The synthesis, characterisation and electronic structure of *N*-heterocyclic carbene adducts of P^I cations†

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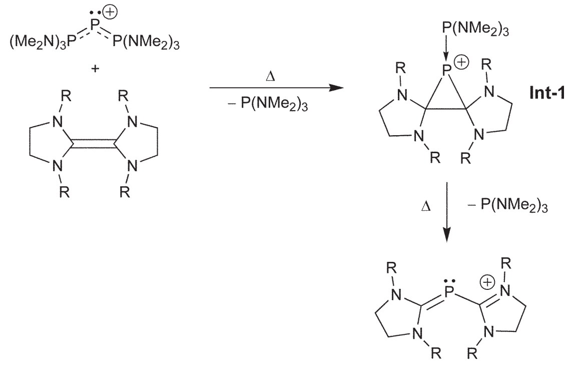
Two different syntheses of *N*-heterocyclic carbene complexes of P^I cations are presented; the structural features of these phosphamethine cyanine salts, in conjunction with the results of computational investigations, provide insight into the nature of the bonding of these heavy allene analogues.

The chemistry of phosphamethine cyanine cations, $[P(CZNR_2)_2]^+$ (Z = CR_3, NR_2, SR, *etc.*), and other phospha-allylic compounds occupies an important position in the history of phosphorus chemistry.[1] These dyes comprised one of the first families of phosphorus compounds reported that contained unambiguous dicoordinate P centers.[2,3] Such compounds are typically made through the reaction of suitable chloro-carbon precursors with explosive or pyrophoric reagents such as $P(CH_2OH)_3$ or $P(SiMe_3)_3$, respectively. In 1983, Schmidpeter *et al.* reported that the triphosphenium salt $\{P[P(NMe_2)_3]_2\}[BPh_4]$ reacts with particular electron rich olefins at elevated temperatures to produce phosphamethine cyanine salts and they proposed that the reaction proceeds in the manner shown in Scheme 1.[4]

Since Arduengo's report of stable *N*-heterocyclic carbenes (NHCs) in 1991,[18] the analogy between phosphines and NHCs has been well documented.[5,6] In the interim, a large number of stable NHCs and related carbenes have been synthesised and characterised. In light of the relationship between phosphines and NHCs, and our recent report of the facile synthesis of diphosphine-stabilized P^I and As^I salts,[7] we have commenced an investigation of carbene-stabilized P^I salts. Herein we present two new synthetic approaches to phosphamethine cyanine salts, which appear to be more accurately considered as NHC-stabilized P^I salts, we provide rare structural data for one example and we offer computational models to elucidate the bonding in such species.

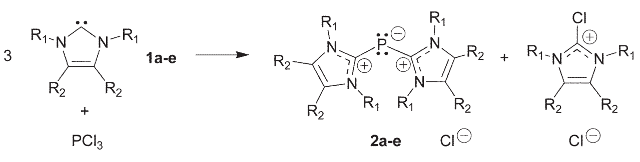


Scheme 1 Schmidpeter's proposed P^+ alkene insertion (R = Me or Et).[4]

As illustrated in Scheme 2, the reaction of phosphorus trichloride with three equivalents of NHC produces salts of the type $[(NHC)_2P][Cl]$, **2**[Cl], in essentially quantitative yield.‡ The additional equivalent of NHC is required to sequester the reactive Cl_2 by-product that is generated during the reduction of the P^{III} centre. As outlined in Table 1, this method works for a variety of NHCs bearing relatively small (R_1 = Et, ^{i}Pr) and certain larger (R_1 = Mes) substituents at the nitrogen centres. In contrast, the reactions of NHCs bearing considerably bulkier substituents (R_1 = ^{t}Bu, adamantyl) on nitrogen do not produce the desired products. Preliminary results indicate that this approach also works with other types of stable carbenes and with the heavier pnictogen trihalides; the details will be presented in a forthcoming full publication. The progress of these reactions is readily monitored by multinuclear (^{1}H, ^{13}C and ^{31}P) NMR spectroscopy given the distinctive signals of the starting materials and products. For example, the ^{31}P chemical shift of **2b** is around −125 ppm and is affected only slightly when the counter anion is changed. It should be noted that the formation of **2** by such a coordination chemistry approach is perhaps surprising given the more typical formation of carbene–phosphenium adducts (*i.e.* $[NHC–PR_2][X]$) from the reaction of an NHC with halophosphines.[8]

An alternative synthetic method, illustrated in Scheme 3, that can be used to obtain salts of **2** is the NHC replacement of 1,2-bis(diphenylphosphino)ethane (dppe) from P^I sources of the type [(dppe)P][X], **3**[X].[7] Thus the treatment of halide salts of **3** with at least two equivalents of various NHCs results in the formation of salts **2**[X] and the concomitant liberation of dppe. This approach is conceptually similar to that used by Arduengo, Cowley and co-workers for the synthesis of NHC–phosphinidene adducts.[9,10] The major advantages of this method over the one outlined in Scheme 2 are that a reduced amount of NHC is required and that the dppe by-product may be readily removed by washing with non-polar solvents. Furthermore, this method can also be used with salts of **3** with a number of other anions, such as $[BPh_4]$.‡

In addition, a surprising route to the chloride salt of **2b** *via* the decomposition of an NHC adduct of an iminophosphine has been



Scheme 2 Direct synthesis of **2**[Cl] salts from PCl_3 and NHCs (a to e as described in Table 1).

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† Electronic supplementary information (ESI) available: crystallographic data in .cif format and a summary of computational results. See http://www.rsc.org/suppdata/cc/b5/b500692a/

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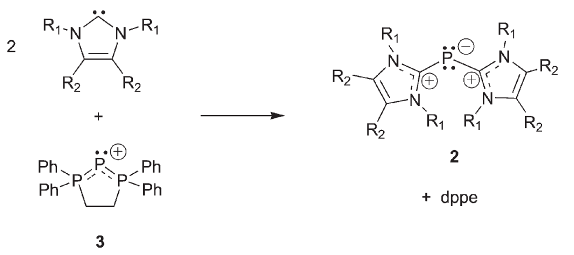
Table 1 Results of the reactions outlined in Schemes 2 and 3

NHC label	R_1	R_2	Scheme 2[a]	Scheme 3[a,b]
1a	Et	Me	Y (−129.2)	Y (−126.7)
1b	^{i}Pr	Me	Y (−126.2)	Y (−124.2)
1c	^{t}Bu	H	N	BP
1d	1-Ad	H	N	BP
1e	Mes	H	Y (−124.2)	BP

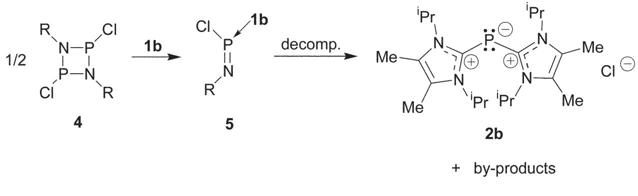
[a] Where the reaction proceeds as described in the given scheme: Y = the reaction proceeds as depicted and the ^{31}P NMR chemical shift (in ppm) of the product **2** is listed in parentheses; N = the reaction does not proceed as depicted in the scheme; BP = the expected by-products are observed, however **2** is not detected by ^{31}P NMR. [b] Data are presented for $[X]^-$ = $[BPh_4]^-$, almost identical chemical shifts are observed for $[X]^-$ = $[I]^-$.



Scheme 3 Ligand replacement synthesis of **2**[X] salts from **3**[X] and NHCs.

discovered. As proposed in Scheme 4, the product of the reaction of 2 equivalents of **1b** with the dichlorophosphetidine **4** (R = 2,6-dimethylphenyl) is an NHC–iminophosphine adduct **5**.[11] A toluene solution of **5** produced small amounts of yellow crystalline material containing **2b** (characterised by ^{31}P NMR) upon standing for two weeks. While the mechanism of the decomposition process and the identity of the by-products have yet to be confirmed, the decomposition reaction did produce crystals suitable for analysis by single crystal X-ray diffraction experiments.§

A depiction of the molecular structure of the cation in the salt **2b**[Cl]·toluene is presented in Fig. 1. There are no unusually short interionic contacts and the metrical parameters in the cation provide insight into the nature of the bonding in such species. With regard to the P$^{\rm I}$ cation, the C–P bonds of 1.823(2) and 1.824(2) Å are typical of P–C$_{\rm aryl}$ single bonds and are significantly longer than those reported previously [1.746(4)–1.794(2) Å] for NHC–phosphinidene adducts.[9,10] The bond distances and angles within the heterocycles are consistent with those of related NHC–P adducts found in the Cambridge Structural Database.[12] The C–P–C angle of 97.35(9)° is much smaller than the angles observed in the only three somewhat comparable cations that have been structurally characterised.[13–15] Perhaps the most notable feature in the structure of the cation is the twisting (*ca.* 50–60°) of the NHC heterocycles from the C–P–C plane. Such twisting should diminish or preclude the interaction of the π-system on the NHC rings with the filled 3p orbital on the P atom.



Scheme 4 Synthesis of **2b**[Cl] from the decomposition of **5** (R = 2,6-dimethylphenyl).

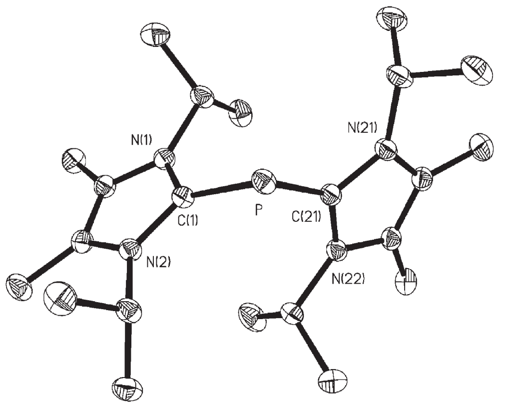
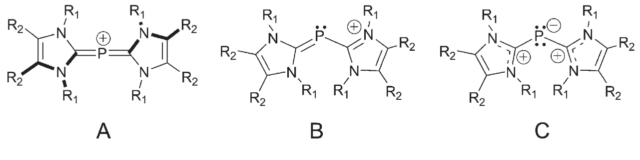


Fig. 1 Thermal ellipsoid plot (30% probability surface) of **2b**, for clarity hydrogen atoms are not shown. Selected distances (Å) and angles (°): P–C(1) 1.824(2), P–C(21) 1.823(2), C(1)–N(1) 1.359(2), C(1)–N(2) 1.361(3), C(21)–N(21) 1.368(3), C(21)–N(22) 1.357(3), C(1)–P–C(21) 97.35(9), C(21)–P–C(1)–N(1) −61.6(2), C(1)–P–C(21)–N(21) 131.2(2).

Given that the observed P–C bond lengths and the twisting of NHC heterocycles from the C–P–C plane are not consistent with the presence of multiple-bonding, we performed a series of density functional theory (DFT) calculations to elucidate the nature of the electronic structure in cations such as **2** using the model **2f** ($R_1 = R_2 = H$).† The bending at the P atom in **2** is inconsistent with a classical allene-type "P$^{\rm V}$" bonding model (**A** in Scheme 5) thus some more probable bonding models for such cations are depicted in Scheme 5.

The twisting of the NHC heterocycles is accurately predicted by the calculations (the C_2 symmetry isomer being the only true minimum on the potential energy surface) and such distortions diminish the effective overlap of the π-systems on the NHC fragments with the 3p orbital on P. Thus the twisting of the NHC fragments and the long P–C distances (1.799 Å calculated for **2f**) would suggest that the "P$^{\rm I}$" model, **C** in Scheme 5, is the best representation of the electronic structure in such cations. However, it must be noted that, in spite of the calculated *ca.* 36° C–P–C–N torsion angle, there is clear evidence for some interaction between the π systems on the NHC ligands and the 3p orbital on P, in both the appearance of the HOMO-2 orbital in **2f** (Fig. 2) and in the results of the electron population analyses. The presence of π-delocalization is also evident in the distinctive bright yellow colours exhibited by the real ions, thus it appears that a "P$^{\rm III}$" canonical structure of the type **B** is not completely prevented by the distortion of the cation from planarity.†

The apparent relative unfavourability of the cations **2c** and **2d** may be rationalized using the results of semi-empirical calculations that were performed with Fujitsu's CAChe 6.1 suite of programs.†



Scheme 5 Some possible Lewis-type drawings of cation **2**.

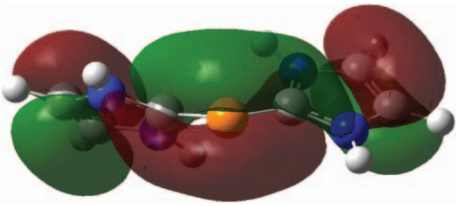


Fig. 2 Gaussview® depiction of the third highest occupied molecular orbital (HOMO-2) for **2f**.

The optimization of complete model cations at the PM3 level of theory suggests that bulky substituents on N result in much longer P–C distances (>1.9Å) and C–P–C angles (>111°). Single-point DFT calculations on appropriate models derived from the semi-empirical results reveal that such distortions in the metrical parameters destabilize the cations and thus may render them more amenable to decomposition.

The experimental results outlined above suggest that an alternative mechanism to that outlined in Scheme 1 is conceivable for the formation of phosphamethine cyanine salts from the reaction of electron rich olefins with P^{I} sources such as **3**. It appears possible that the reaction may occur by way of NHCs generated *in situ* by the thermolysis of the electron rich olefins.[16]

In conclusion, we have shown that NHCs can be used as effective ligands for P^{I} cations and that a number of new, convenient and safe synthetic approaches can be used to obtain salts of such species. We are currently proving the generality of these synthetic approaches with other stable carbenes and other group 15 elements. We have also presented structural and computational evidence for an improved understanding of the nature of the bonding in this historically important type of phosphorus cation.

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Notes and references

‡ Representative data for the salts **2b**[Cl] and **2b**[BPh_4]; chemical shifts are reported in ppm and coupling constants are given in Hertz.

2b[Cl]: A solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1b**)[17] (0.282 g; 1.564 mmol) in 10 mL of THF was slowly added *via* cannula to a solution of PCl_3 (0.072 g; 0.521 mmol) in 10 mL of THF. The solution immediately precipitated a yellow material and was allowed to stir for 30 min. The solvent was removed *in vacuo*. The by-product [NHC–Cl][Cl] was unable to be separated because its solubility is similar to that of **2b**[Cl]. Yield: 0.196 g (87% isolated, quantitative by ^{31}P NMR). ^{31}P NMR (CD_2Cl_2) δ: −124.2 (s). ^{13}C NMR (CD_2Cl_2) δ: 128.1 (s), 51.5 (s), 21.2 (s), 11.0 (s). ^{1}H NMR (CD_2Cl_2) δ: 4.50 (septet, 4H, ^{3}J = 6.8), 2.25 (s, 12H), 1.66 (d, 24H, ^{3}J = 6.7). HR-ESI-MS: calcd. for $C_{22}H_{40}ClN_4P$ $[M - Cl]^+$ m/z = 391.2991, found 391.2986 (1.2 ppm).

2b[BPh_4]: A solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1b**) (0.069 g; 0.383 mmol) in 10 mL of THF was slowly added *via* cannula to a solution of [(dppe)P][BPh_4] (0.143 g; 0.191 mmol) in 10 mL of THF. The solution immediately became intensely yellow-coloured and was allowed to stir for 30 min. The solvent was removed *in vacuo*, followed by washing with toluene (3 × 5 mL) to remove the free dppe. Yield: 0.098 g (72% isolated, quantitative by ^{31}P NMR). ^{31}P NMR (CD_2Cl_2) δ: −126.1 (s). ^{11}B NMR (CD_2Cl_2) δ: −6.9 (s). ^{13}C NMR (CD_2Cl_2) δ: 164.6 (q, $^{1}J_{BC}$ = 49), 136.5 (s), 127.9 (s), 127.2 (s), 122.2 (s), 51.6 (s), 21.2 (s), 11.0 (s). ^{1}H NMR (CD_2Cl_2) δ: 7.33 (m, 20H), 4.41 (m, 4H), 2,12 (s, 12H), 1.58 (d, 24H, ^{3}J = 6.6). HR-ESI-MS: calcd. for $C_{46}H_{60}BN_4P$ $[M - BPh_4]^+$ m/z = 391.2991, found 391.2978 (3.2 ppm).

§ A suitable single crystal of **2b**[Cl]·toluene was covered with mineral oil and mounted in the 198 K N_2 stream of a Bruker AXS P4/SMART 1000 CCD diffractometer equipped with a Mo Kα radiation (λ = 0.71073 Å) source. The structure was solved by direct methods and refined using full matrix, least squares on F^2. Crystal data for **2b**[Cl]·toluene: $C_{29}H_{48}ClN_4P$, triclinic, $P\bar{1}$, a = 10.134(3), b = 12.243(3), c = 13.037(3) Å, α = 103.358(4)° β = 99.906(5)°, γ = 100.772(4)°, V = 1506.3(7) Å^3, Z = 2, D_{calcd} = 1.145 g cm^{-3}, μ (Mo Kα) = 0.203 mm^{-1}. A total of 10,360 reflections was collected in the range $2.30 < 2\theta < 54.98$. Of these, 6,428 were independent; wR_2 = 0.1560, R = 0.0524. CCDC 261141. See http://www.rsc.org/suppdata/cc/b5/b500692a/ for crystallographic data in .cif or other electronic format.

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