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A Simple Route to Phosphamethine Cyanines from *S*,*N*-Heterocyclic Carbenes

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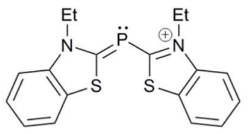
Although salts of thiazolium cations are known, many readily prepared iodide salts have eluded spectroscopic and structural characterization; herein, data for a variety of such salts are reported. It has been demonstrated that thiazolium cations can be deprotonated to generate *S,N*-heterocyclic carbenes and their "electron rich olefin" dimers, but use of the former has been largely overshadowed by that of the more common *N*-heterocyclic carbenes. We report herein that the deprotonation of thiazolium iodides and their subsequent reaction with a conveniently prepared triphosphenium precursor grants phosphamethine cyanine cations with solid-state geometry and electronic structure unlike those of NHC-stabilized cations. Protection of the phosphorus atom in such ions with elemental sulfur provides an air- and moisture-stable dithiophosphinium salt.

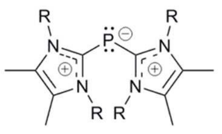
Introduction

Phosphamethine cyanine dyes are compounds of historic importance in main group chemistry and inorganic chemistry as a whole.[1] The crystal structure of cation **A** exhibited one of the first reported dicoordinate phosphorus environments and it furnished the first concrete evidence of 3p-2p π-bonding![2] In spite of their significance, until recently few examples of these cations had been crystallographically characterized and the study of their reactivity has remained relatively unexplored. The dearth of invetigations was likely a consequence of the synthetic challenges associated with their isolation and because of their being very air- and moisture-sensitive. Nearly 50 years after this report, we presented the safe, high yielding synthesis of cations of the type $^{\mathbf{R}}$**B** (where $^{\mathbf{R}}$ denotes the *N*-alkyl groups) starting from *N*-heterocyclic carbenes (NHCs) and a readily prepared triphosphenium precursor **C**.[3,4] In contrast to the planarity observed in the solid state structure of **A**–which remains one of the few crystallographically characterized phosphamethine cyanines until this time–the structure of $^{\mathbf{R}}$**B** is distinctly non-planar so we characterized these systems as being NHC-ligated P^{I} cations.[5]

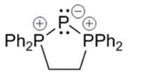
More recently, we discovered that a chelating framework enhances the stability of these cations and thus may finally allow for the widespread development and application of such species as functional dyes.[6] The short methylene bridge of $^{\mathbf{R}}$**D** also has a substantial effect on the molecular and electronic structures of the cations. As one might anticipate, the bridge enforces a much more co-planar arrangment of the NHC fragments and the C-P-C plane, but $^{\mathbf{R}}$**D** takes on a butterfly conformation and Natural Bond Orbital (NBO) analysis suggests that the P^{I} assignment is still most accurate for these cations.



A



$^{\mathbf{R}}$**B**



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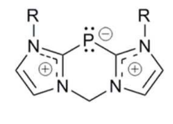
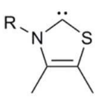


$^{\mathbf{R}}$**D**



E

Over the last 20 years, carbenes have proven to be capable stabilizing ligands for main group moieties.[7] In most of these cases, the carbenes employed were either NHCs or cyclic (alkyl) (amino) carbenes (CAACs). In contrast, thiazol-2-ylidenes (SNHCs) (**E**) have not seen much use in this regard and most of the research involving SNHCs has been focused on their role as organo-catalysts such as in benzoin condensations.[8] While some transition metal-SNHC systems have emerged in recent years,[9] these few examples still pale in comparison to the tremendous number of transition metal-NHC systems currently known. This disparity is presumably because replacement of one :NR fragment with the isolobal :S: fragment has a drastic effect on the properties of SNHCs (most importantly, their stability).[10] The less electronegative sulfur atom is not as efficient at stabilizing the σ-type lone pair on carbon, and the lack of an exocyclic group on sulfur decreases kinetic stability of the carbenic centre. In fact, SNHCs with *N*-substituents smaller than 2,6-diisopropylphenyl will dimerize rapidly in solution as described by the Wanzlick equilibrium[11] and only the resultant electron-rich olefin (ERO)[12] can be isolated in the solid state. Furthermore, the introduction of the large sulfur atom into the heterocyclic framework distorts the very stable geometry found in NHCs.[10] Interestingly, the π-accepting ability of SNHCs is significantly greater than that of their more stable *N*-heterocyclic counterpart but they still retain strong σ-donating ability.[13,14] In spite of the dearth of comparative studies of NHCs and SNHCs, their different steric and electronic properties suggest that they might engender different types of compounds when coordinated to interesting main group species.

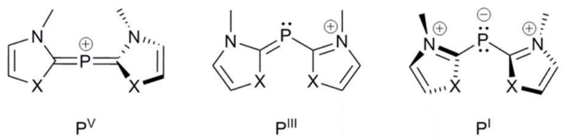


Fig. 1 Possible canonical forms of phosphamethine cyanine cations (X = NR, S).

A simple route to generation of SNHCs is by deprotonation of thiazolium salts. Though these have been know for many years,[15] many easily prepared *N*-alkylthiazolium iodide salts have eluded structural and in some cases spectroscopic characterization. In this work, we report upon the synthesis, spectroscopic and structural data for a variety of these SNHC precursors. Most importantly, we report that SNHCs can be employed in our P^+ transfer approach to yield low-coordinate

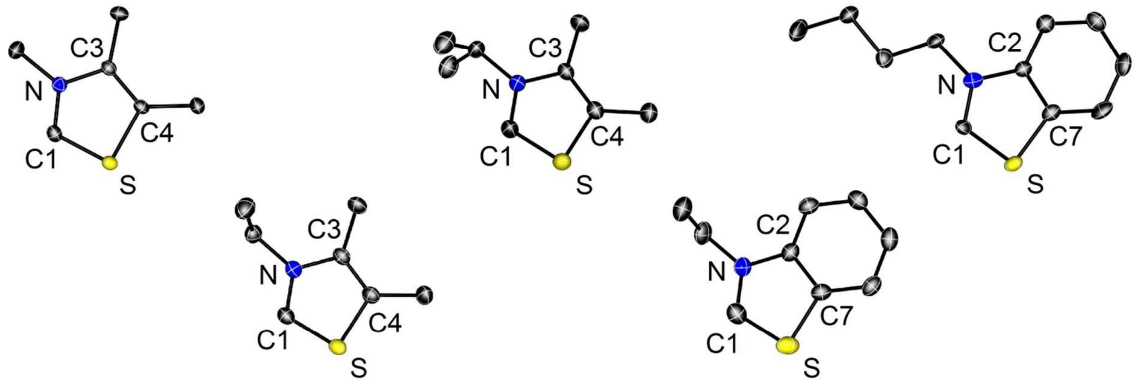


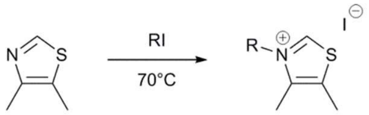
Fig. 2 Crystal structures of thiazolium iodide salts from left to right, selected distances (Å) and angles (º): **[$^{\mathrm{Me}}$TZ][I]**: C1-S, 1.681(2); C1-N, 1.393(3); C3-C4, 1.355(3); S-C1-N, 111.90(15). **[$^{\mathrm{Et}}$TZ][I]**: C1-S, 1.680(2); C1-N, 1.322(3); C3-C4, 1.354(3); S-C1-N, 112.21(18). **[$^{\mathrm{iPr}}$TZ][I]**: C1-S, 1.675(4); C1-N, 1.314(5); C3-C4, 1.350(5); S-C1-N, 113.0(3). **[$^{\mathrm{Et}}$BTZ][I]**: C1-S, 1.690(4); C1-N, 1.312(5); C2-C7, 1.400(5); S-C1-N, 114.5(3). **[$^{\mathrm{nBu}}$BTZ][I]**: C1-S, 1.695(11); C1-N, 1.306(13); C2-C7, 1.411(14); S-C1-N, 114.7(8). Ellipsoids are drawn using the 50% probability surface. Hydrogen atoms and anions are omitted for clarity.

phosphamethine cyanine salts.[16] The features of the cations in these salts are quite different than those bearing imidazolyl substituents.

Results and discussion

Synthesis and characterization of *N*-alkyl thiazolium salts

The systematic synthesis of *N*-alkylbenzothiazolium iodides through the treatment of benzothiazole with alkyl iodides was described by Nigrey and Garito,[17] and more recently this has been expanded upon by Rogers and co-workers.[18] Thus, spectroscopic data for a large library of these has been compiled but crystallographic data for many of these reported compounds were never reported. During the course of our investigations, we were able to obtain crystal structures for several of these known compounds. Unlike the benzannulated derivatives, many *N*-alkyl-4,5-dimethylthiazolium iodides lack both crystallographic and spectroscopic data. For completeness, we have included full characterization data for all of the dimethyl-backbone derivatives we prepared (Scheme 1). All of these salts were synthesized in the same solvent-free conditions as described by Rogers *et al.* for the benzannulated analogues, and their ^{1}H and ^{13}C NMR data show similar features, namely, the very large deshielding of the C1 carbon (ca. 145 ppm) and its bound proton (ca. 10.5 ppm).



Scheme 1 Synthesis of *N*-alkyl-4,5-dimethylthiazolium iodides (R = Me, Et, iPr, nBu).

As one would anticipate, the thiazolium salts are all structurally very similar (Figure 2). The C-N bonds in all these examples range from 1.306(13) to 1.324(2) Å, and the C-S bonds range from 1.675(4) to 1.695(11) Å. The angle formed by these two bonds ranges from 111.90(15)º to 114.7(8)º, and is slightly more obtuse for the benzannulated cations. All of these parameters are consistent with known thiazolium cations reported in the Cambridge Structural Database (CSD),[19] and furthur discussion of their metrical parameters is not warranted.

Attempts to synthesize benzannulated phosphamethine cyanines

Initially, the synthesis of benzannulated cations analogous to **A** was targetted. It is by now well-known that deprotonation of azolium salts generates electron-rich olefins or carbenes, as described by the Wanzlick equilibrium. This relationship, once the source of much controversy,[20] is by now well documented[21,22] and has recently been exploited by Bertrand and coworkers to isolate the first carbene-carbene heterodimer.[23] In fact, for SNHCs, it was shown by Arduengo that even with the relatively large mesityl groups on nitrogen, this equilibrium favours the olefin in solution and in the solid state.[10] Consequently, we found that deprotonation of **[$^{\mathrm{Et}}$BTZ][I]** with potassium hydride grants the known dithiadiazafulvalene **($^{\mathrm{Et}}$BTZ)$_2$**,[24,25] with no trace of the carbene monomer observed in the ^{13}C NMR spectrum.

The olefin **($^{\mathrm{Et}}$BTZ)$_2$** was recrystallized from a concentrated toluene solution to provide crystals suitable for analysis by single crystal X-ray diffraction. Although this dithiadiazafulvalene has been know for a long time,[24] **($^{\mathrm{Et}}$BTZ)$_2$** is only the second of this type to be crystallographically characterized; the other being Arduengos bis(3,4,5-trimethylthiazol-2-ylidene). Interestingly, as with its analogue, the olefin **($^{\mathrm{Et}}$BTZ)$_2$** features structurally inequivalent thiazole rings which are not coplanar, as illustrated in Figure 3. One of the nitrogen atoms (N2) is distinctly pyramidal (the sum of the angles about N2 is 341.8(5)º) while the other (N1) is planar (the sum of the angles about N1 is 359.8(5)º). There are no apparent packing features in the structure which could cause such distortions to the geometry of the molecule, and the experimental structure is accurately predicted by the geometry optimized structure calculated at the PBE1PBE/TZVP level of theory (Figure 4). It has been suggested[10] that such a non-planar geometry is indicative of the non-least motion dimerization pathway for singlet carbenoid dimerization.[26–28]Furthermore, the pyramidalization of only one of the nitrogen atoms is consistent with a more extreme donor-acceptor dimer model (Figure 4) in which the thiazolyl fragment with a planar nitrogen acts as a donor and the thiazolyl moiety featuring the pyramidal nitrogen acts as an acceptor.[10]

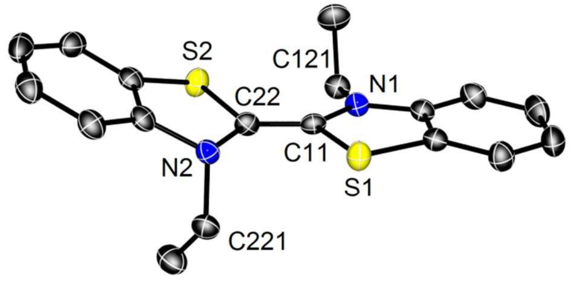


Fig. 3 Thermal ellipsoid plot of (**^{Et}BTZ)$_2$**. Ellipsoids are drawn using the 50% probability surface. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (^{o}): C11-C21, 1.336(4); C11-S1, 1.771(3); C11-N1, 1.399(3); N1-C121, 1.451(3); C21-S2, 1.786(3); C21-N2, 1.436(4); N2-C221, 1.475(4); C21-C11-N1-C121, 6.2(5); C11-C21-N2-C221, 74.4(3).

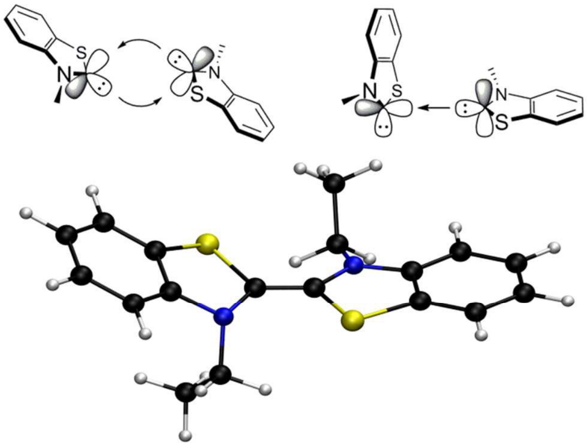


Fig. 4 Top left: Schematic symmetrical non-least motion pathway model for the dimerization of singlet SNHCs. Top right: extreme donor-acceptor non-least motion dimerization model. Bottom: Optimized geometry of **(EtBTZ)$_2$** (PBE1PBE/TZVP level of theory).

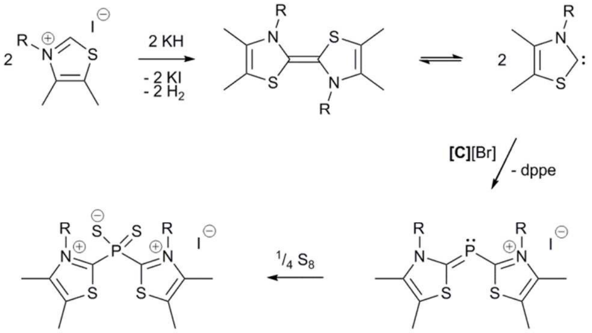
When **(^{Et}BTZ)$_2$** is treated with phosphorus triiodide, a broad mixture of products is observed in the ^{31}P NMR spectrum, none of which could be attributed to the desired phosphamethine cyanine cation. This prompted us to use our conveniently prepared triphosphenium precursor **C**[I] as a source of P^{+} but, even under reflux, the target phosphamethine cyanine cation **[^{Et}BTZ$_2$P]$^{+}$** (**A**) was not observed; this result contrasts with observations of Schmidpeter for bis(imidazolyl) EROs.[29] Thus it appeared as if an in-situ approach to carbene generation would be required.

^{31}P NMR spectra reveal that the reaction of potassium hydride with *N*-ethylbenzothiazolium iodide in the presence of **C**[I] also results in a mixture of products. This time however, the NMR data featuring a peak at 33 ppm suggested that cation **[^{Et}BTZ$_2$P]$^{+}$** was indeed present in the mixture. This conclusion was confirmed by HR-ESI-MS analysis, which featured a peak at 357.0649 m/z consistent with the cation.

With this result in hand, we were able to extend this procedure to the 4,5-dimethyl-backbone thiazolium salts, giving the cations **[^{R}TZ$_2$P]$^{+}$** (R = Me, Et, ^{i}Pr, ^{n}Bu) in reasonable yield (Scheme 2) on the basis of ^{31}P NMR and HRMS investigations. Unfortunately, these triphosphenium salts are not indefinitely stable in the presence of harsh bases and a stepwise approach proved to be more appropriate.

Synthesis and characterization of [^{Et}TZ$_2$P][I]

The ethyl-substituted variant **[^{Et}TZ$_2$P][I]** was the most easily purified and crystallized in our hands so the following sections concentrate on the properties and chemistry of that salt. The iodide salt **[^{Et}TZ$_2$P][I]** is a deep red solid that is thermally robust–melting at 186 ºC–but that is extremely unstable towards moisture and air. Solutions of the salt exposed to air decompose in minutes, and solids exposed show no trace of the cation by NMR spectroscopy over the course of hours. While it may be concievable for this one-pot approach to give mixed anion species (bromide and iodide), elemental analysis shows unequivocally that the isolated bulk material is the iodide salt. From a practical standpoint, we wish to note that if residual thiazolium salt remains present in the crude material, treatment of the crude salt mixture with additional potassium hydride in THF followed by the described workup grants analytically pure **[^{Et}TZ$_2$P][I]**.



Scheme 2 Synthesis of **[^{R}TZ$_2$P][I]** and **[^{R}TZ$_2$PS$_2$][I]** (R = Me, Et, ^{i}Pr, ^{n}Bu).

The ^{31}P NMR spectrum of **[^{Et}TZ$_2$P][I]** features a singlet at 17 ppm. This is remarkably deshielded when compared to chelated (bis)NHC (-82 ppm)[6] and acyclic (bis)NHC (-112 to -127 ppm)[4,30] ligated variants, and gives the first indication that the phosphorus environments of these species are quite dissimilar. This deshielding is undoubtedly a result of the far superior π-accepting ability of SNHCs as compared to NHCs. The phosphorus environment of **[^{Et}TZ$_2$P][I]** is more shielded than that of the benzanullated analogue **A** (26 ppm), in line with observation made by Heinicke *et al*.[31] for NHCs and benzannulated NHCs. The carbenic carbon atoms resonate at 179 ppm in the ^{13}C NMR spectrum, consistent with trends observed for reported SNHC-phosphinidene adducts.[13] The ^{1}J-couplings of phosphorus to the carbenic carbon atoms is 87 Hz and is thus comparable to those of acyclic (bis)NHC-ligated P^{I} cations.[4,30]

Pleochroic deep red/yellow crystals of **[^{Et}TZ$_2$P][I]** suitable for single crystal X-ray diffraction were grown by slow evaporation of an acetonitrile solution. Remarkably, this is only the second bis(thiazolyl) phosphamethine cyanine salt ever structurally characterized! The salt crystallizes in the space group *C2/c* with half of each ion present in the asymmetric unit and the phosphorus atom sits on a C_2 axis (Figure 5). The crystallographically identical P-C bonds in **5** of 1.7866(15) Å are typical of delocalized 2-phosphaallylic species, and fall between the bond lengths observed in **A** (1.75(4) Å and 1.75(7) Å)[2] and **^{iPr}B** (1.824(2) and 1.823(2) Å)[4]. Similarly, the C-P-C angle in **[^{Et}TZ$_2$P][I]** of 102.23° fits between the more obtuse C-P-C angle in **A** (104.6°) and the more acute C-P-C angle in **^{iPr}B** (97.35(9)°). In our recent report of bis-NHC-ligated P^{I} cations, we included a table comparing the metrical parameters of most crystallographically characterized phosphamethine cyanines and related species, and made note of the twisting of the heterocycles from the C-P-C plane in each of the compounds.[6] For **[^{Et}TZ$_2$P]$^{+}$**, this twisting is 10.61°, which, while slightly greater than what is observed in **A** (2.66° and 4.39°),[2] is very small compared to that seen in **^{iPr}B** (51.7° and 60.2°) and even bis-NHC-ligated **^{R}D** (18.7° and 25.5°).[4,6] In an important comparison, the P-C bond lengths of **[^{Et}TZ$_2$P]**$^+$ are slightly longer than those observed in the N-H tautomer of the neutral di(benzothiazol-2-yl)phosphane, crystallographically characterized by Stalke and coworkers. However for the latter case, hydrogen-bonding draws the nitrogen atoms of the heterocycles close together, leading to a much more acute C-P-C angle (98.7(2)º) and an even more planar overall structure (twisting of 3.77º and 6.77º).[32] When all of these metrical parameters are considered, it is clear that the replacement of one :NR fragment by :S: has a dramatic effect on the phosphorus environment in these systems: in contrast to all of the NHC analogues, the P^{III} canonical structure seems to be the most appropriate description for this ion. One other metrical parameter which is of interest in this system is the very short S-S distance of 2.970 Å that is much shorter than the sum of the van der Waals radii (3.6 Å),[33] consistent with an S···S closed-shell interaction, especially when considering the much longer S-S distances of 3.8 Å which have been considered weakly bonding closed-shell S-S interactions.[34]

As it has previously been shown by Weigand *et al.* and by ourselves that NHC-stabilized P^I cations are suitable ligands for coinage metal complexes,[6,35] cyclic voltammetry was performed on **[^{Et}TZ$_2$P][I]** in order to rank its donor ability against that of **^{Me}D**, however the two show very different redox properties. Whereas **^{Me}D** shows a single irreversible oxidation at +0.341 V (versus Fc/Fc+)[6], **[^{Et}TZ$_2$P][I]** shows two quasi-reversible oxidations at +0.241 V and -0.142 V, and suggests that it should be a stronger donor than **^{Me}D**.

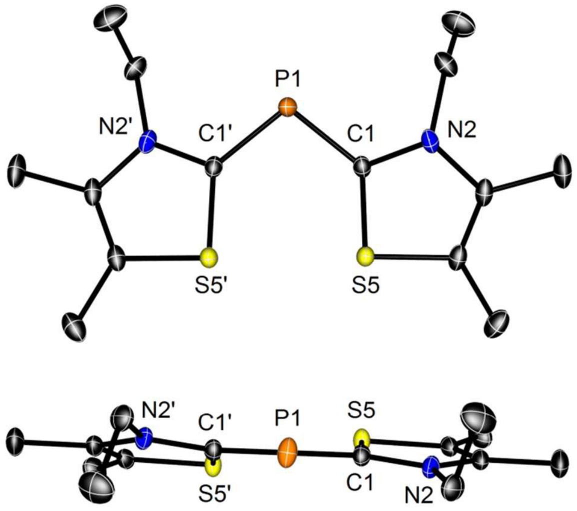


Fig. 5 Thermal ellipsoid plot of **[^{Et}TZ$_2$P][I]** from top-down (top) and side-on (bottom) views. Ellipsoids are drawn using the 50% probability surface. Hydrogen atoms and anion are omitted for clarity. Selected distances (Å) and angles (º): P1-C1, 1.7866(15); C1-N2, 1.3573(18); C1-S5, 1.7177(15); S5-S5', 2.970; C1-P1-C1', 102.23(10).

Computational investigations

In order to rationalize the structure and bonding of **[^{Et}TZ$_2$P]**$^+$, DFT calculations were performed at the PBE1PBE/TZVP level of theory. The geometry optimization correctly predicts the modest twisting of the heterocycles from the C-P-C plane and all of the other metrical parameters in very good agreement with the crystallographically determined structure. In contrast to the results obtained for the acyclic and even chelated bis-NHC-coordinated ions,[6] NBO analysis of the optimized structure of **[^{Et}TZ$_2$P]**$^+$ finds only one lone pair of electrons on phosphorus (in an orbital with 66.3% s-character and 33.7% p-character) and identifies the presence of both σ- and π-bonds between P and C. This is in good accord with all of the experimental results and together provides a solid basis for characterization of **[^{Et}TZ$_2$P]**$^+$ as a P^{III} compound. It is also worth noting that AIM analysis identifies a bond-critical point between the two sulfur atoms consistent with the presence of an S···S interaction that likely contributes to the almost planar conformation (see the Supporting Information).

Synthesis and characterization of [^{Et}TZ$_2$PS$_2$][I]

Protection of the phosphorus centre in **[^{Et}TZ$_2$P][I]** is accomplished by treatment with elemental sulfur, resulting in a colour change from deep red to bright yellow. The newly dithionated cation displays a ^{31}P NMR resonance at 31 ppm. To our delight, this cation remains resistant towards air and moisture even after weeks of exposure.

Slow evaporation of acetonitrile or dichloromethane solutions of **[^{Et}TZ$_2$PS$_2$][I]** grants bright yellow crystals suitable for X-ray diffraction. The salt crystallizes in the space group *P2$_1$/n* and the molecular structure of the cation is illustrated in Figure 6. The P-C bond lengths of 1.8522(12) Å and 1.8494(13) Å are considerably longer than those of **[^{Et}TZ$_2$P][I]**, and the C-P-C angle of 95.86(5)º is much more accute, both of which are anticipated upon the loss of multiple bonding at the phosphorus centre. The S-P distances of 1.9514(5) and 1.9538(5) are typical of those seen in dithiophosphinates.[36–38] Interestingly, the SNHC rings are aligned almost perpendicularly to one another, precluding any type of S···S interaction between the two rings. There is however a close S···S distance between one of the SNHC sulfur atoms and a sulfur atom on phosphorus (3.2305(5) Å). **[^{Et}TZ$_2$PS$_2$][I]** represents a rare examples of a cationic dithiophosphinate (a pyridyl analogue was described as perhaps being a donor-stabilized [PS$_2$]$^+$ ion[39]). Investigations of **[^{Et}TZ$_2$P]**$^+$ salts as potential *Janus head* ligands[40] are underway.

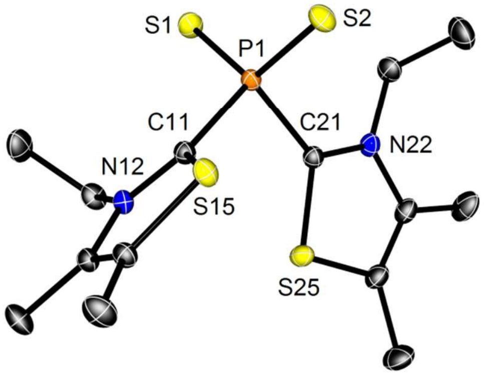


Fig. 6 Thermal ellipsoid plot of **[^{Et}TZ$_2$PS$_2$][I]**. Ellipsoids are drawn using the 50% probability surface. Hydrogen atoms and anion are omitted for clarity. Selected distances (Å) and angles (º): P1-S1, 1.9514(5); P1-S2, 1.9538(5); P1-C11, 1.8522(12); P1-C21, 1.8494(13); C11-S12, 1.6939(13); C21-S22, 1.6903(13); C11-N15, 1.3433(16); C21-N25, 1.3390(16); C11-P1-C21, 95.86(6); S1-P1-S2, 122.06(2).

Conclusions

In conclusion, we have reported spectroscopic and crystallographic data for a variety of *N*-alkyl thiazolium iodide salts which have hitherto eluded characterization. We have shown that in spite of the small substituents on nitrogen, the SNHCs resulting from deprotonation of these salts are present in solution in amounts allowing for ligand displacement reactions with our conveniently prepared triphosphenium precursor. The resultant phosphamethine cyanine cations have spectroscopic,

Table 1 Summary of crystallographic data and refinement details.

Compound	**[^{Et}BTZ][I]**	**[^{nBu}BTZ][I]**	**[^{Me}TZ][I]**	**[^{Et}TZ][I]**
CCDC	1413985	1413986	1413982	1413983
Empirical formula	$C_9H_{10}NSI$	$C_{11}H_{14}NSI$	$C_6H_{10}NSI$	$C_7H_{12}NSI$
Formula weight	291.14	319.19	255.11	269.14
Temperature/K	173(2)	173(2)	150(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	*P 2$_1$/c*	*P n a 2$_1$*	*P 2$_1$/c*	*P -1*
a/Å	7.3740(9)	17.471(3)	8.5748(2)	7.2083(10)
b/Å	16.650(2)	13.112(2)	7.6434(2)	8.0237(11)
c/Å	8.6559(10)	5.2955(9)	13.3454(3)	8.8800(12)
α/°	90	90	90	78.7720(10)
β/°	103.4220(10)	90	92.1710(10)	82.5190(10)
γ/°	90	90	90	73.7020(10)
Volume/Å^3	1033.8(2)	1213.1(3)	874.04(4)	481.96(11)
Z	4	4	4	2
ρ_{calc}g/cm^3	1.871	1.748	1.939	1.855
μ/mm^{-1}	3.247	2.775	3.824	3.473
F(000)	560	624	488	260
Crystal size/mm^3	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.308 × 0.155 × 0.140	0.50 × 0.40 × 0.40
2Θ range for data collection/°	2.446 to 28.111	2.802 to 27.486	3.072 to 27.500	2.346 to 27.485
Index ranges	$-9 \le h \le 9$,	$-22 \le h \le 22$,	$-11 \le h \le 11$,	$-9 \le h \le 9$,
	$-21 \le k \le 21$,	$-16 \le k \le 16$,	$-9 \le k \le 9$,	$-10 \le k \le 10$,
	$-11 \le l \le 11$	$-6 \le l \le 6$	$-17 \le l \le 17$	$-12 \le l \le 12$
Reflections collected	11380	12749	16440	5441
Independent reflections	2402 [R_{int} = 0.0249]	2730 [R_{int} = 0.0868]	1997 [R_{int} = 0.0354]	2144 [R_{int} = 0.0213]
Data/restraints/parameters	2402 / 0 / 109	2730 / 1 / 127	1997 / 0 / 86	2144 / 0 / 96
Goodness-of-fit on F2	1.295	1.143	1.278	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0354,	R_1 = 0.0498,	R_1 = 0.0242,	R_1 = 0.0207,
	wR_2 = 0.0684	wR_2 = 0.0946	wR_2 = 0.0661	wR_2 = 0.0472
Final R indexes [all data]	R_1 = 0.0386,	R_1 = 0.0733,	R_1 = 0.0243,	R_1 = 0.0222,
	wR_2 = 0.0698	wR_2 = 0.1032	wR_2 = 0.0665	wR_2 = 0.0481
Largest diff. peak/hole / e Å-3	0.753/-0.644	1.999/-0.921	0.755/-0.884	0.531/-0.385
Refinement method	Full-matrix least-squares on F^2			
Data completeness	1.000	0.998	0.998	0.997

structural and electronic properties that are consistent with the original assignment as P^{III} species. Although the phosphamethine cyanine iodide salts are highly air-sensitive, oxidation of the phosphorus centre by sulfur gives a protected dithiophosphinium cation which is air and moisture stable. Detailed investigations of the ligand chemistry and photophysical behavior of these compounds are ongoing.

Experimental section

General Remarks

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich and used without further purification. Deuterated solvents were dried according to literature procedure when necessary, and all other solvents were dried over a series of Grubbs'-type columns and degassed prior to use.[41] **C**[Br][3], **C**[I],[42] **C**[BPh$_4$],[42] **[^{Et}BTZ][I]**[18] and **[^{nBu}BTZ][I]**[18] were synthesized according to literature procedures. NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz, Bruker Avance Ultrashield 300 MHz or Bruker Avance DPX 300 MHz spectrometers. Chemical shifts are reported in ppm relative to internal standards for ^{1}H and ^{13}C (the given deuterated solvent) and external standards for and ^{31}P (85% H_3PO_4). Coupling constants |J| are given in Hz. Elemental Analysis was performed at the University of Windsor Mass Spectrometry Service Laboratory using a Perkin Elmer 2400 combustion CHN analyzer. High-resolution electrospray ionization mass spectrometry was performed either at the University of Windsor Mass Spectrometry Sevice Laboratory using a Micromass LCT mass spectrometer or at the McMaster Regional Centre for Mass Spectrometry. Melting points were determined in sealed (under nitrogen) or open capillary tubes using an Electrothermal Mel-Temp® melting point apparatus. Cyclic voltammetry was performed in dry MeCN solutions using a [NBu$_4$][PF$_6$] (0.1 M) electrolyte with analyte concentration of about 0.01 M. A glassy carbon electrode, a platinum wire, and an Ag/AgCl electrode were used as the working, auxiliary, and reference electrodes, respectively. The experiments were run with a scan rate of 100mV/s and a sensitivity of 100 μA/V and the potentials reported are referenced to ferrocene/ferrocenium ($E^1/_2$ = 0.0 V). The voltammogram is depicted in the Supporting Information.

Crystallographic Details

Crystals for investigation were covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXII software suite[43] on a Bruker Photon 100 CMOS diffractometer or using the SMART software on a Bruker APEX CCD diffractometer using a graphite monochromator with MoK$_\alpha$ radiation (λ = 0.71073 Å). For each sample, data were collected at low temperature. APEXII software was used for data reductions and SADABS[44] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the spacegroup and the structures were solved and refined using the SHELX[45] software suite as implemented in the WinGX[46] or OLEX2[47] program suites. Validation of the structures was conducted using PLATON.[48]

Table 2 Continued summary of crystallographic data and refinement details.

Compound	**[^{iPr}TZ^{Me}][I]**	**(^{Et}BTZ)$_2$**	**[^{Et}TZ$_2$P][I]**	**[^{Et}TZ$_2$PS$_2$][I]**
CCDC	1413984	1413987	1413988	1413989
Empirical formula	$C_8H_{14}NSI$	$C_{18}H_{18}N_2S_2$	$C_{14}H_{22}N_2PS_2I$	$C_{14}H_{22}N_2PS_4I$
Formula weight	283.16	326.46	440.32	504.44
Temperature/K	173(2)	173(2)	173.19	173.2
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*P n m a*	$P\ 2_1\ 2_1\ 2_1$	*C2/c*	$P2_1/n$
a/Å	12.0281(14)	8.4609(10)	14.6665(7)	11.8142(7)
b/Å	7.7753(9)	9.3845(11)	10.2797(5)	7.1440(4)
c/Å	11.5619(13)	20.267(2)	13.4062(7)	24.3816(13)
α/°	90	90	90	90
β/°	90	90	118.4096(18)	103.289(2)
γ/°	90	90	90	90
Volume/Å^3	1081.3(2)	1609.2(3)	1777.80(15)	2002.7(2)
Z	4	4	4	4
ρ_{calc}g/cm^3	1.739	1.347	1.645	1.673
μ/mm^{-1}	3.101	0.328	2.119	2.094
F(000)	552	688	880.0	1008.0
Crystal size/mm^3	0.40 × 0.40 × 0.20	0.70 × 0.50 × 0.30	0.104 × 0.086 × 0.046	0.206 × 0.16 × 0.094
2Θ range for data collection/°	2.443 to 28.234	2.392 to 27.497	6.316 to 61.112	5.956 to 77.306
Index ranges	$-15 \leq h \leq 15$, $-10 \leq k \leq 10$, $-15 \leq l \leq 15$	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-26 \leq l \leq 26$	$-20 \leq h \leq 20$, $-14 \leq k \leq 14$, $-19 \leq l \leq 19$	$-20 \leq h \leq 20$, $-12 \leq k \leq 12$, $-42 \leq l \leq 42$
Reflections collected	11622	18137	43169	94035
Independent reflections	1386 [R_{int} = 0.0274]	3648[R_{int} = 0.0473]	2726 [R_{int} = 0.0497]	11356 [R_{int} = 0.0389]
Data/restraints/parameters	1386 / 0 / 73	3648 / 0 / 199	2726/0/95	11356/0/205
Goodness-of-fit on F2	1.115	1.048	1.092	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0254, wR_2 = 0.0521	R_1 = 0.0388, wR_2 = 0.0834	R_1 = 0.0235, wR_2 = 0.0429	R_1 = 0.0340, wR_2 = 0.0612
Final R indexes [all data]	R_1 = 0.0291, wR_2 = 0.0539	R_1 = 0.0468, wR_2 = 0.0872	R_1 = 0.0342, wR_2 = 0.0455	R_1 = 0.0515, wR_2 = 0.0657
Largest diff. peak/hole / e Å-3	0.662/-0.458	0.283/-0.185	0.55/-0.62	1.44/-1.08
Refinement method	Least-Squares Minimization			
Data completeness	1.000	0.999	0.998	0.997

Crystallizations of *N*-alkylbenzothiazolium iodide salts

Crystals suitable for single crystal X-Ray diffraction were grown from a 1:1 solution of MeCN:EtOH.

Synthesis and crystallization of bis(*N*-ethylbenzothiazol-2-ylidene)

A suspension of potassium hydride (5.334 g, 13.30 mmol) in THF (25 mL) was added to a stirring suspension of *N*-ethylbenzothiazolium iodide (3.850 g, 13.20 mmol) in THF (50 mL) and refluxed overnight. After cooling, all volatiles were removed under reduced pressure, and the resulting residue was extracted with toluene and filtered through celite. Removal of most of the solvent from the filtrate under reduced pressure granted a dark red oil from which crystals of the olefin grew over a period of 5 days. Spectroscopic data are consistent with previous reports.[24,25]

General synthesis of *N*-alkyl-4,5-dimethyl thiazolium iodides

Thiazolium iodide salts were synthesized using a variation of a method reported by Rogers *et al.*. 4,5-dimethyl thiazole and a small excess of the given alkyl iodide were stirred and heated to 70 ºC under nitrogen until most or all of the liquid mixture had been replaced by a white to off-white solid (1 to 4 days, depending on the alkyl iodide). Once cooled to room temperature, this solid was triturated and washed with toluene, then dried under vacuum, affording the analytically pure *N*-alkyl-4,5-dimethyl thiazolium iodide salt as an off-white to white solid. Crystals suitable for single crystal X-ray diffraction were grown from a solution of 1:1 EtOH:MeCN.

N-methyl-4,5-dimethylthiazolium iodide [^{Me}TZ][I]

Synthesis and spectroscopic data for this compound has been reported.[49] Spectroscopic data reported therein are identical to those aquired. Recrystallization by slow evaporation of dichloromethane affords crystals suitable for X-Ray diffraction.

N-ethyl-4,5-dimethylthiazolium iodide [^{Et}TZ][I]

Reagents: 4,5-dimethylthiazole (4.815 g, 42.54 mmol); ethyl iodide (7.372 g, 47.27 mmol). Yield: 99% (11.300 g, 41.98 mmol). Mp: 118 ºC. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 12.38 (s), 13.29 (s), 15.32 (s), 49.67 (s), 133.30 (s), 141.63 (s), 155.06 (s). ^{1}H NMR ($CDCl_3$) δ: 1.60 (t, 3H, $^3J_{H\text{-}H}$ = 7), 2.64 (s, 3H), 2.67 (s, 3H), 4.65 (q, 2H, $^3J_{H\text{-}H}$ = 7), 10.68 (s, 1H). Elemental Analysis: calcd. for $C_7H_{12}NSI$: C, 31.24; H, 4.49; N, 5.20, found: C, 31.55; H, 4.74; N, 5.32. HR-ESI-MS: calcd. for $[(C_7H_{12}NS)_2I]^+$ *m/z* = 411.0426, found: 411.0439.

N-isopropyl-4,5-dimethylthiazolium iodide [^{iPr}TZ][I]

Reagents: 4,5-dimethylthiazole (5.350 g, 47.26 mmol); isopropyl iodide (9.639 g, 56.70 mmol). Yield: 29% (3.911 g, 12.81 mmol). Mp: 157 ºC. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 12.81 (s), 13.15 (s), 23.03 (s), 56.98 (s), 133.31 (s), 141.46 (s), 154.50 (s). ^{1}H NMR ($CDCl_3$) δ: 1.63 (d, 6H, $^3J_{H\text{-}H}$ = 6.5), 2.48 (s, 3H), 2.50 (s, 3H), 4.91 (sept, 1H, $^3J_{H\text{-}H}$ = 6.5), 10.54 (s, 1H). Elemental Analysis: calcd. for $C_8H_{14}NSI$: C, 33.93; H, 4.98; N, 4.95, found: C, 34.26; H, 5.05; N, 5.05. HR-ESI-MS: calcd. for $[C_8H_{14}NS]^+$ *m/z* = 156.0847, found: 156.0855.

N-^{n}butyl-4,5-dimethylthiazolium iodide [^{nBu}TZ][I]

Reagents: 4,5-dimethylthiazole (5.029 g, 44.43 mmol); *n*-butyl iodide (8.895 g, 48.33 mmol). Yield: 90% (11.860 g, 39.91 mmol). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 12.30 (s), 13.15 (s), 13.35 (s), 19.21 (s), 31.50 (s), 53.80 (s), 133.17 (s), 141.50 (s), 155.30 (s). ^1H NMR ($CDCl_3$) δ: 0.96 (t, 3H, $^3J_{H\text{-}H}$ = 7.4), 1.43 (m, 2H), 1.89 (m, 2H), 2.51 (s, 3H), 2.55 (s, 3H), 4.63 (t, 2H, $^3J_{H\text{-}H}$ = 7.5), 10.76 (s, 1H). Elemental Analysis: calcd. for $C_9H_{16}NSI$: C, 36.37; H, 5.43; N, 4.71, found: C, 35.46; H, 5.62; N, 4.73. HR-ESI-MS: calcd. for $[C_9H_{16}NS]^+$ *m/z* = 170.1003, found: 170.0996.

Observation of in situ generated [^{Et}BTZ$_2$P]$^+$

A suspension of potassium hydride (0.069 g, 0.52 mmol) in THF (15 mL) was transferred to a mixture of *N*-ethyl-benzothiazolium iodide (0.151 g, 0.52 mmol) and [dppeP][BPh_4] (0.195 g, 0.26 mmol) in THF (15 mL). The reaction mixture was allowed to stir under nitrogen for one half hour, and then at reflux for four hours. Removal of all volatiles under reduced pressure granted a red mixture from which the desired cation was detectable by HR-ESI-MS and ^{31}P NMR. $^{31}P\{^1H\}$ NMR (MeCN) δ: 33.0 (s). HR-ESI-MS: calcd. for $[C_{18}H_{18}N_2S_2P]^+$ *m/z* = 357.0649, found: 357.0648.

Observation of in situ generated [^{Me}TZ$_2$P]$^+$

Potassium tert-butoxide (0.176 g, 1.57 mmol) in THF (3 mL) was transferred to a suspension of *N*,4,5-trimethyl thiazolium iodide (0.400 g, 1.57 mmol) in THF (5 mL) and reacted for two hours. The resulting mixture was centrifuged and the solution added to a suspension of [dppeP][Br] (0.399 g, 0.78 mmol) in THF (10 mL) and allowed to stir overnight. Removal of all volatiles under reduced pressure granted a red mixture from which the desired cation was detectable by ^{31}P NMR. $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ: 17.7 (s). HR-ESI-MS: calcd. for $[C_{12}H_{18}N_2S_2P]^+$ *m/z* = 285.0649, found: 285.0644.

Observation of in situ generated [^{iPr}TZ$_2$P]$^+$

A suspension of potassium hydride (0.146 g, 1.09 mmol) in THF (15 mL) was transferred to a mixture of *N*-isopropyl-4,5-dimethylthiazolium iodide (0.310 g, 1.09 mmol), and [dppeP][BPh_4] (0.402 g, 0.54 mmol) in THF (15 mL). The reaction mixture was allowed to stir under nitrogen for one half hour, and then at reflux for four hours. Removal of all volatiles under reduced pressure granted a red mixture from which the desired cation was detectable by HR-ESI-MS and ^{31}P NMR. $^{31}P\{^1H\}$ NMR (CD_3CN) δ: 9.9 (s). HR-ESI-MS: calcd. for $[C_{16}H_{26}N_2S_2P]^+$ *m/z* = 341.1275, found: 341.1258.

Observation of in situ generated [^{nBu}TZ$_2$P]$^+$

A suspension of potassium hydride (0.110 g, 0.82 mmol) in THF (15 mL) was transferred to a mixture of *N*-n-butyl-4,5-dimethylthiazolium iodide (0.238 g, 0.80 mmol) and [dppeP][BPh_4] (0.300 g, 0.40 mmol) in THF (15 mL). The reaction mixture was allowed to stir under nitrogen for one half hour, and then at reflux for four hours. Removal of all volatiles under reduced pressure granted a red mixture from which the desired cation was detectable by ^{31}P NMR. $^{31}P\{^1H\}$ NMR (MeCN) δ: 17.5 (s). HR-ESI-MS: calcd. for $[C_{18}H_{30}N_2S_2P]^+$ *m/z* = 369.1593, found: 369.1588.

Synthesis of [^{Et}TZ$_2$P][I]

A suspension of *N*-ethyl-4,5-dimethylthiazolium iodide (0.716 g, 2.660 mmol) in THF (25 mL) was added to a suspension of potassium hydride (0.160 g, 3.989 mmol) in THF (25 mL) at -78 ºC. After two hours, a suspension of [dppeP][Br] (0.677 g, 1.329 mmol) was added to the mixture, and the reaction vessel was allowed to warm slowly to room temperature and react for 12 hours. All volatiles were removed from the red mixture under reduced pressure, and diethyl ether (100 mL) was added to the residue and sonicated. The insoluble material was collected by filtration and washed with diethyl ether (2 x 5 mL), and dried under reduced pressure. Acetonitrile (30 mL) was then slowly added to the collected material. Some gas evolution was observed upon addition of acetonitrile, but this ceased after a few seconds. The solution was filtered and any volatiles were removed from the filtrate under reduced pressure. Toluene (50 mL) was added to the resulting residue and sonicated giving a suspension, from which the insoluble product was collected by filtration and washed with toluene (3 x 5 mL). If necessary, the product can be further purified by recrystallization from a saturated acetonitrile solution, affording crystals suitable for single crystal X-Ray diffraction. Yield: 54% (0.160 g, 0.363 mmol). Mp: 186 ºC. $^{31}P\{^1H\}$ NMR (CD_3CN) δ: 17.2 (s). $^{13}C\{^1H\}$ NMR (CD_3CN) δ: 12.20 (s), 12.28 (s), 12.6 (d, $^4J_{P\text{-}C}$ = 5.0), 46.82 (d, $^3J_{P\text{-}C}$ = 25.7), 125.25 (d, $^3J_{P\text{-}C}$ = 3.6), 140.84 (d, $^3J_{P\text{-}C}$ = 2.3), 178.79 (d, $^1J_{P\text{-}C}$ = 87.0). ^1H NMR (CD_3CN) δ: 1.38 (t, 6H, $^3J_{H\text{-}H}$ = 7.5), 2.34 (s, 6H), 2.38 (s, 6H), 4.30 (dq, 4H, $^3J_{H\text{-}H}$ = 7.5, $^4J_{P\text{-}C}$ = 1.0). Elemental Analysis: calcd. for $C_{14}H_{22}N_2S_2PI$: C, 38.18; H, 5.04; N, 6.37, found: C, 38.14; H, 4.82; N, 6.38. HR-ESI-MS: calcd. for $[C_{14}H_{22}N_2S_2P]^+$ *m/z* = 313.0962, found: 313.0952. Cyclic Voltammetry: $E^1/_2$ = +0.241 V, -0.142 V.

Synthesis of [^{Et}TZ$_2$PS$_2$][I]:

Dichloromethane (5 mL) was added to a stirring mixture of **[^{Et}TZ$_2$P][I]** (0.030 mg, 0.068 mmol) and sulfur (S_8)(0.004 g, 0.017 mmol) and allowed to stir overnight. The resulting reaction mixture was centrefuged and the clear yellow supernatant solution was decanted and left to recrystallize. Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation of either dichloromethane or acetonitrile. Yield: Quantitative by multinuclear NMR. Mp: 192 ºC (dec.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 31.2 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 13.28 (s), 14.08 (s), 14.38 (d, $^4J_{P\text{-}C}$ = 5.0), 50.62 (d, $^3J_{P\text{-}C}$ = 25.7), 138.18 (d, $^3J_{P\text{-}C}$ = 2.9), 149.13 (d, $^3J_{P\text{-}C}$ = 3.5), 170.57 (d, $^1J_{P\text{-}C}$ = 57.2). ^1H NMR (CD_2Cl_2) δ: 1.54 (t, 6H, $^3J_{H\text{-}H}$ = 7.2), 2.54 (s, 6H), 2.57 (s, 6H), 4.85 (q, 4H, $^3J_{H\text{-}H}$ = 7.2). Elemental Analysis: calcd. for $C_{14}H_{22}N_2S_4PI$: C, 33.33; H, 4.40; N, 5.55, found: C, 33.55; H, 4.17; N, 5.69. HR-ESI-MS: calcd. for $[C_{14}H_{22}N_2S_4P]^+$ *m/z* = 377.0403, found: 377.0405.

Computational Details

Calculations were performed with the Gaussian 09 suite of programs[50] using Compute Canada's Shared Hierarchical Academic Research Computing Network (SharcNet). Model complexes were fully optimized with no symmetry constraints using the PBE1PBE density functional theory (DFT) method[51–53] in conjunction with the TZVP basis sets for all atoms.[54,55] Geometry optimizations were started using models in which the relevant phosphorus, nitrogen and carbon atoms were placed a the positions found experimentally using X-ray crystallography and the hydrogen atoms were placed in geometrically appropriate positions using Gaussview.[56] Frequency calculations were also performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface and to determine thermochemical information. Natural bond orbital (NBO) analyses[57] to determine orbital contributions, Wiberg Bond Indicies and orbital energies were obtained using the routine included in the Gaussian distributions.[58] Atoms In Molecules (AIM) analysis was done using AIM2000.[59] Summaries of the calculated results, including Cartesian coordinates are presented in the supplementary material.

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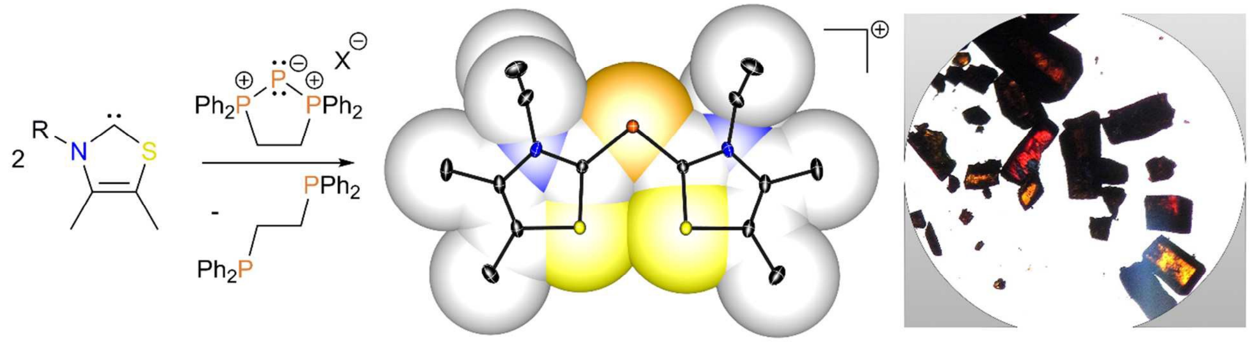
Graphical Abstract

The reaction between a triphosphenium salt and *S*,*N*-heterocyclic carbenes grants phosphamethine cyanines with a different electronic structure than those of their NHC-ligated analogues.