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2022-05-03

Cicac-Hudi , M , Kaaz , M , Birchall , N , Nieger , M & Gudat , D 2022 , ' A neutral analogue of a phosphamethine cyanine ' , Dalton Transactions , vol. 51 , no. 17 , pp. 6533-6536 . https://doi.org/10.1039/d2dt0

http://hdl.handle.net/10138/356974
https://doi.org/10.1039/d2dt00837h

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COMMUNICATION

A neutral analogue of a phosphamethine cyanine

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Reaction of an imidazolio-phosphide with a N-heterocyclic bromoborane and NaH afforded a neutral analogue of a phosphamethine cyanine cation. DFT studies were used to analyse the dative bonding across P–C/B bonds and the conformational preferences and imply that the observed conformation is imposed by sterics.

Phosphamethine cyanines I (Chart 1) are considered a historic landmark as the first stable compounds featuring double bonding between phosphorus and carbon atoms.[1] Their short P–C distances and planar conformation[1b,2] are well in accord with the presence of a conjugated π-electron system represented by superposition of the canonical formulae Ia - Ib.

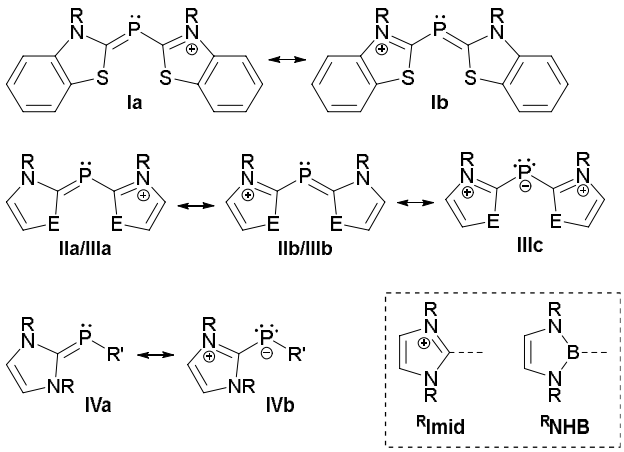

Chart 1: Molecular structures of phosphamethine cyanines (I), their analogues (II, E = S; III, E = NR), imidazolio-phosphides (IV), and generic structures of imidazolio (^{R}Imid) and N-heterocyclic boryl (^{R}NHB) substituents (R = alkyl, aryl; R' = H, alkyl).

The development of N-heterocyclic carbene (NHC) chemistry stimulated further the exploration of phosphamethine cyanine analogues such as II[3] and III,[4] which differ from I in the lack of the benzene anellation and an additional formal replacement of the sulfur atoms by two more imino (NR) moieties in III. While the solid-state structures and bonding description of II match those of I,[3] steric interference between the extra N-substituents enforces a helical distortion of the heterocycles in III.[4,5] With this layout being expected to disrupt π-conjugation, cations III were no longer iconified as phosphorus-containing multiple bond systems, but rather as carbene-stabilised phosphorus(I) species.[5] In contrast to I, the bonding is now depicted by overlaying a leading zwitterionic resonance structure IIIc with contributions from the already familiar formulae IIIa,b reflecting stabilisation of the P-centred lone-pairs by hyperconjugation with the imidazole rings (Chart 1).[6] This description allows not only rationalising the ability of the phosphorus atom in III to bind to two transition metal centres,[7] but reveals as well close parallels to the mono-NHC-derivatives IV.[8,9] By analogy to the identification of the latter as onio-substituted phosphides,[10] the cations III may as well be pictured as bis-imidazolio-substituted phosphides.[6]

The range of phosphamethine cyanine analogues was recently widened by swapping thiazolyl or imidazolyl units for further isoelectronic moieties like triazolyls.[11] As a cationic imidazolio-substituent (^{R}Imid) is as well isoelectronic to a neutral N-heterocyclic boryl unit (^{R}NHB, Chart 1), introducing the latter would in principle allow to prepare also analogues of cations I – III in different charge states. We report here on the synthesis of a neutral phosphamethine cyanine analogue with mixed NHB/imidazolio-substitution.

Building on known protocols for the functionalisation of PH-bonds in primary imidazolio-phosphides (IV, R' = H) with strong electrophiles and base,[10,12] we set out to access a neutral analogue of III by condensation of 1 with bromoborane 2 in the presence of triethylamine. Formation of borylated 3 was observed as anticipated, but the reaction was unselective and furnished free and NHB-decorated PH_3 and P_2H_4 along with imidazolium ions and intractable solids as further products (Scheme 1). Notably, consumption of 2 remained incomplete when stoichiometric amounts of both reactants were used, and the same products were also obtained without NEt_3.

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Electronic Supplementary Information (ESI) available: Experimental procedures, representations of NMR spectra, results of crystallographic and computational studies. CCDC-2133603. See DOI: 10.1039/x0xx00000x

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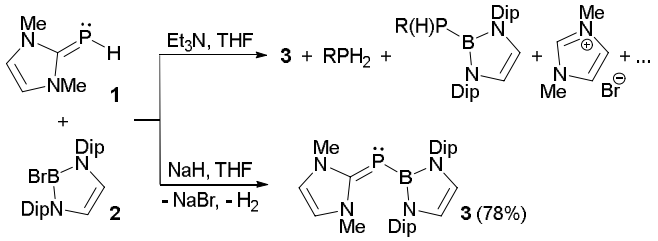


Scheme 1: Condensation of 1 and 2 with Et_3N or NaH as base (R = H, PH_2, Dip = iPr$_2$C$_6$H$_3$)

The unselective reaction can be rationalised in the light of our findings on base-induced alkylations of IV.[10] Acting as stronger proton scavengers than tertiary amines, zwitterions like 1 are protonated during the reaction, and the cationic phosphines formed undergo autocatalytic dismutation to yield PH_3/P_2H_4, imidazolium ions, and intractable solids. Boryl-(di)phosphines may then arise from condensation of PH_3/P_2H_4 with residual 2.[13] Having found that the side reactions can be avoided by using strong anion bases,[10] we optimized the reaction of 1 and 2 along these lines and succeeded in generating 3 with >80% selectivity (by integration of ^{31}P NMR spectra) using sodium hydride as base and isolating the product as red crystals in very reasonable yield (78%). For a clean reaction, it is best to slowly add electrophile 2 to a suspension of 1 and NaH in a polar solvent (MeCN) to ensure rapid dehydrohalogenation and inhibit a direct reaction of the hydride with the bromoborane.

Identity and purity of 3 were established by analytical and spectroscopic data and XRD. The ^{31}P NMR chemical shift (δ^{31}P -177) is more negative than in 1 (δ^{31}P -149[6]) and cations III (δ^{31}P -124 to -129[4,5]), revealing that the NHB-moiety exerts in this respect the same effect as in phosphines.[13] The ^{11}B NMR chemical shift of 32.3 ppm slightly exceeds the reported values of NHB-substituted phosphines (δ^{11}B 23 to 27.5[13]).

The interpretation of the XRD data is burdened with a disorder of the whole P-imidazolio-unit (and one iPr-group in the NHB unit, Figure S1) over two positions, which foils the evaluation of precise metrics in the BPC-triad. Still, the structure confirms the constitution of 3 and reveals a similar bent coordination at phosphorus and helical alignment of the N-heterocycles (Figure 1) as in III.[4-6] Comparable features were also reported for a P-borylated phosphaguanidinato-complex of scandium sharing a common N_2C-P-NHB unit with 3.[14] In line with the results of DFT studies (see below), we attribute the disorder to the presence of conformers with differing torsional orientation of the P–C-bond relative to the NHB plane (Figure S2). Notably, the twist of the N-heterocycles is not symmetrical as in III, but differs in both halves of the molecule: while the imidazole ring approaches orthogonality with respect to the C27-P1-B1-plane (interplanar angles 67°/82° for both disordered fragments), the torsion remains much smaller for the NHB unit (16°/31°).

Facing the lack of clear structural data, we turned to DFT studies to gain further insight into the electronic structure of 3. The energy optimized (B3LYP-D3BJ/def2-SVP level) molecular structure complies with the bent geometry (B–P–C 98.4°) and helical conformation found experimentally (see Figure S9). Shorter P–C (1.785 Å) and P–B distances (1.902 Å) than in ^{Me}Imid–PH_2 (1.845 Å) and ^{Dip}NHB-PH_2 (1.927 Å) are, as in III[4-6] and in line with calculated bond orders (Table S2), indicative of (hyper)conjugative interactions between P-centred lone-pairs and heterocyclic π-systems. However, while these interactions affect in III both substituents (cf. P–C 1.802 and 1.823 Å for the isosteric cation [(^{Dip}Imid)(^{Me}Imid)P]$^+$), they seem to focus in case of 3 mainly on the imidazole fragment.

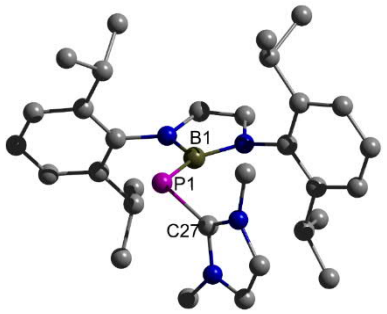
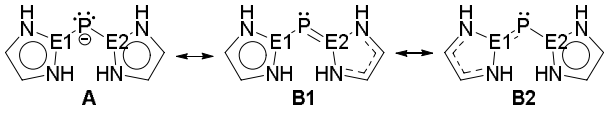


Figure 1: Ball-and-stick representation of the molecular structure of 3 in the crystal. For clarity, only one of the disordered positions (occupation 0.56) of the P-imidazole unit and the disordered iPr-group in one of the Dip-substituents is displayed, and hydrogen atoms were omitted. Thermal ellipsoids as well as selected distances and angles for the complete disordered structure are displayed in the ESI (Figure S2).

For a more detailed assessment, we turned to a computational analysis of the less crowded permethylated (3^{Me}) and parent (3^H) analogues of 3 and symmetric bis-imidazolio-phosphide cations $(4^R)^+$ and diboryl-phosphide anions $(5^R)^-$ (R = H, Me), respectively. All species display shortened (compared to pure single bonds) P–B/C distances and a helical alignment of the N-heterocycles. The skew falls off with decreasing steric bulk of the N-substituents, but the assembly remains distinctly non-planar even for R = H (Figure S10). Natural Resonance Theory[Error! Reference source not found.] (NRT) analysis of the bonding in 3^H – $(5^H)^-$ relates the bond shortening to (hyper)conjugative interactions described by the familiar resonance between 'phosphido' (A) and 'conjugated' (B) canonical structures as dominant contributors (Figure 2).



compd	E1	E2	rel. weight (%)			nat. bond order [a]	
			A	B1	B2	P-E1	P-E2
$(4^H)^+$	C$^+$	C$^+$	58.3	41.6		0.77	0.77
3^H	B	C$^+$	38.4	43.7	11.5	0.92	0.92
$(5^H)^-$	B	B	23.8	71.0		1.00	1.00

[a] covalent contribution

Figure 2: Dominant resonance structures, their relative contributions, and covalent natural bond orders obtained from NRT analyses of the B3LYP-D3BJ/def2-SVP densities of 3^H – $(5^H)^-$. Each structure displayed represents the overlay of several canonical formulae with different electron distribution in the π-systems of the N-heterocycles. For a full account on the NRT results, see Figure S5 in the ESI.

The trends in the relative weights of these resonance structures and in Natural Bond Orders imply that the dative bonding fades with increasing total charge, presumably due to growing electrostatic stabilization of the 'phosphido' lone-pairs. As in case of 3, the (hyper)conjugation in 3^H focuses

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mainly on the P–C bond. Accordingly, the electronic structure bears close similarity to that of IV and insinuates addressing compounds 3 as borylated imidazolio-phosphides.

Additional insight into the trade-off between hyperconjugation (with P-centred lone-pairs of sp-hybrid character) and full π-conjugation (involving pure p-Orbitals at P) across the P–C/B bonds is available from an analysis of the energetics of bond rotation processes. Relaxed potential energy scans imply that rotations around P–B/C bonds in 3^{Me} – $(5^{Me})^-$ occur preferably in a concerted manner, and that enantiotopic ($(4^{Me})^+$, $(5^{Me})^-$) or enantiomeric (3^{Me}) conformers may readily interconvert via transition states in which one heterocycle aligns orthogonally and one parallel with the central EPE plane (E = B, C; Figure 3).

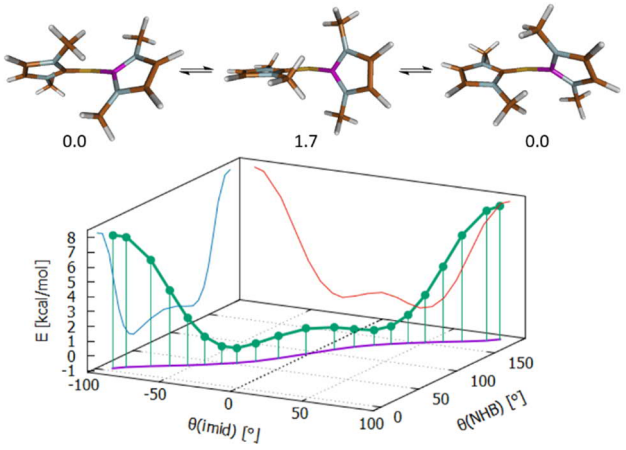

Figure 3: Top: Computed molecular structures of two enantiomeric rotamers of 3^{Me} and the transition state with θ(imid) = 0° and θ(NHB) = 90° (θ(X) denotes the torsional angle of substituent X relative to the central CPB-plane) with relative Gibbs enthalpies ΔG^0 in kcal/mol. Bottom: result of a relaxed potential energy scan illustrating the concerted variation of torsional angles θ(imid) and θ(NHB) (purple trace) and the corresponding B3LYP-D3BJ/def2-SVP energies (green trace); red and blue traces indicate projections of the energy on the two independent coordinates. Further details are given in the ESI.

The rotational barrier in $(4^{Me})^+$ ($\Delta E^{\neq,rot}$ = 4.0 kcal/mol) is still lower than in imidazolio-phosphides (^{Me}imid-PH (IV, R = Me, R' = H): $\Delta E^{\neq,rot}$ = 12.2 kcal/mol), revealing that disrupting full π-conjugation to one imidazole ring has a minor energetic penalty. An even smaller barrier results for $(5^{Me})^-$ ($\Delta E^{\neq,rot}$ = 2.3 kcal/mol). The computed P–C rotational barrier in neutral 3^{Me} ($\Delta E^{\neq,rot}$ = 7.9 kcal/mol) implies that conjugation with the NHB-unit stabilizes the rotational transition state, but less so than interaction with an imidazole ring. In contrast, NHB-rotation in 3^{Me} has only a negligible energy barrier ($\Delta E^{\neq,rot}$ = 0.7 kcal/mol), indicating that B–P hyperconjugation and full conjugation are equally proficient and torsional motions proceed basically in a double-well potential allowing easy swapping between two mirror symmetrical helical conformers (Figure 3). Intriguingly, this setting can also explain the disorder in crystalline 3 if one reflects that the two different positions of the imidazole-unit embody principally a pair of such conformers. Last, but not least, we note that the observed conformation of 3, in which the torsion of the imidazole ring out of the CPB-plane exceeds that of the NHB-moiety and π-conjugation across the P–C bond seems to be largely blocked, is intrinsically disfavoured and likely imposed by the steric demand of the N-substituents.

Conclusions

Synthesis and characterisation of a first neutral analogue of phosphamethine cyanine cations were reported. DFT studies suggest describing its electronic structure as boryl-substituted imidazolio-phosphide in which (hyper)conjugation of P-centred lone-pairs affects predominantly the imidazole unit.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank B. Förtsch for elemental analyses, Dr. W. Frey and J. Trinkner (Institute of Organic Chemistry, Univ. of Stuttgart) for recording X-ray data and mass spectra, and acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation through grant no INST 40/575-1 FUGG (JUSTUS 2 cluster).

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