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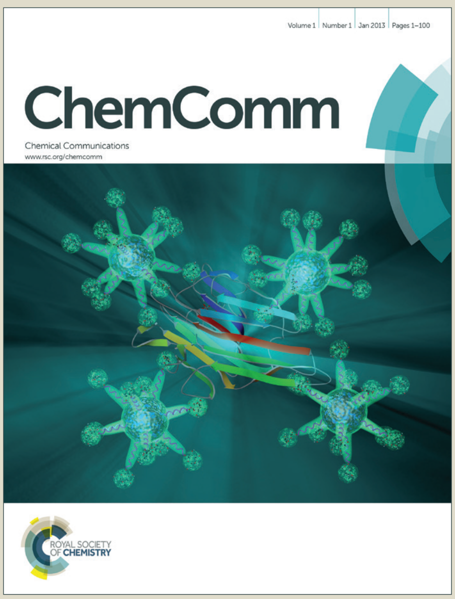

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Two C_2-Symmetric Chelating P_2-Bisphosphazene Superbases Connected *via* a Binaphthyl Backbone – Synthesis, Structural Features and Preparation of a Cationic Alkyl Aluminum Complex

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Two P_2-phosphazenyl groups were linked via a C_2-symmetric binaphthyl backbone resulting in two novel chiral superbases with dimethylamino and pyrrolidino substituents. We investigated their basic properties and coordination chemistry towards a cationic alkyl aluminum fragment. The outstanding basicity of the chiral tetrasphosphazenes presented herein leads to interesting perspectives for the application in asymmetric Brønsted base catalysis

Chiral amines play a very important role in asymmetric catalysis - especially with regard to extensive scientific activities in the field of organocatalysis during the past decade.[1] However, due their low basicity the role of chiral amines to enantioselective reactions in which they act as Brønsted-bases is strongly limited to comparably acidic substrates. Thus, chiral representatives of all classes of organic superbases such as amidines,[2] guanidines,[3] azaphosphatranes,[4] proton sponges[5] or phosphazenes[6] have been prepared and investigated with respect to their applicability to asymmetric synthesis.[7] This renaissance of well-established concepts of superbasicity becomes manifest in a cluster on superbases published in Synlett quite recently.[8] So far, the class of chiral guanidines is the most advanced with respect to its structural variety and utilization in enantioselective reactions. The area has already been the subject of review articles by Ishikawa and Tan.[9] Chiral guanidines were applied to asymmetric Michael addition, silylation, nucleophilic epoxidation and TMS cyanation reactions.[3a,b] Taking into consideration that the pK_{BH}^+ values of organic superbases range from 25 to about 45 on the acetonitrile scale, it must be stated that chiral guanidines presented to date only populate the very low end of the basicity scale (pentamethylguanidine: pK_{BH}^+ (MeCN) = 25.00[10]). Extension of the synthetic scope of chiral superbases requires the design of compounds with higher pK_{BH}^+ values by making use of the high intrinsic basicity of phosphazenes with multiple PN units or the combination of several superbasic features in one molecule. In this context Terada *et al.* recently published helically chiral spirocyclic P_3 phosphazenes and a series of highly basic chiral guanidinophosphazenes that were used in enantioselective amination reactions of ketones.[11] Raab[12] and Himmel *et al.*[13] linked two guanidinyl moieties *via* a C_2-symmetric binaphthyl backbone allowing the formation of an energetically favorable [N-H···N] hydrogen bond after protonation. Since we have thoroughly studied the basicity-enhancing effect of proton chelation,[14] we were interested to combine this proton pincer ligand concept with a chiral binaphthyl skeleton to achieve a unique interaction of two amino-substituted Schwesinger-P_2 bases in a chiral environment. A related bis(monophosphazene) with two PPh_3 units was prepared by Reetz *et al.* in 1998, but the electron-withdrawing triphenylphosphonio substituents are not able to grant a high basicity or even superbasicity with a pK_{BH}^+ value (MeCN) > 25.00.[15]

We chose a Kirsanov condensation to achieve the linkage between two P_2 fragments and the aromatic diamine. The required bromophosphonium bromide precursors **1** and **2** were prepared by

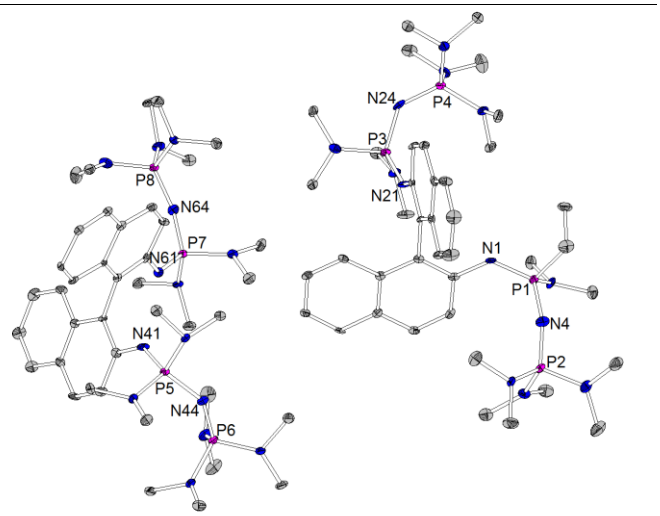
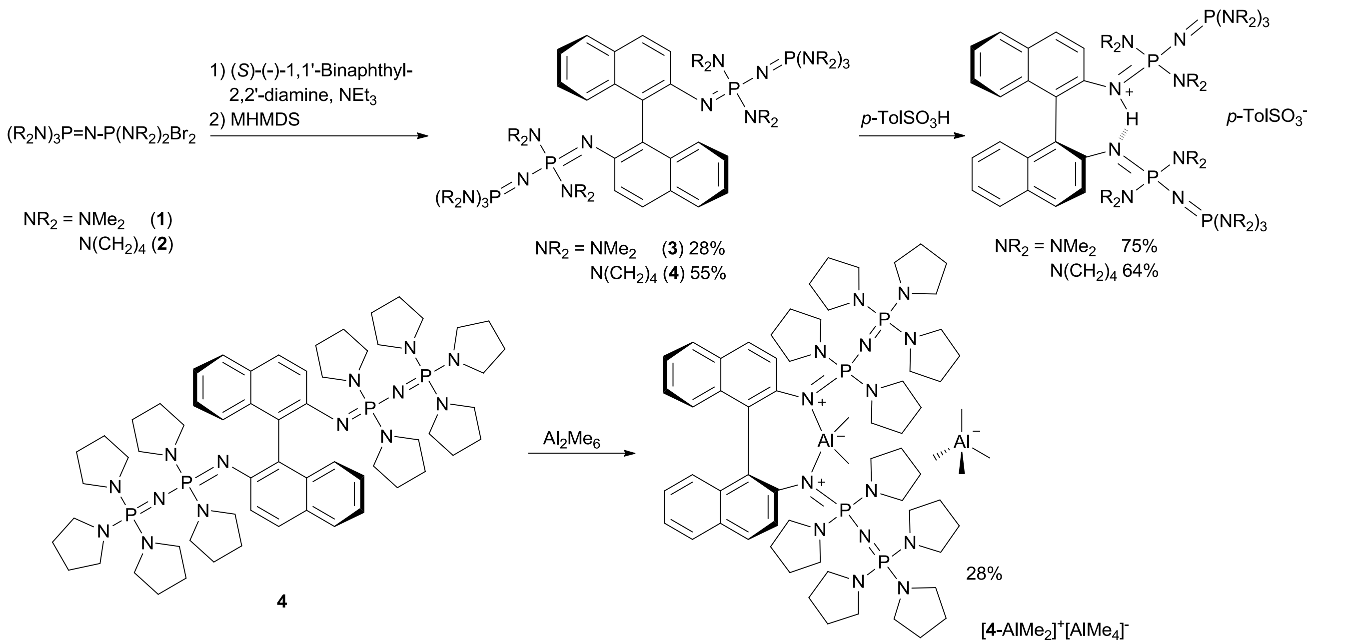


Fig 1. Molecular structure of **3** (ellipsoids with 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: d(N1···N21) 3.98(1), d(N1-P1) 1.567(6), d(P1-N4) 1.593(7), d(N4-P2) 1.536(7), d(N21-P3) 1.561(6), d(P3-N24) 1.627(7), d(N24-P4) 1.545(7), d(N41···N61) 4.10(1), d(N41-P5) 1.557(6), d(P5-N44) 1.609(6), d(N44-P6) 1.549(6), d(N61-P7) 1.542(7), d(P7-N64) 1.596(6), d(N64-P8) 1.539(7).[16]



Scheme 1. Preparation of the chiral tetraphosphazenes **3** and **4** *via* a Kirsanov reaction, protonation with *para*-toluenesulfonic acid and reaction of **4** with trimethylaluminum.

the bromination of the literature known P(III) compounds that were accessible *via* three-step procedures from tris(dimethylamino) phosphane and tris(pyrrolidino)phosphane.[14b, 17, 18] The reaction of (*S*)-(–)-1,1'-binaphthyl-2,2'-diamine with the bromophosphonium bromides in presence of the auxiliary base triethylamine and subsequent deprotonation with metal bis(trimethylsilyl)amides gave the two chiral tetraphosphazenes **3** and **4**. They were characterized *via* ^{1}H, ^{13}C and ^{31}P spectroscopy, ESI mass spectrometry, elemental analysis and in case of the dimethylamino-substituted species also X-ray crystallographic analysis (Figure 1). The two independent molecules found in the asymmetric unit reveal a large distance of 3.98(1) and 4.10(1) Å between the two basicity centers. Unlike in proton sponges, their N-centered lone pairs avoid each other by suitable torsion of the two naphthalene moieties around the axial carbon-carbon bond. Hence, no steric strain in the aromatic

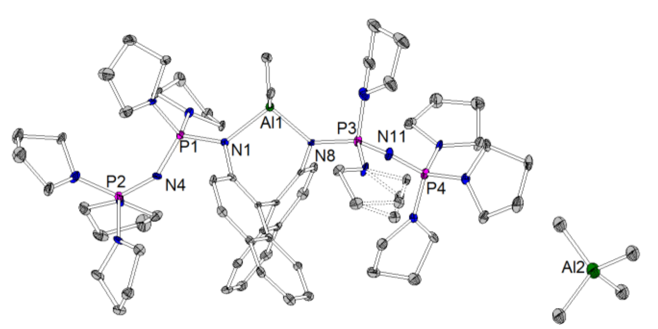


Fig 2. Molecular structure of $[\mathbf{4}\text{-AlMe}_2]^+[AlMe_4]^-$ (ellipsoids with 30% probability). The disorder in the $[AlMe_4]^-$ anion is not displayed. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: d(N1-Al1) 1.938(5), d(N1-P1) 1.633(5), d(P1-N4) 1.582(5), d(N4-P2) 1.558(4), d(N8-Al1) 1.938(5), d(N8-P3), d(P3-N11) 1.576(5), d(N11-P4) 1.548(5), N1-Al1-N8 98.3(2).[19]

backbones or repulsion of the nitrogen atoms' lone pairs destabilizing the tetraphosphazene's free base form is observed.

Protonation of the two tetraphosphazenes was studied with *p*-toluenesulfonic acid. It is accompanied by a low-field shift of the signals in the ^{31}P NMR spectrum and an increase in the $^{2}J(P,P)$ coupling constants. In case of the pyrrolidino-substituted species, the acidic proton exhibits a triplet with a $^{2}J(P,H)$ coupling constant of 7.4 Hz indicating interaction with two phosphorous atoms and thus the formation of an intramolecular [N-H···N] hydrogen bond.

The pK_{BH}^{+} values were determined *via* NMR titration experiments *versus* bisphosphazene proton sponges.[20] As expected, **4** exhibits a higher pK_{BH}^{+} value of 30.8 on the acetonitrile scale than its dimethylamino-substituted counterpart **3** which possesses a pK_{BH}^{+} value of 29.3. These results also suggest the energetically favorable chelation of the acidic proton since the basicity of **4** exceeds the pK_{BH}^{+} value of the non-chelating naphthalene-substituted P_2 Schwesinger base (pyr)P_2-1-Naph (pK_{BH}^{+} (MeCN) (calc.) = 26.0)[14b] by nearly five orders of magnitude. For Terada's chiral guanidinophosphazenes pK_{BH}^{+} values (THF) close to 26.8 were estimated.[11]

The coordination behavior of proton sponges[21] or other chelating superbases towards electrophiles other than protons has attracted considerable scientific interest.[13, 22] However, whereas metal complexes of macrocyclic phosphazenes have been reported, [23] the coordination chemistry of classical open chain Schwesinger superbases is widely unexplored.[24] We were interested to demonstrate the use of the title compounds not only as base but also as chiral donor ligand towards Lewis acids of catalytic interest. The reaction of 4 with two equivalents of trimethylaluminum resulted in the asymmetric dissociation and formation of $[\mathbf{4}\text{-AlMe}_2]^+[AlMe_4]^-$ (Scheme 1) which could be investigated concerning its structural features (Figure 2). An angle of 69.3(9)° is observed between the two naphthalene planes. The cationic fragment $[AlMe_2]^+$ is chelated by the two basic nitrogen atoms showing an N-Al-N angle of 98.3(2)° and a non-bonding N···N distance of 2.931(6) Å.

Conclusions

In the state of the art the concept of Schwesinger polyphosphazene superbases has not been extended to chelating chiral representatives, favorably with a rigid backbone. Furthermore, Schwesinger polyphosphazene bases have not been used as superstrong chelating neutral donor ligands in coordination chemistry and catalysis. In this respect the chiral tetraphosphazenes communicated herein add valuable perspectives to the highly topical field of chiral superbases with expected applications as enantioselective organocatalysts with an extraordinarily high Brønsted-basicity and as chiral superdonor ligands for cationic metal complexes of catalytic interest.

Notes and references

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Electronic Supplementary Information (ESI) available: The ESI contains detailed synthetic procedures and analytical data. The CIF files belonging to the crystal structures presented herein are available free of charge at the Cambridge Crystallographic Data Centre under the deposition numbers CCDC 977138 to 9771340. For ESI see DOI: 10.1039/c000000x/

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16 **3** crystallizes in the triclinic space group *P*1 with the unit cell constants a = 10.5097(10) Å, b = 13.3588(14) Å, c = 16.9068(17) Å, α = 87.901(4)°, β = 89.867(4)° and γ = 82.976(4)°. Detailed crystal data and experimental conditions are given in the supplementary information.

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18 A molecular structure of **1** is presented in the supplementary information (Figure S1).

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20 NMR titration experiments were performed in THF due to the low solubility of the free base forms in acetonitrile. **4** competed with HMPN and TPPN for protons while an unpublished *iso*-propyl-substituted bisphosphazene proton sponge with a pK_{BH^+} value of 30.4 in acetonitrile was used in case of **3**. A linear correlation between the THF and the acetonitrile scale can be assumed by approximation. The procedure is described in ref. 14a.

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