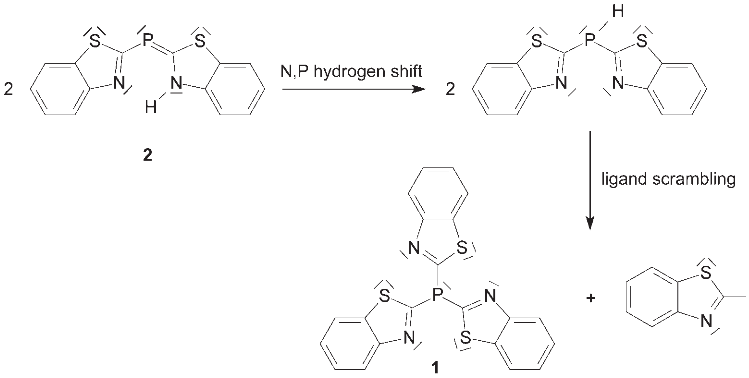


Figure 1. Glass apparatus used to hydrolyse [LiP(bth)$_2$] and extract **2** from the reaction mixture.

Surprisingly, the NMR data from solutions of **2** already show the phosphorus atom to be divalent because the hydrogen atom of the *sec*-phosphane is not located at the phosphorus atom but is placed at a ring nitrogen atom. Hence, the connectivity in **2** is different from that of pyridyl (Py)-substituted Janus-head ligands like $HPPy_2$[18] or H_2CPy_2.[19] In the first, the hydrogen atom is bonded to the phosphorus atom, as clearly shown by NMR and IR spectra (^{31}P NMR: $^1J_{(P,H)} = 225$ Hz; IR: $\tilde{\nu}_{(P,H)} = 2312$ cm^{-1}). Phosphane **2** is reminiscent of diacylphosphanes, which show keto–enol tautomerism in solution.[20] The N−H tautomer is stable in diethyl ether causing a signal in the ^{31}P NMR spectrum at $\delta = 6.81$ ppm with a $^3J_{P,H}$ coupling constant of 8 Hz. If, for example, tetrahydrofuran is used as the solvent, a second signal at $\delta = -65.77$ ppm starts growing, which can be assigned to the P−H tautomer. The $^1J_{P,H}$ coupling constant is 226 Hz and therefore close to that of di(pyrid-2-yl)phosphane. Surprisingly, the P−H tautomer is not stable and a transformation to tris(benzothiazol-2-yl)phosphane and the primary (benzothiazol-2-yl)phosphane occurs. The absence of any common organic solvent other than diethyl ether seems to be of vital importance for the stability of **2**. In any other solvent tested so far (e.g., pentane, hexane, toluene, THF, dioxane), ligand scrambling takes place as shown in Scheme 3.



Scheme 3. Ligand scrambling of **2** in any solvent other than diethyl ether.

Consequently, all reactions starting from di(benzothiazol-2-yl)phosphane (**2**) have to be carried out in diethyl ether. The solid parent phosphane **2** decomposes gradually, as indicated by a colour change from bright yellow to orange. Simultaneously, the consistency changes from a powder to a paste with reduced solubility and reactivity. Therefore, the starting material needs to be stored in a sealed flask at −38 °C under a dry, inert gas atmosphere.

sec-Phosphane **2** was allowed to react with elemental caesium in a 1:1 ratio in diethyl ether at −78 °C to obtain the metal phosphanide $[\{CsP(bth)_2\}_n]$ (**3**) (Scheme 2d). The reaction mixture turned deep red while gas was evolved. After four hours of being stirred at this temperature, the solution was allowed to warm to ambient temperature. After reducing the amount of solvent the reaction mixture was stored at +4 °C and red crystals suitable for single-crystal X-ray diffraction analysis were yielded.

Crystal-structure determinations of 1 and 2: Tris(benzothiazol-2-yl)phosphane (**1**) crystallises in the rhombohedral space group *R*3*c* with a third of the two molecules in each asymmetric unit. The phosphorus atoms are located at the threefold axis. The solid-state structure of one stereoisomer of **1** is depicted in Figure 2. The two stereoisomers are distinguished by the rotation direction of the propeller-like molecules. The sequence of the heteroatoms around the phosphorus atom as the hub is S–N–S–N–S–N. In the lattice the molecules are stacked with the lone pair on each phosphorus atom pointing in the same direction but with a ring nitrogen atom on top of a sulfur atom and vice versa. The P−C distance of 182.0(2) pm is in accordance with that in PPy_3.[21] The relatively acute C-P-C angle of 101.87(7)° is a result of the stereochemically active lone pair at the phosphorus atom.

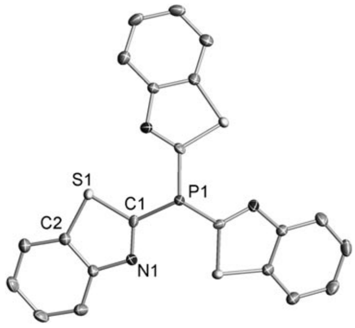


Figure 2. Structure of tris(benzothiazol-2-yl)phosphane (**1**). The anisotropic displacement parameters are depicted at the 50 % probability level. Selected bond lengths [pm] and angles [°]: P(1)−C(1) 182.0(2), C(1)−N(1) 129.3(2), C(1)−S(1) 174.3(2); C(1)-P(1)-C(1A) 101.87(7).

Di(benzothiazol-2-yl)phosphane (**2**) crystallises in the orthorhombic space group *Pbca* with the whole molecule in the asymmetric unit. The solid-state structure of **2** is depicted in Figure 3. The structure shows that the phosphorus atom is divalent and that the hydrogen atom is located at one of the ring nitrogen atoms. The position was taken from a difference Fourier map and refined freely.

Interestingly, this protonation of one ring causes no structural differences of the bth rings. The hydrogen atom H2 is additionally linked to the second nitrogen atom by a hydrogen bond. The bond length of 192(5) pm for the hydrogen bond N1···H2 is rather short.[22] The atoms N1···H2−N2 include an angle of 140(4)°. The sums of the angles around

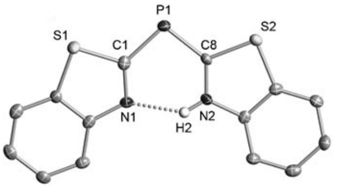
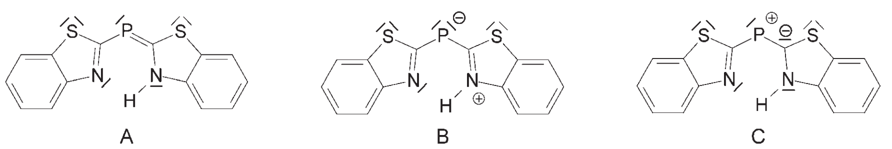


Figure 3. Solid-state structure of di(benzothiazol-2-yl)phosphane (**2**). The anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [pm] and angles [°]: P1–C1 178.4(5), P1–C8 177.8(4), N1···H2 192(5), N2–H2 85(5), C1–N1 133.1(6), C8–N2 133.4(5), N1···N2 262.3(5); C1-P1-C8 98.7(2), N2-H2···N1 140(4); C8-N2-H2 119(3), C14-N2-H2 124(3), C1-N1···H2 104(1), C7-N1···H2 143(1), planes (bth)/(bth′) 169.4°.

the nitrogen atoms N1 and N2 are close to 360° and are in accordance with sp^2 hybridisation. The P–C bond lengths of 178 pm on average are equal within their estimated standard deviations but are considerably shorter than those in **1**. Considering the mere distances, they are half-way between a single and a double bond,[23] thus supporting the canonical diagram A in Scheme 4. Clearly, further reduction of the C-P-C angle to 98.7(2)° relative to **1** is caused by reduced steric crowding and by the intramolecular hydrogen bond. However, there might be two lone pairs located at the central phosphorus atom causing the acute angle. The Lewis diagram B in Scheme 4 might contribute considerably to explaining the bonding in the *sec*-phosphane **2**.



Scheme 4. Lewis diagrams to rationalise the bonding in *sec*-phosphane **2**.

This is substantiated by the fact that we recently determined by means of experimental charge-density determination two lone pairs to be present in the metallaphosphane [$AlMe_2P(\mu\text{-}Py)_2$] containing a divalent P^{III} atom. In the *sec*-phosphane $PPy_2(H)$, the hydrogen atom was found to be located at the ring nitrogen atom as well and can be employed in unusual μ-bridging to two $W(CO)_5$ moieties in an unsupported dinuclear complex [$\{(OC)_5W\}_2(\mu\text{-}P)Py_2(H)$], thus mimicking a four-electron donor.[24] Moreover, the phosphorus atom in the caesium phosphanide [$\{CsP(bth)_2\}_n$] (**3**) is coordinated to two metal atoms in positions where the two lone pairs are anticipated (Figure 5c).

Theoretical studies of 2: The solid-state structure shows di(benzothiazol-2-yl)phosphane (**2**) to be the N–H tautomer of the P–H form anticipated for *sec*-phosphanes. In particular, in view of the decomposition channel via the P–H tautomer, it was of great interest to get information about the energy differences of both forms. Theoretical calculations are an excellent tool to determine the relative energies of various conformers. Geometries were optimised at the B3LYP/6-311++G** level of theory and the total energies were calculated.[25] The X-ray structure was used as the starting geometry. As reference geometries, the P–H tautomer was calculated in *trans–trans*, *cis–trans*, and *cis–cis* arrangements (Figure 4).

The optimised structure derived from the experimentally determined geometry turned out to be the energetically most favourable. Although bond lengths and angles in this structure differ from those found in **2**, the experimental geometry is almost reproduced. Whereas the P–C bond lengths in **2** are identical within estimated standard deviations (P1–C1 178.4(5), P1–C8 177.8(4) pm), they differ more significantly in the calculated geometry (P1–C1 181.6, P1–C8 175.5 pm). All of the bond lengths are between those for P–C double and single bonds. The average bond length of 178.6 pm matches that of the experimentally determined structure very well. Similarly, the C_{ipso}–N bond lengths differ more significantly in the calculated structure (C1–N1 131.2, C8–N2 135.4 pm) than in the experimental structure (C1–N1 133.1(6), C8–N2 133.4(5) pm). Although the merge of distances in both parts of the experimental structure might suggest the superposition of protonated and deprotonated

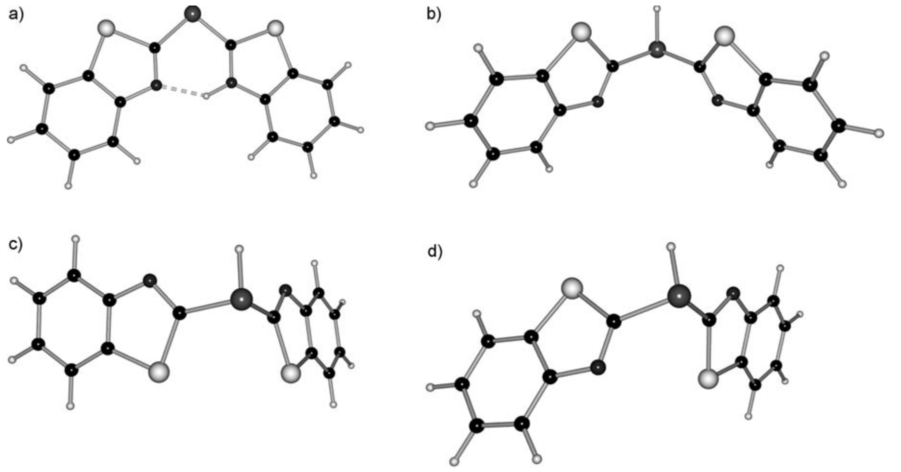


Figure 4. Optimised geometries for the tautomeric forms of **2**: a) optimised X-ray structure (0.0 kJ mol^{-1}); b) *trans–trans* (25.07 kJ mol^{-1}); c) *cis–cis* (28.65 kJ mol^{-1}); d) *cis–trans* (22.54 kJ mol^{-1}).

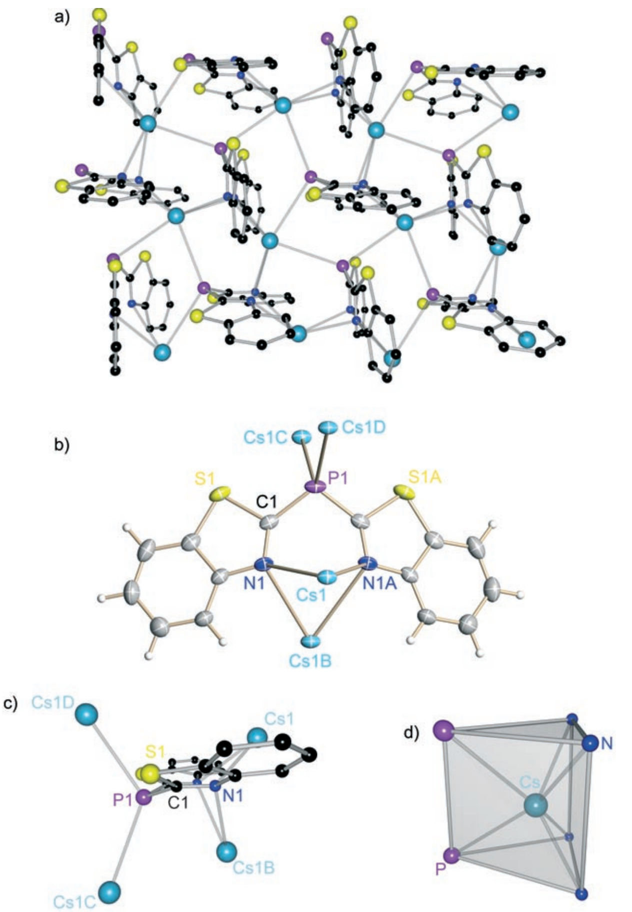


Figure 5. Crystal structure of $[\{Cs(bth)_2P\}_n]$ (**3**): a) the coordination polymer; b) the metal coordination of a single phosphanide; the anisotropic displacement parameters are depicted at the 50% probability level; c) the butterfly arrangement of the anion; d) the coordination polyhedron of the caesium cation. Selected bond lengths [pm] and angles [°]: P1−C1 179.2(4), C_{ipso}−N 131.3(5), N1−Cs1 321.4(4), N1−Cs1B 318.6(3), P1−Cs1C 367.2(2), P1−Cs1D 361.6(2), N1···N1A 321.4(7), C-P-C 103.3(3), N_{bth}-Cs1-$N_{bth'}$ 60.0(1), N_{bth}-Cs1B-$N_{bth'}$ 60.6(1), Cs1C-P-Cs1D 126.1(1), planes (bth)/(bth′) 147.5°.

rings or a double minimum for the hydrogen bond, the structure shows no indication of two hydrogen sites of 0.5 occupation factor. The total energy of the optimised X-ray structure was defined to be zero. The energies for the P−H isomers span the range from 22.54 kJ mol^{-1} for the *cis–trans* arrangement to 28.65 kJ mol^{-1} for the *cis–cis* conformation. In all non-planar geometries the heteroaromatic rings are rotated about the P−C bonds. The angles included by the ring systems range from 33.4 (*cis–cis* conformer) through 102.4 (*trans–trans* conformer) to 104.1° (*cis–trans* conformer). The crystal structure of **2** displays an almost planar molecule. The total energy of the system clearly decreases through the formation of a strong N−H···N hydrogen bond.

Crystal-structure determination of 3: $[\{CsP(bth)_2\}_n]$ (**3**) crystallises in the orthorhombic space group $Cmc2_1$ with the asymmetric unit consisting of half the monomer. The di(benzothiazol-2-yl)phosphanide is generated by a mirror plane.

In the coordination polymer (Figure 5a) each anion is coordinated to four caesium cations and vice versa. The central phosphorus atom is coordinated to two caesium cations above and below the mean plane of the anion. Two additional metal atoms μ-bridge the nitrogen ring atoms (Figure 5b). Conjugation in the anion is precluded because of the butterfly arrangement of the substituents. Both bth mean planes intersect at an angle of 147.5° (Figure 5c). The coordination polyhedron of each caesium cation can be best described as a trigonal prism. One of the rectangles is made up of four nitrogen atoms. The two rectangles forming the sides of the triangle are derived from the same anion. The prism is completed by the edge opposite the N_4 rectangle occupied by the two phosphorus atoms (Figure 5d).

The P−C bond length in the anionic ligand is slightly elongated relative to **2** to 179.2(4) pm because the electron density at the phosphorus atom is occupied by two caesium cations and not coupled into the heteroaromatic rings. The bond lengths match those in $[\{CsP(py)_2(pmdeta)\}_2]$[26] (pmdeta = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) almost perfectly, although the phospha-aza-allylic π-coordination in the latter is not observed in **3**. The P−Cs bond lengths in **3** are 367.2(2) and 361.6(2) pm. Corresponding bond lengths listed in the CSD span a wide range from 342 to 411 pm.[27] This is particularly emphasised in $[Cs([18]crown\text{-}6)P(H)\mathit{t}Bu_3C_6H_2]$ with two independent molecules present in the asymmetric unit. The P−Cs bond lengths of 384.7(2) and 406.9(3) pm in two otherwise almost identical molecules vary by 20 pm.[28] The N−Cs bond lengths are 321.4(4) and 318.6(3) pm. In polymeric $[(Cs_2(\mu\text{-thf})\{Ph(Me_3SiN)P\}_2)_n]$ a similar bonding situation with two μ-bridging Cs cations across N···N is present and the N−Cs bond lengths range from 309.5(4) to 316.2(4) pm.[29] The N1···N1A distance in **3** is 321.4(7) pm. This is the largest distance observed for the bite distance in di(benzothiazol-2-yl)phosphanides so far. The benzothiazol-2-yl rings are rotated about the P−C_{ipso} bonds in the same direction. The best planes defined by the atoms of the heteroaromatic rings include an angle of 147.5°. The maximum in bite distance in this compound is caused by the maximum rotation of the heteroaromatic rings about the P−C bonds (Figure 5c). The butterfly arrangement is a compromise between planarity required for conjugation and the affinity of the cationic metals to the maxima of electron density. The rotation of the heteroaromatic rings about the P−C_{ipso} bonds facilitates close proximity of the caesium cations to the sulfur atoms. The S1···Cs1D distance is 412.7(1) pm. This is at the long end of the published range.[28] Only a few S···Cs distances are listed. Thiolato complexes show the shortest distances from approximately 330 to 360 pm.[30] Distances for dative bonds found in thioethers or thioketones range from approximately 370 to 390 pm.[31] However, there is no doubt that the S···Cs interactions enhance the formation of the butterfly arrangement.

Conclusion

In conclusion, di(benzothiazol-2-yl)phosphane is a rare example of a phosphane containing a divalent phosphorus atom in the centre and accommodating the hydrogen atom in the ligand periphery. Computational investigations prove this conformer to be about 22 kJ mol^{-1} more stable than the best P–H tautomer. However, owing to its decomposition in any common solvent other than diethyl ether, this phosphane has to be prepared and handled with special care. An individual Soxhlet extractor and low temperatures are required to ascertain reasonable yields. Both faces of the Janus-head ligand in **3** are coordinated to the same number of caesium cations but in a different way. The central phosphorus atom in the coordination polymer is bound to two metal atoms above and below the mean plane of the anion in positions where the two lone pairs are anticipated, thus mimicking a four-electron donor. Two additional cations μ-bridge both ring nitrogen atoms. Long-range Cs···S distances help to establish the solid-state structure. Hence, the ligand is a promising anionic staple in heterobimetallic complexes, simultaneously suiting various coordination requirements like radius, polarisability and haptisity of a variety of organometallic residues.

Experimental Section

General procedures: All experiments were carried out in a dry nitrogen or an argon atmosphere by using modified Schlenk techniques and a dry box. Solvents were freshly distilled from a sodium–potassium alloy prior to use. The reactants used were either procured commercially or synthesised according to published procedures.

NMR spectra were recorded at room temperature on a Bruker DRX 300 spectrometer at 300.1 (^{1}H), 75.5 (^{13}C), or 121.5 MHz (^{31}P). Chemical shifts are in δ relative to the solvent used for ^{1}H and to H_3PO_4 (85 %) for ^{31}P. Elemental analyses were performed at the Mikroanalytisches Labor des Instituts für Anorganische Chemie der Universität Würzburg. The melting and decomposition points were determined by using differential thermo analysis (DTA) on a Thermal Analyzer 9000 (Du Pont) instrument and a Differential Scanning Calorimetry (DSC) cell. IR spectra were recorded on a Bruker IFS 25 spectrometer.

Synthesis of tris(benzothiazol-2-yl)phosphane (1): The compound was synthesised and characterised by following the procedure published in ref. [15].

Synthesis of di(benzothiazol-2-yl)phosphane (2): Tris(benzothiazol-2-yl)phosphane (12.00 g, 27.71 mmol) was dissolved in THF (60 mL) and allowed to react with an excess of elemental lithium. The colourless solution turned red. After two hours of stirring the remaining metal was removed and THF was replaced by diethyl ether. The solution was diluted with diethyl ether and dried over magnesium sulfate. Storing the solution at –40 °C yielded pale yellow needles (7.24 g, 87 %) suitable for single-crystal X-ray diffraction analysis. M.p. 102 °C; ^{1}H NMR (300.1 MHz, $C_4D_{10}O$): $\delta = 6.78$ (dd, $^3J_{H3,H4} = 7$ Hz, $^3J_{H5,H4} = 8$ Hz, 2H; H4, H11), 6.92 (dd, $^3J_{H4,H5} = 8$ Hz, $^3J_{H6,H5} = 8$ Hz, 2H; H5, H12), 7.22 (d, $^3J_{H5,H6} = 8$ Hz, 2H; H6, H13), 7.28 (d, $^3J_{H4,H3} = 7$ Hz, 2H; H3, H10) 8.05 ppm (d, $^3J_{P,H} = 8$ Hz, 1H; H2); ^{13}C NMR (75.5 MHz, $C_4D_{10}O$): $\delta = 121.6$ (s, 2C; C3, C10), 123.3 (s, 2C; C6, C13), 124.2 (s, 2C; C4, C11), 126.4 (s, 2C; C5, C12), 137.8 (s, 2C; C2, C9), 155.4 (s, 2C; C7, C14), 155.5 ppm (s, 2C; C1, C8); ^{31}P NMR: 6.81 ppm (s, 1P; P1); elemental analysis calcd (%) for **2**: C 55.99, H 3.02, N 9.33, S 21.35; found: C 56.25, H 3.31, N 9.20, S 20.77.

Synthesis of [{Cs(bth)$_2$P}$_n$] (3): Elemental caesium (1.00 g, 7.52 mmol) in diethyl ether (60 mL) was reacted with **2** (2.00 g, 6.66 mmol) in diethyl ether (60 mL) at –78 °C. The reaction mixture turned deep red while evolving gas. After the solution had been stirred for 4 h at this temperature it was allowed to warm up to ambient temperature. After the amount of solvent was reduced, the reaction mixture was stored at 4 °C. Red crystals (2.07 g, 73 %) suitable for single-crystal X-ray diffraction analysis were obtained. M.p. 234 °C (decomp); ^{1}H NMR (300.1 MHz, C_6D_6): $\delta = 6.92$ (ddd, $^3J_{H3,H4} = 7.44$ Hz, $^3J_{H5,H4} = 7.44$ Hz, $^4J_{H6,H4} = 1.14$ Hz, 2H; H4, H11), 7.12 (ddd, $^3J_{H4,H5} = 7.09$ Hz, $^3J_{H6,H5} = 8.14$ Hz, $^4J_{H3,H5} = 1.27$ Hz, 2H; H5, H12), 7.53 (d, $^3J_{H5,H6} = 8.14$ Hz, 2H; H6, H13), 7.60 ppm (d, $^3J_{H4,H3} = 7.44$ Hz, 2H; H3, H10); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 120.6$ (s, 2C; C3, C10), 121.0 (s, 2C; C6, C13), 125.2 (s, 2C; C4, C11), 126.8 (s, 2C; C5, C12), 131.8 (s, 2C; C2, C9), 155.1 (s, 2C; C7, C14), 156.9 ppm (s, 2C; C1, C8); ^{31}P NMR (121.5 MHz, H_3PO_4 (85 %)): $\delta = 14.23$ ppm (s, 1P; P1); elemental analysis calcd (%) for **3**: C 38.90, H 1.87, N 6.48, S 14.83; found: C 41.89, H 3.97, N 3.97, S 9.06.

Theoretical studies: Zero-temperature vacuum DFT calculations were performed by employing Becke's three-parameter exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP)[32,33] in combination with a 6-311++G** Gaussian basis set included in the Gaussian 98 program. No symmetry restrictions were imposed. Using the crystal structure coordinates of **2** as a starting point for geometry optimisations gave a planar configuration. The topological analyses were performed with the AIM2000 program package[34] by using the converged densities from the geometry optimisation.

Structure determination of 1–3: Crystallographic data for **1**–**3** are listed in Table 1. All data were measured at low temperature[35] by using graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda = 71.073$ pm) on a Bruker D8 goniometer platform, equipped with a Smart Apex CCD detector. Cell parameters were determined and refined by using the SMART software.[36] Series of ω scans were performed at several φ settings. Raw frame data were integrated by using the SAINT program.[37] The structures were solved by using direct methods and refined by means of full-matrix least-squares cycles on F^2 by using SHELXTL.[38] Data of **2** and **3** were empirically absorption corrected with SADABS 2.[39] The position of the hydrogen atom H2 at N2 in **2** was taken from the difference Fourier map and

Table 1. Crystallographic data for compounds **1**–**3**.

	1	**2**	**3**
formula	$C_{21}H_{12}N_3PS_3$	$C_{14}H_9N_2PS_2$	$C_{14}H_8CsN_2PS_2$
M_r [g mol^{-1}]	433.49	300.32	432.22
CCDC no.	618731	618732	618734
T [K]	173(2)	100(2)	173(2)
crystal system	rhombohedral	orthorhombic	orthorhombic
space group	*R*3*c*	*Pbca*	$Cmc2_1$
a [pm]	2009.6(3)	1460.7(5)	2579.61(15)
b [pm]	2009.6(3)	727.2(3)	732.46(4)
c [pm]	1552.4(3)	2447.8(8)	806.45(5)
V [nm^3]	5.429(2)	2.6001(16)	1.52376(15)
Z	12	8	4
ρ_{calcd} [Mg m^{-3}]	1.591	1.534	1.884
μ [mm^{-1}]	0.511	0.517	2.798
$F(000)$	2664	1232	832
crystal size [mm]	0.5 × 0.3 × 0.3	0.2 × 0.1 × 0.01	0.4 × 0.03 × 0.02
θ range [°]	3.35 to 25.01	2.17 to 25.04	2.89 to 26.37
reflections collected	11 162	15 966	6839
independent reflections	2240	2655	1719
absorption correction	–	empirical	empirical
max/min transmission	–	1.000/0.581	1.000/0.822
data/restraints/param.	2240/1/164	2292/0/175	1587/1/94
final R index [$I > 2\sigma(I)$]	0.0244	0.0561	0.0262
R index (all data)	0.0653	0.0926	0.0285
largest diff. peak/hole [e nm^{-3}]	299/–257	497/–335	758/–493
flack x parameter[40]	0.01(6)	–	0.02(2)

refined freely. All other hydrogen atom positions were refined by using a riding model. The U_{iso} values for the hydrogen atoms of a CH_3 group were set to 150 %, those of all other hydrogen atoms to 120 % of the U_{eq} values of the corresponding C atoms. All non-hydrogen atoms were refined anisotropically. The absolute structures of **1** and **3** were refined successfully by refining the Flack x parameter.[40] CCDC-618731, -618732 and -618734 (see Table 1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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