Ferrocenylmethylation reactions with a phosphinoferrocene betaine†

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A phosphinoferrocene betaine, \(N^\prime-\{(\text{diphenyolphosphino})\text{ferrocenyl}\}(\text{methyl})-N, N\)-dimethyl-3-sulfo-1-propanaminium, inner salt, \(\text{Ph}_2\text{PfcCH}_2\text{NMe}_2(\text{CH}_3)_2\text{SO}_3\) \((2; \text{fc} = \text{ferrocene}-1,1\text{-diyl})\), was prepared by alklylation of \(\text{Ph}_2\text{PfcCH}_2\text{NMe}_2\) \((1\) with 1,3-propanesultone, and was studied as a ferrocenylmethylation agent. The treatment of \(2\) with \(\text{NaOH}\) in hot water—dimethyl sulfoxide produced phosphinoalcohol \(\text{Ph}_2\text{PfcCH}_2\text{OH}\) \((3\) in a 64% yield, whereas a similar reaction with \(\text{MeONa}\) in dimethylsulfoxide—methanol furnished the corresponding ether, \(\text{Ph}_2\text{PfcCH}_2\text{OMe}\) \((4)\), in a 47% yield. In subsequent experiments, betaine \(2\) was employed in the synthesis of phosphinoferrocene sulfones, \(\text{Ph}_2\text{PfcCH}_2\text{SO}_2\text{R}\), where \(\text{R} = \text{Me} (6a), \text{Ph} (6b),\) and 4-tolyl \((6c)\). Compounds \(6a\)–c and some by-products of the ferrocenylmethylation reactions, namely alcohol \(3, 1\prime-\{(\text{diphenyolphosphino})\text{1-methylferrocene} (5)\), and \(1\prime-\{(\text{diphenyolphosphino})\text{ferrocene} (7)\) structurally characterised. Reactions of \(6a\) as the representative with \(\text{ZnX}_2/\text{NaX} (X = \text{Br} \text{and I})\) afforded unique coordination polymers \([\text{ZnNaX}_2(6a)(\text{CH}_3\text{OH})_n]\), featuring tetrahedral \(\text{Zn}(i)\) and octahedral \(\text{Na}(i)\) centres bridged by halide ions, solvating methanol and the sulfone ligands. The reaction of \(6a\) with \(\text{ZnBr}_2/\text{KBr}\) produced an analogous product, \([\text{ZnKBr}_3(6a)(\text{CH}_3\text{OH})_n]\), while that with \(\text{ZnBr}_2/\text{LiBr}\) furnished a different, pseudodimeric complex \([\text{Zn}_2\text{Li}_2\text{Br}_6(6a)_2(\text{CH}_3\text{OH})_4(\text{H}_2\text{O})]\), featuring tetrahedrally coordinated \(\text{Zn}(i)\) and \(\text{Li}(i)\) centres bridged by \(6a\). Reactions of \(6a\) with \(\text{ZnBr}_2/\text{MBr} (M = \text{Rb, Cs}\) and \(\text{NaCl}/\text{ZnCl}_2\) did not yield similar products because of an easy precipitation (low solubility) of the respective alkali metal halides.

In the synthesis of phosphinoferrocene donors, ferrocenylmethylation reactions have been applied only rarely because of competitive reactions affecting the phosphate moieties (alkylation). Therefore, the \([1\prime-\{(\text{diphenyolphosphino})\text{ferrocene-1-yl}\}-\text{methyl}\) derivatives have typically been synthesised either indirectly (e.g., via late-stage lithiation/phosphinylation) or from P-protected building blocks, such as \(\text{Ph}_2\text{P}[\text{fcCH}_2\text{O}]^+\) or the borane adduct \(\text{Ph}_2\text{PfcCH}_2\text{OH-BH}_3\). In view of our recent work focusing on the preparation and coordination properties of \(1\prime-\{(\text{diphenyolphosphino})\text{-1-\{(\text{dimethylamino})\text{methyl}\)}\text{ferrocene} (1)\), and other \(1\prime\)-functionalised phosphinoferrocene derivatives possessing an inserted methylene group, we wanted to extend the hitherto explored synthetic chemistry of the former compound, which led us to attempt the preparation of ammonium salts derived from \(1\) and study their prospective synthetic applications. In this contribution, we describe the selective synthesis and structural characterisation of the phosphinoferrocene betaine \(\text{Ph}_2\text{PfcCH}_2\text{NMe}_2(\text{CH}_3)_2\text{SO}_3^- (2; \text{fc} = \text{ferrocene}-1,1\text{-diyl})\) and its utilisation in the preparation of the known and some new \(1\prime\)-functionalised phosphinoferrocene donors such as \(1\prime-\{(\text{diphenyolphosphino})\text{ferroceny}l\text{methyl} \}\text{sulfones} \(\text{Ph}_2\text{PfcCH}_2\text{SO}_2\text{R}\). Furthermore, we report on the reactions of the representative ligand, \(\text{Ph}_2\text{PfcCH}_2\text{SO}_2\text{Me}, \) with zinc(i) and alkali metal...
Results and discussion

Synthesis of betaine 2 and initial reaction tests

Betaine 2 was synthesised similarly to its non-phosphinylated analogue (Scheme 1)\textsuperscript{13} by the reaction of phosphinoamine 1\textsuperscript{10} with 1,3-propanesultone (1,2-oxathiolane-2,2-dioxide) in dry benzene. The compound was isolated by column chromatography, resulting as an air-stable orange solid in an 81\% yield (at the 10 mmol scale).\textsuperscript{14} Crystallisation from methanol–tetrahydrofuran–diethyl ether afforded the stoichiometric solvate 2·CH\textsubscript{3}OH, which was structurally characterised by single-crystal X-ray diffraction analysis (\textit{vide infra}).

The \textsuperscript{1}H and \textsuperscript{13}C NMR spectra of 2 combine the signals due to the phosphinoferrocenyl moiety with those of the NMe\textsubscript{2} group and the propane-1,3-diyl bridge. The \textsuperscript{31}P NMR resonance is observed at $\delta_P -18.1$ ppm, suggesting that the phosphine moiety remained intact. In its IR spectrum, betaine 2 shows strong signals attributable to the vibrations of the terminal sulfonate moiety ($\nu_s 1037$ cm\textsuperscript{-1} and $\nu_{as} 1189$ cm\textsuperscript{-1}), whereas the electrospray ionisation (ESI) mass spectrum reveals signals of the pseudomolecular ions [M + X]+, where M = H, Na, and K, and of the characteristic fragment\textsuperscript{15} ions due to the substituted ferrocenylmethylium cation [Ph\textsubscript{2}PfCH\textsubscript{2}]\textsuperscript{+} at $m/z$ 383.

The possible synthetic applications of betaine 2 were first examined by its conversion into the known alcohol 3\textsuperscript{12a} and the corresponding methyl ether 4\textsuperscript{9} \textit{via} reactions with the respective nucleophiles (Scheme 1). These ferrocenylmethylation reactions were carried out similarly to the literature\textsuperscript{13,16} but carefully optimised. For solubility reasons, dimethyl sulfoxide was chosen as the solvent, and the reactions were performed at temperatures above 100 °C since lower reaction temperatures markedly reduced the yield of the substitution product (N.B. unreacted 2 could be recovered from the reaction mixture in such cases). The reaction time was maintained at minimum (typically 1 h) in order to prevent decomposition and oxidation of the phosphate moiety.

For the preparation of alcohol 3, the best reaction conditions were found to consist of refluxing the solution of betaine 2 in a mixture of DMSO and 2 M aqueous NaOH (1 : 1; the concentration of NaOH in the resulting solution was 1 M) for 1 h. Product 3 was isolated by extraction and purified by column chromatography, resulting in a 64\% yield (at the 2 mmol scale). A small amount of a less polar side-product was also isolated, being identified as 1′-(diphenylphosphino)-\textsuperscript{1}-methyl-ferrocene, Ph\textsubscript{2}PfMe (5; typically ca. 5\%). This rather unexpected product probably results \textit{via} “quenching” of the intermediate cation Ph\textsubscript{2}PfCH\textsubscript{2}+ upon attack of other C–H bonds (acid–base equilibria) rather than by interaction with any proton source in the reaction system.

The etherification reaction was similarly performed in a mixture of dimethyl sulfoxide and methanolic MeONa (1 M MeONa in the reaction system) at lower temperatures (but still under reflux conditions) for 2 h, affording phosphinoether 4 in a 47\% isolated yield.

The crystal structures of 2·CH\textsubscript{3}OH and 5

The solvate 2·CH\textsubscript{3}OH, isolated after crystallisation by liquid-phase diffusion of tetrahydrofuran and diethyl ether into a solution of the betaine in methanol, crystallises with the symmetry of the triclinic space group \textit{P}1\textbar. Its structure is presented in Fig. 1, and the relevant geometric data are summarised in Table 1.

Fig. 1. PLATON plot of the phosphinobetaine molecule in the structure of 2·CH\textsubscript{3}OH showing the atom-labelling scheme and displacement ellipsoids at a 30\% probability level.
The ferrocene unit in the structure of \( \text{2} \) shows similar Fe–C distances \( (2.019(1)–2.051(1) \, \text{Å}) \) and, accordingly, practically negligible tilting (the dihedral angle of the least-squares planes of the cyclopentadienyl ring is \( 1.40(8)° \)). The substituents attached to the ferrocene moiety adopt a nearly ideal synclinal eclipsed conformation, as evidenced by the torsion angle \( C1–C1g1–Cg2–C6 \) of \( -73.49(9)° \) (cf. the ideal value of \( 72° \)).

The carbons surrounding the positively charged nitrogen atom in \( \text{2} \) constitute a regular tetrahedral environment, with the C–N distances and associated bond angles (C–N–C) in the range of \( 1.497(2)–1.525(2) \, \text{Å} \) and 106.3(1)–111.0(1)°, respectively. The environment of the sulfur atom is somewhat distorted, presumably because of the different sizes of the bonded atoms and, also, a repulsion of the oxygen atoms (S-C > S=O and O=S=O > C=S=O; see parameters in Table 1).

The individual molecules constituting the crystals of \( \text{2-CH}_3\text{OH} \) assemble into dimers of inversion-related molecules through charge-supported hydrogen bonds between two oxygen atoms of the negatively charged sulfonate group and the \( \text{CH}_3 \) hydrogens polarised by the positively charged nitrogen atom (Fig. 2). The solvating methanol forms an O–H⋯O hydrogen bond with the remaining sulfonate oxygen. Additional C–H⋯O interactions further interconnect the \( (\text{CH}_3\text{OH})_2 \) units into columnar stacks oriented along the crystallographic \( a \)-axis.

The solid-state structure of 5 (Fig. 3) resembles that of the corresponding borane adduct \( 5\text{BH}_3 \).\(^9\) Whereas the C1–C11 bond lengths \( (1.497(2) \, \text{Å}) \) in both compounds are practically identical (within the three-sigma level), the P–C bonds in 5 \( (\text{P}-\text{C}6 1.810(2), \text{P}-\text{C12} 1.841(2), \text{P}–\text{C18} 1.834(2) \, \text{Å}) \) are slightly but statistically significantly longer (by ca. 0.02 Å) than those in the mentioned reference compound, reflecting the electronic changes associated with the adduct formation \( (\text{R}, \text{P} \rightarrow \text{BH}_3) \). The Fe–C distances in the molecule of 5 span a narrow range of \( 2.037(1)–2.051(2) \, \text{Å} \), which is in turn reflected in an insignificant tilting of the cyclopentadienyl rings (the tilt angle is as low as \( 1.1(1)° \)). As indicated by the torsion angle \( C1–Cg1–Cg2–C6 \) of \( -77.8(1)° \), the ferrocene unit has a synclinal eclipsed conformation, which is also similar to that of the aforementioned borane adduct.

**Synthesis and characterisation of phosphine-sulfoxones 6**

Aiming at the preparation of new phosphinoferrocene ligands \( \text{via} \) ferrocenylmethylation, betaine 2 was subsequently reacted with sodium sulfinates to give the respective phosphino-ferrocene sulfoxones 6 (Scheme 2). The reactions were performed with an excess of the sulfinate salts \( (2 : \text{RSO}_2\text{Na} = 1 : 2.5) \) in refluxing DMSO-water for 2 h, similarly to the synthesis of ferrocenylmethyl sulfoxides \( \text{FeCH}_2\text{SO}_2\text{R} \) from simple ferrocenylmethylation agents.\(^{13,17}\)
The yields of the sulfones after chromatographic purification were ca. 30% for 6a and approximately 50% for the compounds bearing the aromatic substituents (6b and 6c), which are less than in the reactions leading to FcSO2R. Therefore, we sought for other reaction products to gain more detailed information regarding the course of these particular ferrocenylmethylation reactions.

In the case of the reaction of betaine 2 with MeSO2Na, a careful chromatographic purification of the reaction mixture led to the isolation of alcohol 3 (2%) and phosphonium 7 (Scheme 3; 12%). Together with 6a, compounds 3 and 7 account for nearly 45% of the starting material. The reactions leading to aryl sulfones 6b and 6c are more selective (isolated yields: ca. 50%) but afford identical by-products (isolated yields of 3 and 7 are ca. 3% and 10–15%, respectively). Apparently, the cation Ph2PfcCH2\(^+\) generated in situ from 2 enters into reactions with all other available nucleophiles, including OH\(^-\) or phosphines. Interaction with the latter provides ionic products (i.e., phosphonium salts arising from “self-alkylation” of the parent 2 with Ph2PfcCH2\(^+\)) and, consequently, also their decomposition products such as 7. The fact that no 7 could be detected in the reaction mixtures obtained after treatment of 2 with NaOH and NaOMe (vide supra) can well reflect the higher relative amounts of these nucleophilic reagents, that suppress the competing reactions with other nucleophiles. Attempts to isolate the anticipated cationic (and hence more polar) side products or to recover unreacted 2 during the course of chromatographic purification of crude sulfones 6 failed.

The formulation of 6a-c and 7 was inferred from NMR and IR spectra, ESI mass spectra, and elemental analysis and was unequivocally confirmed by single-crystal X-ray diffraction. The NMR spectra of sulfones 6 comprise the signals due to the (diphenylphosphino)ferrocenyl unit and its attached methylene linker (CH2: \(\delta_{\text{H}}/\delta_{\text{C}}\) 3.59/36.65 for 6a, and ca. 3.68/58.3 for 6b and 6c). The signals of the sulfone substituents, as well as the \(^{31}\text{P}\) NMR resonances (\(\delta_{\text{P}}\approx -17\text{ ppm}\)), are observed in the usual ranges. The IR spectra of the sulfones display the characteristic strong bands of the sulfone moieties centred at approximately 1310 (\(\nu_{\text{as}}\)) and 1145 cm\(^{-1}\) (\(\nu_{\text{s}}\)).\(^{17a}\)

The \(^1\text{H}\) and \(^13\text{C}\) NMR spectra of the by-product 7 contain signals of the 1,1'-disubstituted ferrocene moiety and two sets of resonances of the non-equivalent PPh2 groups, which is also reflected in the \(^{31}\text{P}\) NMR spectrum showing two singlets at \(\delta_{\text{P}}\approx 16.9\) and 10.1. The presence of the cyclopentadienylidene unit\(^{18}\) in 7 is manifested by a pair of triplets at \(\delta_{\text{H}}\) 6.12 and 6.40 and a pair of doublets at \(\delta_{\text{C}}\) 13.92 and 115.83 in the \(^1\text{H}\) and \(^13\text{C}\) NMR spectra, respectively. The \(^13\text{C}\) NMR signal due to Cipso in the P=C\(_2\)H4 moiety is observed at \(\delta_{\text{C}}\) 78.21 as a phosphorus-coupled doublet (\(^{3}J_{\text{PC}} = 110\text{ Hz}\)). The signals of the connecting methylene group are found at \(\delta_{\text{H}}\) 3.59 (doublet with \(^{3}J_{\text{PH}} = 12.7\text{ Hz}\)) and \(\delta_{\text{C}}\) 30.01 (dd, \(^{3}J_{\text{PC}} = 53, ^{3}J_{\text{PFc}} = 1\text{ Hz}\)).

Crystallisation of 6a from ethyl acetate–hexane provided crystals of a triclinic modification (denoted as 6a). Crystals of another polymorph, 6a’, were serendipitously isolated during an attempted preparation of Zn(n) complexes, i.e., upon crystallization of a 6a/ZnBr2 mixture from methanol–diethyl ether (vide infra). The polymorphs differ by the symmetry of the crystal lattice (6a: triclinic, \(P\overline{1};\) 6a’: monoclinic, \(P2_1/c\)) and by the overall conformation of the molecules constituting their crystals (Fig. 4 and Table 2).

![Scheme 3](image_url)  
**Scheme 3** Canonical forms of compound 7.

![Fig. 4](image_url)  
**Fig. 4** PLATON plots of the molecular structures of the triclinic (top; 6a) and monoclinic (bottom; 6a’) polymorphs of 1-[(diphenylphosphino)-1-[(methy1sulfonyl)methyl]ferrocene. The displacement ellipsoids enclose the 30% probability level.
Thus, whereas the molecular structures of the two polymorphs are expectedly very similar in terms of interatomic distances and angles, they differ in the mutual orientation of the substituted cyclopentadienyl rings, which are nearly synclinal eclipsed in 6a and exactly halfway between anticalinal eclipsed and antiperiplanar staggered in 6a’ (compare the C1–Cg1–Cg2–C6 angles in Table 1).19 Another less pronounced difference can be observed in the orientation of the PPh2 units resulting from different rotations along the pivotal C6–P bond and from the tilting of the phenyl rings.

The geometry of the (methylsulfonyl)methyl moiety in 6a and 6a’ agrees well with that of, e.g., phenyl methyl sulfone, 4-methoxyphenyl methyl sulfone,20 and (benzylsulfonyl)-methanol.21 Similar to these compounds, the O1–S–O2 angle is the most opened and the C11–S–C24 angle is the most acute among the bond angles around the sulfur atoms in 6a and 6a’, most likely due to an electrostatic repulsion of the electronegative oxygen atoms.

The main difference between the molecular structures of sulphones 6b and 6c (Fig. 5 and Table 2) can also be found in the conformation of the 1,1′-disubstituted ferrocene unit, which is intermediate between anticalinal staggered and anticalinal eclipsed for 6b and synclinal eclipsed for 6c. In both cases, the CH2SO2Ar (Ar is an aryl) moieties extend away from the ferrocene core but adopt different orientations as indicated by the torsion angle C1–C11–S–C24 (see Table 2) and the dihedral angles of the C(1–5) and C(24–29) ring planes of 45.93(8)° and 33.5(1)° for 6b and 6c, respectively. On the other hand, the PPh2 units and the dihedral angles suggest different orientations of the PPh2 units resulting from different rotations along the pivotal C6–P bond and from the tilting of the phenyl rings.

The ferrocene cyclopentadienyls in the structure of byproduct 7 (Fig. 6) are tilted by 2.6(1)° and assume a conformation near synclinal eclipsed, as evidenced by the C1–Cg1–Cg2–C6 torsion angle of 79.3(1)°. The individual Fe–C distances are in the range of 2.026(2)–2.050(2) Å. The cyclopenta-
The similar bond in the phosphonium salt [FcPPh2(CH2Ph)]Cl
length of the P2 rings to the partly positively charged P2. In contrast, the P2 length to those in MePh2P
metal cation in ZnBr2/MBr (M = Li, Na, K, Rb, and Cs).

1.839(2), P1 1.382(3), C33 crystals of monoclinic 6a 
1:1 molar ratio in methanol 
avigation to the preparation of a Zn(II) complex by reacting ZnBr2 and 
halides with 6a via 

The reactions of 6a with ZnBr2 with other alkali metal bromides were performed similarly to the preparation of the mentioned Na–Zn complexes but in solvent mixtures with an optimised chloroform/methanol ratio to ensure sufficient solubility of the alkali metal halide and not suppress separation of the product after the addition of methyl tert-butyl ether. Attempted reactions with RbBr and CsBr did not afford any M–Zn complex because these salts separated from the reaction mixture, whereas the analogous reaction of 6a with ZnBr2 and KBr produced K–Zn complex 9a (Scheme 4), which adopts the structure of its sodium congener. In contrast, the reaction 6a with ZnBr2 and LiBr produced a Zn–Li complex [ZnLi2·Br6(6a)2(CH3OH)(H2O)]·CH3OH (10a·CH3OH). In its structure, the phosphinoferrocene ligands coordinate the terminal ZnBr2 units via their phosphate groups (similarly to the mentioned Na–Zn and K–Zn complexes) and further bind solvated Li+ ions via the sulfone oxygens to form a discrete pseudodimeric assembly (Scheme 5).

The M–Zn complexes (M = alkali metal cation) disintegrate upon dissolving in donor solvents. This was evidenced by the 1H and 31P[1H] NMR spectra recorded for solutions of crystal-
line 8a in CD$_3$OD that reveal the exclusive presence of uncoordinated 6a in solution ($\delta_p$ $-16.3$ ppm) and also by the ESI mass spectra showing only signals due to 6a and its fragments (see Experimental). The same applies to the elusive 6a-ZnBr$_2$ complexes (intermediates) as similar features have been observed in the NMR and ESI MS spectra of a residue obtained by evaporation of a 1:1 mixture of 6a-ZnBr$_2$. Hence, the characterisation of the mixed-metal complexes had to be confined to solid-state techniques. Nonetheless, unequivocal structural information was gained (see Experimental). The same applies to the elusive mass spectra showing only signals due to coordinated 6a.

Nonetheless, unequivocal structural information was gained from single-crystal X-ray diffraction analysis. Compounds 8a and 8b were very similar, suggesting analogous structures for these compounds, and displayed additional broad bands attributable to $\nu_{OH}$ vibrations at ca. 3470–3490 cm$^{-1}$, attributable to the “solvating” methanol. Nonetheless, unequivocal structural information was gained from single-crystal X-ray diffraction analysis.

Compounds 8a and 8b are essentially isostructural, and the minor differences in the lattice parameters and atomic coordinates are associated with the different sizes of the halide anions. Compound 9a also has practically the same structure, albeit described by different cell parameters because even a small variation in the cell angles near 90° as in this particular case can result in another reduced triclinic cell setting. The structure of 8a is depicted in Fig. 7, and the displacement ellipsoid plots for all three compounds are presented in the ESI (Fig. S2–S4†). Pertinent geometric parameters are given in Table 3.

Compounds 8a and 8b are one-dimensional coordination polymers in which the ZnX$_3$(6a-KP) units coordinate the Na(i) ions via two halide ions (bridging X2 and X3) and the sulfate oxygen O1. The coordination sphere of the Na(i) ion is completed by the sulfone O2 located in an adjacent ZnX$_3$(6a-KP) moiety, related by crystallographic inversion, and also by a methanol molecule and its inversion-related counterpart. The solvating methanol further stabilises the structure through a hydrogen bond with the Zn-bound halide (O1S⋯H1O).

The Zn(i) ions in the structures of 8a and 8b have the usual, albeit distorted, tetrahedral donor environment (donor set: PX$_3$), where two Zn-X distances are somewhat shorter than the remaining one (Zn–X1/2 < Zn–X3). The associated interligand angles increase in the following order: X1–Zn–X3 < X2–Zn–X3 < X1–Zn–X2 < X3–Zn–P (cf. the ranges of 102.64(2)–114.50(2)$^\circ$ and 101.61(1)–114.68(3)$^\circ$ for 8a and 8b, respectively). In contrast, the sodium cation, as the second metal centre in the structures, has an unsymmetric octahedral coordination (donor set: cis-X$_2$O$_4$), wherein the extreme Na-donor distances differ by ca. 0.8 and 1.1 Å and the interligand angles (cis-only) span the ranges of 78.25(7)–101.12(8)$^\circ$ and 77.1(1)–104.7(1)$^\circ$ for 8a and 8b, respectively. In both cases, the Na atoms appear displaced from the geometrical centre of the octahedron towards O1S$^{ii}$ and O2$^{ii}$ in heavily twisted pseudoequatorial planes {Na, X2, X3, O1S$^{ii}$/iv, O2$^{ii}$/iv}. The observed angular distortions of the coordination spheres around both the Zn(ii) and Na(i) ions appear to result from an interplay between the unlike metal–donor distances, steric requirements of the individual donors, constraints imposed by the doubly bridged fragments [Zn(μ-Br)$_2$Na and Na(μ-CH$_3$OH)$_2$Na], and the hydrogen-bond interactions.

### Table 3 Selected distances and angles for 8a, 8b, and 9a (in Å and $^\circ$)*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>8a (M/X = Na/Br)</th>
<th>8b (M/X = Na/I)</th>
<th>9a (M/X = K/Br)</th>
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<td>2.6610(4)</td>
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<td>3.3218(6)</td>
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<td>2.399(3)$^a$</td>
<td>2.730(2)$^a$</td>
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</table>

*a For definitions, see the footnote to Table 2. Symmetry codes: (i) $2-x,-y,-z$, (ii) $1-x,-y,-z$, (iii) $1-x,1-y,-z$, (iv) $-x,1-y,-z$. 

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*Fig. 7 Section of the infinite coordination chain in the structure of 8a (for a conventional displacement ellipsoid plot; see the ESI†). For clarity, the CH hydrogens are omitted, and the CH$_2$OH–Br hydrogen bond is indicated by a red dotted line (O1S⋯Br1 = 3.599(2) Å). The corresponding distance in the structures of 8b and 9a are as follows: 8b, O1S⋯I1 = 3.828(3) Å; 9a, O1S⋯Br1 = 3.540(2) Å.*
As indicated above, the structure of 9a is very similar to its Na congener 8a, with the observed differences reflecting the larger size of the alkali metal cation present in the structure. The geometry of the PZnBr₃ moiety remains virtually unchanged upon going from 8a to 9a; the interligand angles span the range 102.97(1)–113.11(2)° and follow the trend described for 8a though not with the same differences between the individual values. Although the overall coordination environment of the K⁺ ion also remains seemingly the same (cis-interligand angles: 74.02(1)–107.97(5)°), the coordination sphere is expanded because of the longer potassium-donor bonds (by approximately 0.21–0.34 Å in the respective pairs).

The structure of 10a·CH₃OH (Fig. 8, parameters in Table 4) reveals that the replacement of Na⁺ with the Li⁺ ion, which is smaller and prefers a tetrahedral coordination environment, results in an opening of the polymeric structure and incorporation of solvent molecules as additional donors into the structure. One of the Li⁺ cations (Li1) is coordinated by a sulfonate oxygen (O2) and three methanol molecules (O1S, n = 1–3) constituting a tetrahedral donor set. The other Li⁺ cation (Li2) has a similar coordination, binding two sulfonate oxygens (from different molecules of 6a), methanol (O4S) and water molecule (O1W). It is noteworthy that the asymmetric environment of the sulfur atoms renders the structure chiral.

On the other hand, the halide anion is transferred to the zinc(ii) centre, which thus gains a distorted tetrahedral PBr₄ coordination as observed for the Na/K–Zn complexes discussed above. Both ZnBr₃ units in the structure of 10a assume a sterically loose staggered orientation with respect to their bonding PC₃ moieties and do not exert any pronounced angular distortion (cf. the interligand angles ranging 105.64(4)–114.28(4)° for Zn1 and 104.54(3)–112.79(4)° for Zn2).

### Conclusion

Alkylation of phosphinoamine 1 with 1,3-propanesultone proceeds selectively under alkylation of the hard nitrogen group to afford the quaternary ammonium salt 2. Betaine 2, possessing an intact phosphine substituent, is an attractive functionalised starting material for ferrocenylmethylation reactions with nucleophiles, which was demonstrated in this paper by model reactions leading to 3 and 4, and by the synthesis of the phosphinosulfones 6 representing new entries among hybrid phosphinoferrocene donors possessing flexible methylene spacers.6–11 Compound 6a, chosen as a representative phosphinosulfone donor, was shown to form unprecedented alkali metal–Zn coordination polymers of the general formula [ZnMX₄(CH₃OH)₄](M/X = Na/Br, Na/I, and K/Br), in which the ferrocene-based ligand coordinates the softer Zn(ii) ion via its phosphine substituent and the alkali metal cation through the sulfone oxygen atoms, while the methanol molecules complete octahedral coordination around the alkali metal ions. These compounds are zwitterions combining negatively charged ZnBr₃ units with cationic centres represented by the alkali metal cations in their structures. In the case of ZnBr₂–LiBr, the analogous reaction with 6a provides [Br₂Zn(6a)Li₂(CH₃OH)₄(H₂O)(6a)ZnBr₃] (methanol solvate), a pseudodimeric complex comprising two chemically different, tetrahedral Li⁺ centres coordinated by the sulfonate oxygens, solvating methanol and a water molecule, and the phosphine-coordinated ZnBr₃ units.

### Experimental

#### Materials and methods

All reactions were performed under an argon atmosphere by standard Schlenk techniques. Amine 1 was prepared as reported previously.10 Benzene and chloroform were dried by standing over sodium metal and CaH₂, respectively, and distilled under argon. Dimethyl sulfoxide was distilled under vacuum. Methanol was dried with an in-house PureSolv MD5
solvent-drying system (Innovative Technology, USA). A solution of sodium methoxide was prepared by dissolving the appropriate amount of sodium metal in anhydrous methanol. Other chemicals and solvents were obtained from commercial suppliers (Sigma-Aldrich or Lachner, Czech Republic) and were used without any additional purification.

NMR spectra were recorded at 25 °C on a Varian Unity INOVA spectrometer operating at 399.95 MHz for 1H, 100.58 MHz for 13C, and 161.92 MHz for 31P. The chemical shifts (δ in ppm) are given relative to internal tetramethylsilane (1H and 13C) or to external 85% aqueous H3PO4 (31P). IR shifts (in cm−1) are indicated as follows: s (strong), v (very), m (medium), w (weak), and vw (very weak).

Analytical data for betaine 2. A solution of propane-1,3-sultone (1.221 g, 10 mmol) in dry benzene (30 mL) was slowly introduced into a solution of amine 1 in the same solvent (4.272 g, 10 mmol in 20 mL). The resultant mixture was stirred at room temperature overnight (15 h), during which time a fine yellow precipitate deposited. The reaction mixture was diluted with methanol (50 mL) and carefully evaporated. The residue was purified by column chromatography over silica gel, eluting first with dichloromethane–methanol (5:1) to remove the less polar impurities. The polarity of the eluent was then increased (dichloromethane–methanol 3:1) to elute a salt containing the protonated amine 1 as the cation, very likely hydrochloride [HCl][Cl]. Finally, the eluent was changed to dichloromethane–methanol 1:1, which removed the major orange band of the desired product. Following evaporation and drying under vacuum over sodium hydroxide, betaine 2 was isolated as an air-stable orange solid (4.476 g, 81%). An analytical sample, in vacuo over sodium hydroxide, betaine 2 was identified by NMR spectroscopy.12

Analytical data for 5. 1H NMR (CDCl3): δ 1.81 (s, 3 H, CH3), 3.92 (vt, J′ = 1.8 Hz, 2 H), 3.99 (vt, J′ = 1.8 Hz, 2 H), 4.00 (vt, J′ = 1.9 Hz, 2 H) and 4.29 (vt, J′ = 1.9 Hz, 2 H) ppm. 13C{1H} NMR (CDCl3): δ 11.75 (s), 25.36 (s), 28.81 (s), 36.60 (s), 47.97 (s), 72.04 (s), 128.21 (s), 139.24 (s), 191.27 (s) ppm. The signal of CH3SiH2 was obscured by the solvent resonance. MS (ESI+): m/z 200 [Ph2PfCH3]+, 384 [Ph2PfCH2Si]++. Anal. calc. for C14H15FeP (357.3): C 71.83, H 5.64%. Found: C 71.72, H 5.41%.

Preparation of ether 4. Betaine 2 (1.101 g, 2.0 mmol) was dissolved in dimethyl sulfoxide (25 mL) at 100 °C, and the solution was treated with 2 M MeONa in methanol (25 mL). The resulting mixture was heated under reflux for 2 h and cooled to room temperature. Then, it was diluted with water (50 mL) and extracted with dichloromethane (3 × 50 mL). The organic extracts were washed with water (2 × 200 mL), dried over magnesium sulfate, and evaporated. The crude product was purified by chromatography over a silica-gel column using diethyl ether–hexane 1:1 as the eluent. The major band due to the product was collected and evaporated under vacuum to yield ether 4 as a yellow-orange solid. Yield: 388 mg (47%). The NMR spectra of the product were identical with those reported in the literature.13

Preparation of 6a. A solution of sodium methanesulfinate (0.534 g, 5.0 mmol) in degassed water (25 mL) was added to a
solution of betaine 2 (1.097 g, 2.0 mmol) in dimethylsulfoxide (25 mL) kept in an oil bath preheated to 130 °C. The resulting solution was heated under reflux for 2 h, whereupon it turned brown, and a yellow-brown precipitate separated. The reaction mixture was cooled to room temperature, diluted with water (50 mL), and extracted with dichloromethane (3 × 50 mL). The combined organic layers were diluted with dichloromethane (50 mL), washed with water (2 × 200 mL), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was purified by chromatography over a silica-gel column, first using dichloromethane–methanol 50:1 to elute the main orange band of 6a and a small tailing band containing alcohol 3. The mobile phase was then changed to dichloromethane–methanol 20:1, which led to the development of an additional broad yellow band containing the side product 7. The complete separation of 3 and 6a was achieved through additional chromatography over silica gel using ethyl acetate/hexane. Yields: 6a – off-white solid (272 mg, 29%); 3 – orange, slowly crystallising oil (14 mg, 2%); and 7 – rusty brown oil (74 mg, 12%).

Analytical data for 6a. 1H NMR (CDCl3): δ 6.26 (s, 3 H, SO2Me), 3.59 (s, 2 H, C2H5CH2), 4.10 (vq, 1H, 1.8 Hz, 2 H) 4.19 (vt, 1H, 1.9 Hz, 2 H), 4.26 (vt, 1H, 1.9 Hz, 2 H) 4.40 (vt, 1H, 1.8 Hz, 2 H) (4 × CH in fc); 7.31–7.41 (m, 10 H, PPh2), 71.73 (s, CH of fc), 71.49 (s, CH of PPh2), 70.59 (s, CH of CH2C5H4), 71.07 (s, CH of CH2C5H4), 71.73 (d, 3JPC = 15 Hz, β-CH of PCH2), 3.83 (d of vt, J = 53 Hz, 2 H) (4 × CH in fc); 6.12 (m, 2 H, α-CH of P = C2H5), 6.40 (m, 2 H, β-CH of P = C2H5), 7.25–7.35 (m, 10 H, fcpPh2), 7.41–7.47 (m, 8 H, CHortho and CHmeta of PCH2Ph), 7.55–7.61 (m, 2 H, CHpara of CH2PPh2), 31P{1H} NMR (CDCl3): δ −169.6 (s, fcpPh2), 10.1 (s, CH2P–C5H4). 13C{1H} NMR (CDCl3): δ 30.01 (dd, 3JPC = 53 Hz, JPC = 1 Hz, PCH2), 69.50 (s, CH of fc), 71.49 (s, CH of fc), 71.77 (d, 3JPC = 4 Hz, CH of fc), 73.89 (d, 3JPC = 15 Hz, CH of fc), 77.42 (d, 3JPC = 2 Hz, Cipso of fc), 78.21 (d, 3JPC = 110 Hz, Cipso of P = C2H5), 113.92 (d, 3JPC = 18 Hz, α-CH of P = C2H5), 115.83 (d, 3JPC = 15 Hz, β-CH of P = C2H5), 125.49 (d, 3JPC = 86 Hz, Cipso of CH2PPh2), 128.19 (d, 3JPC = 7 Hz, CHmeta of CH2PPh2), 128.59 (d, 3JPC = 12 Hz, CHortho of fcpPh2), 126.63 (s, CHpara of fcpPh2), 132.54 (d, 3JPC = 3 Hz, CHpara of CH2PPh2), 133.37 (s, CHmeta of fcpPh2), 133.52 (d, 3JPC = 10 Hz, CHortho of CH2PPh2), 138.85 (d, 3JPC = 10 Hz, Cipso of fcpPh2). MS (ESI+): m/z 383 [(PbPfC6H5)]+, 633 [(7 + H)]+. HRMS (APCI+) calc. for C40H35FeP2([M + H]+): 633.1558, found: 633.1561. Anal. calc. for C40H34FeP2·1/8CHCl3 (647.4): C 74.44, H 5.31%. Found: C 74.30, H 5.38%.

Preparation of 6b. Betaine 2 (2.0 mmol) was dissolved in dimethylsulfoxide (25 mL) and the reaction flask was transferred to an oil-bath preheated to 130 °C. After stirring for several minutes at this temperature, an aqueous solution of the corresponding sulfinate (5.0 mmol in 25 mL of degassed water) was added, and the resultant mixture was heated under reflux for 2 h (an orange precipitate separated). The reaction mixture was cooled to room temperature, diluted with water (50 mL), and extracted with dichloromethane (3 × 50 mL). The combined organic layers were diluted with dichloromethane (50 mL), washed with water (2 × 200 mL), dried over magnesium sulfate, and evaporated under vacuum. The products were isolated by column chromatography over silica gel. Initial elution with dichloromethane–methanol 50:1 produced a major orange band due to sulfoxide 6b, followed by a minor band of alcohol 3. Subsequent elution with dichloromethane–methanol 20:1 led to the development of a broad yellow band containing crude 7. Compound 3 was further purified as described above (see the preparation of 3). Particular details are as follows.

The reaction of 2 (1.099 g, 2.0 mmol) with sodium phenylsulfinate [0.838 g, 5.0 mmol] as described above yielded 6b (yellow solid; 524 mg, 50%), 3 (14 mg, 2%), and 7 (61 mg, 10%). Starting with 2 (1.095 g, 2.0 mmol) and sodium 4-toluenesulfinate [0.937 g, 5.0 mmol], an analogous procedure produced 6c (yellow solid; 570 mg, 53%), 3 (25 mg, 3%), and 7 (98 mg, 16%).

Analytical data for 6b. 1H NMR (CDCl3): δ 3.68 (s, 2 H, C2H5CH2), 3.94 (vt, J = 1.9 Hz, 2 H), 4.02 (vq, 1H, 1.8 Hz, 2 H), 4.05 (vt, 1H, 1.9 Hz, 2 H) and 4.32 (vt, J = 1.8 Hz, 2 H) (4 × CH of fc); 7.28–7.35 (m, 10 H, PPh2), 7.42–7.47 (m, 2 H, SO2Ph), 7.57–7.62 (m, 3 H, SO2Ph). 31P{1H} NMR (CDCl3): δ −16.9 (s, 1C{1H} NMR (CDCl3): δ 58.23 (s, C2H5CH2), 70.16 (s, CH of CH2C5H4), 71.30 (s, CH of CH2C5H4), 71.52 (d, 3JPC = 4 Hz, β-CH of PC6H5), 73.81 (d, 3JPC = 15 Hz, α-CH of PC6H5), 74.68 (s, Cipso of CH2C5H4), 76.79 (d, 3JPC = 7 Hz, CHmeta of PPh2), 128.24 (d, 3JPC = 7 Hz, CHortho of PPh2), 128.69 (s, CHortho and CHmeta of SO2Ph + CHpara of PPh2), 133.44 (d, 3JPC = 20 Hz, CHpara of PPh2), 133.51 (s, CHpara of SO2Ph), 137.84 (s, Cipso of SO2Ph), 138.73 (d, 3JPC = 10 Hz, Cipso of PPh2). IR (Nujol): νmax 2723 vw, 2667 vw, 1583 vw, 1568 vw, 1400 w, 1311 s, 1304 vs (vC=O), 1288 s, 1263 w, 1240 w, 1192 w, 1119 s, νC=O (SO2), 1122 s, 1099 s, 1084 s, 1069 s, 1058 s, 1038 s, 983 s, 928 s, 903 s, 835 s, 788 s, 750 s, 742 vs, 704 s, 697 vs, 630 w, 618 w, 603 w, 569 w, 529 m, 510 s, 486 s, 479 vs, 455 s, 441 m, 406 vw cm−1. MS (ESI+): m/z 383 [(PbPfC6H5)]+, 633 [(7 + H)]+. HRMS (APCI+) calc. for C40H34FeP2([M + H]+): 633.1558, found: 633.1561. Anal. calc. for C40H34FeP2·1/8CHCl3 (647.4): C 74.44, H 5.31%. Found: C 74.30, H 5.38%.
C25H25FeO2PS (524.4): C 66.42, H 4.81%. Found: C 66.20, H 4.80%.

**Analytical data for 6c.** $^1$H NMR (CDCl$_3$): $\delta$ 2.43 (s, 3 H, C$_6$H$_3$(CH$_2$)$_3$), 3.67 (s, 2 H, C$_6$H$_2$(CH$_2$)$_3$), 3.95 (vt, $J_f$ = 1.9 Hz, 2 H), 4.02 (vt, $J_f$ = 1.8 Hz, 2 H), 4.06 (vt, $J_f$ = 1.9 Hz, 2 H) and 4.32 (vt, $J_f$ = 1.8 Hz, 2 H) 7.23–7.26 (m, 2 H, C$_6$H$_4$), 7.29–7.35 (m, 10 H, PPh$_2$), 7.46–7.50 (m, 2 H, C$_5$H$_4$). $^{31}$P($^1$H) NMR (CDCl$_3$): $\delta$ –16.9. $^{31}$C($^1$H) NMR (CDCl$_3$): $\delta$ 21.64 (s, C$_6$H$_3$(CH$_2$)$_3$), 58.28 (s, C$_6$H$_2$(CH$_2$)$_3$), 70.14 (s, CH of C$_6$H$_2$(CH$_2$)$_3$), 71.33 (s, CH of CH$_2$C$_6$H$_4$), 71.50 (d, $J_{PC}$ = 4 Hz, $\beta$-CH of C$_6$H$_4$), 73.78 (d, $J_{PC}$ = 14 Hz, $\alpha$-CH of C$_6$H$_4$), 74.86 (s, C$_{ipso}$ of CH$_2$C$_6$H$_4$), 76.77 (d, $J_{PC}$ = 7 Hz, C$_{ipso}$ of C$_6$H$_4$), 128.24 (d, $J_{PC}$ = 7 Hz, C$_{meta}$ of PPh$_2$), 128.69 (s), 128.71 (s) and 129.32 (s) (2 × CH of C$_6$H$_4$ + C$_{para}$ of PPh$_2$), 134.45 (d, $J_{PC}$ = 20 Hz, C$_{ortho}$ of PPh$_2$), 134.96 (s, C$_5$O$_2$ of C$_6$H$_4$), 138.75 (d, $J_{PC}$ = 10 Hz, C$_{ipso}$ of PPh$_2$), 144.43 (s, C$_6$H$_4$ of C$_6$H$_4$). IR (Nujol): $\nu$ max 3650 m composite, 3086 w, 1708 m, 1620 mw, 1468 w, 1323 m, 1294 m, 1277 m, 1257 m, 1239 m, 1216 m, 1186 m, 1168 m, 1146 s, 1127 m, 1105 m, 1087 m, 1058 m, 1056 mw, 1030 m, 1019 m, 1011 m, 971 m, 965 m, 931 w, 915 w, 905 w, 881 m, 857 m, 846 w, 826 w, 790 w, 748 s, 704 w, 692 s, 627 w, 610 w, 543 m, 517 m, 499 m, 490 s, 457 m, 432 vw cm$^{-1}$. MS (ESI+): m/z 383 ([Ph$_2$PfCCH$_2$]+), 463 ([6a + H$^+$]), 485 ([6a + Na$^+$]), 501 ([6a + K$^+$]). Anal. calc. for C$_{25}$H$_{26}$Br$_3$FeKO$_3$PSZn (838.5): C 35.81, H 5.06%. Found: C 36.62, H 5.00%.

**Preparation of 8a.** A methanolic solution of sodium bromide (10.3 mg, 0.10 mmol) was added to solid ZnBr$_2$ (22.5 mg, 0.10 mmol), followed by a chloroform solution of 6a in chloroform (46.2 mg, 0.10 mmol in 0.6 mL). The resulting mixture was stirred for 30 min, filtered through a PTFE syringe filter (0.45 μm pore size), and diluted with additional methanol (0.3 mL) as the top layer. The filtrate was layered with methyl tert-butyl ether to a total volume of 10 mL, and the mixture was set aside for crystallisation. The orange crystals, which separated over several days, were filtered off, washed three times with methyl tert-butyl ether, and dried under vacuum. Yield of 8a: 64.6 mg (79%).

IR (Nujol): $\nu$ max 3495 br m, 3089 m, 1619 w, 1433 m, 1407 w, 1318 m, 1293 s, 1267 m, 1228 w, 1193 w, 1167 m, 1146 s, 1118 m, 1107 m, 1091 m, 1064 w, 1052 w, 1043 v, 1030 m, 1021 m, 1013 s, 971 m, 960 m, 931 w, 905 w, 890 m, 881 s, 857 w, 846 w, 826 w, 790 w, 748 s, 704 w, 692 s, 627 w, 610 m, 543 m, 517 m, 499 s, 489 s, 459 s, 409 w cm$^{-1}$. Anal. calc. for C$_{25}$H$_{27}$Br$_3$FeKO$_3$PSZn (838.5): C 35.81, H 3.25%. Found: C 35.61, H 3.29%.

**Preparation of 10a.** ZnBr$_2$ (22.6 mg, 0.10 mmol) and LiBr (8.7 mg, 0.10 mmol) were dissolved in methanol (0.10 mL). A chloroform solution of ligand 6a (46.3 mg, 0.10 mmol in 0.4 mL) was added and the resultant mixture was stirred for 30 min. Filtration, addition of methanol (0.1 mL), addition of methyl tert-butyl ether (up to 10 mL total volume) and crystallisation as described above gave 10a as an orange crystalline solid, which was obtained by suction, washed with methyl tert-butyl ether, and dried under vacuum. Yield: 42.8 mg (49%).

IR (Nujol): $\nu$ max ca. 3270–3650 m composite, 3086 w, 1708 w, 1623 br s, 1403 w, 1318 m, 1306 w, 1283 s, 1263 m, 1247 w, 1228 w, 1193 v, 1168 m, 1143 s, 1116 s, 1116 s, 1095 m, 1062 w, 1041 w, 1030 m, 1020 m, 973 m, 930 w, 888 s, 857 w, 876 w, 833 v, 828 w, 790 m, 748 vs, 705 w, 692 w, 627 w, 609 w, 542 v, 517 m, 489 br s, 459 s cm$^{-1}$. Anal. calc. for Li$_2$Zn$_2$Br$_7$(6a)$_2$·(MeO)$_2$(H$_2$O)$_2$ (1762.9): C 36.11, H 4.12%. Found: C 35.88, H 3.79% (the sample is slightly hygroscopic).

**X-ray crystallography**

The diffraction data ($\theta_{max} = 27.5\%$; data completeness $\geq 99.3\%$) were recorded with a Nonius Kappa diffractometer equipped with an APEX-II CCD detector (Bruker) and a Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite mono-
chromatized Mo Kα radiation (λ = 0.71073 Å) and were corrected for absorption using routines included in the diffraction-meter software.

The structures were solved by the direct methods (SHELXS97) and refined by full-matrix least squares routines based on F² (SHELXL97).36 The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms residing on the oxygen atoms (OH protons) in the structures of 2·CH₃OH, 8a, 8b, and 9a were identified on the difference electron density maps and refined as riding atoms with Ueq(H) set to 1.2-times Ueq(O). In the case of 10a·CH₃OH, they were placed into positions suitable for the formation of hydrogen bonds and refined similarly. Hydrogen atoms residing on the carbon atoms were included in their theoretical positions and refined analogously.

Description of the crystallization experiments and a listing of relevant crystallographic data and structure refinement parameters are available in the ESI (Table S1†). Geometric data as well as all structural drawings were obtained with a recent version of the PLATON program.37 All numerical values are rounded with respect to their estimated standard deviations (ESDs) given with one decimal. Parameters pertaining to atoms in constrained positions are presented without ESDs.

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Notes and references

6 A proper choice of the alkylation reagent can sometimes eliminate this problem. For an example, see: P. Štěpnička and I. Cisařová, Organometallics, 2003, 22, 1728.
11 For an alternative synthesis of 1, see: M. E. Wright, Organometallics, 1990, 9, 853.
14 In addition to the betaine, the reaction of 1 with the sultone gives rise to other products, namely salt(s) with protonated amines (presumably hydrochloride), which are less polar than 2, and some P-alkylated products (δP 26.7; more polar than 2).


29 The Na⁺ necessary for the formation of **8a** seems to have come from the commercial ZnBr₂ sample, which was shown to contain 0.04 µg Na per 1 mg by atomic absorption spectrometry, or simply from the solvents and/or the glassware.

30 Increasing the chloroform-to-methanol ratio can result in a separation of the alkali metal halide (MX) from the reaction mixture (full or partial), which in turn reduces the yield of the mixed-metal complex or even fully prevents its formation. On the other hand, a low chloroform-to-methanol ratio (i.e., more polar reaction mixture) can significantly reduce the yield of the desired mixed-metal complex by increasing its solubility.

31 We feel that compound **10a** need not necessarily be the only product possibly arising in the **6a/LiBr/ZnBr₂** system as the reaction can, in principle, afford also other, differently solvated species.


34 The search for structurally characterised compounds combining octahedral Na(I) and tetrahedral Zn(II) sites in the Cambridge Structural Database, version 5.36 of November 2014 with updates from November 2014, resulted in 42 hits. These compounds were mostly coordination polymers featuring various O-donors. None of them contained phosphine donors or motifs similar to that encountered in **8a** and **8b**.

35 Dissolution of this by-product in dichloromethane, washing with 5% aqueous NaOH, and subsequent chromatographic purification recovered pure **1**.
