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## COMMUNICATION

# Remarkably Stable Chelating Bis-*N*-Heterocyclic Carbene Adducts of Phosphorus(I) Cations

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Justin F. Binder, Ala'aeddeen Swidan, Martin Tang, Jennifer H. Nguyen and Charles L.B. Macdonald\*

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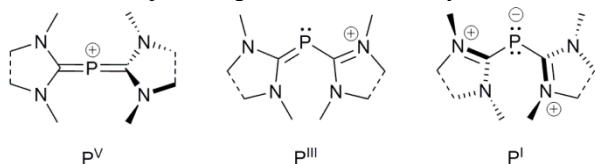
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**A convenient one-pot synthesis of chelating bis-*N*-heterocyclic carbene-ligated P<sup>I</sup> salts is described. The solid state structures of these remarkably stable phosphamethine cyanine dyes with various *N*-alkyl groups and counter-anions are reported, and initial reactivity results are discussed.**

2-Phosphaallylic cations occupy a special place in the history of phosphorus chemistry and main group chemistry as a whole.<sup>1</sup> In particular, the crystal structure of bis(*N*-ethylbenzthiazole(2))-phosphamethine cyanine perchlorate (see Table 1) provided the first structural confirmation of a dicoordinate phosphorus environment **and** concrete evidence for 3p-2p  $\pi$ -bonding!<sup>2-4</sup> From a practical perspective, several of these compounds were investigated as phosphorus analogues of methine cyanine dyes because of the potentially delocalized  $\pi$ -system (Fig. 1, P<sup>III</sup> form). However, although the compounds can be used as dyes, they proved to be relatively unstable with respect to hydrolysis of the P-C bond in the presence of water which precluded the widespread development and application of this promising class of functional dyes.

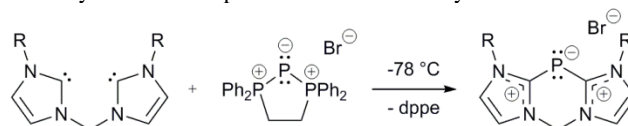


**Fig. 1** Possible canonical structures of bis(NHC)-ligated P cations.

In spite of their importance and long history, only a few examples have been structurally authenticated but some observations are particularly noteworthy: (a) no cumulene-like structures (Fig. 1, P<sup>V</sup> form) have ever been observed; and (b) planar conformations have only been observed in thiazolyl stabilized cations (attributable to S...S interactions),<sup>3</sup> in the N-H tautomers of the neutral di(benzothiazol-2-yl)phosphane<sup>5</sup> and bis(*s*-triazinyl)phosphane<sup>6</sup> (attributable to H-bonding), and in some anionic compounds in which metal coordination enforces butterfly conformations<sup>7-9</sup>. In fact, most of the 2-phosphaallylic species reported actually have non-planar structures featuring “twisting” of the heterocycles with respect to the P-C bond. We subsequently assigned such structural features as being most consistent with the P<sup>I</sup> designation (Fig. 1) and

we described such compounds as *N*-heterocyclic carbene (NHC) complexes of P<sup>+</sup>.<sup>10,11</sup> In fact, the use of NHCs and other carbenes to stabilize low-valent main group fragments has proven tremendously fruitful over the last decade.<sup>12</sup> **Table 1** presents relevant metrical parameters for nearly all of the reported compounds. All 2-phosphaallylic cations featuring imidazolyl-substituents have displayed twisted substituents,<sup>10,13,14</sup> presumably as a result of the steric requirements of the *N*-alkyl groups. In light of the foregoing, we postulated that a cyclic structure might improve the stability of phosphamethine cyanine dyes and simultaneously improve  $\pi$ -delocalization across the molecules. We present herein a convenient method for the generation of such species.

We previously demonstrated that the treatment of triphosphenium iodide P<sup>I</sup> precursors<sup>15,16</sup> with certain *N*-heterocyclic carbenes (NHCs) provides NHC-stabilized P<sup>I</sup> salts. We now report that the reaction of equimolar amounts of the selected (bis)carbene proligand (<sup>R</sup>L: Fig. 2, R = Me, Bn, <sup>t</sup>Bu) with a readily prepared triphosphenium bromide precursor<sup>17</sup> yields orange salts of the type [<sup>R</sup>LP][Br] in excellent yields (Scheme 1). Because free (bis)carbenes of this type are very sensitive to temperature,<sup>18</sup> the generation of <sup>R</sup>L from its imidazolium precursor and the subsequent reaction with the P<sup>I</sup> reagent must be performed at low temperature. Generation of <sup>R</sup>L can be done in the presence of the P<sup>I</sup> precursor but this route leads to lower overall yields. When the reaction is complete, the diphosphine by-product can be removed readily with non-polar solvents to yield analytically pure products that are stable at ambient temperature. In stark contrast to acyclic species, the [<sup>R</sup>LP][Br] salts appear to be stable indefinitely as solids in air and solutions exposed to water show only minor decomposition after several days!



**Scheme 1** Synthesis of [<sup>R</sup>LP][Br] P<sup>I</sup> salts (R = Me, Bn or <sup>t</sup>Bu).

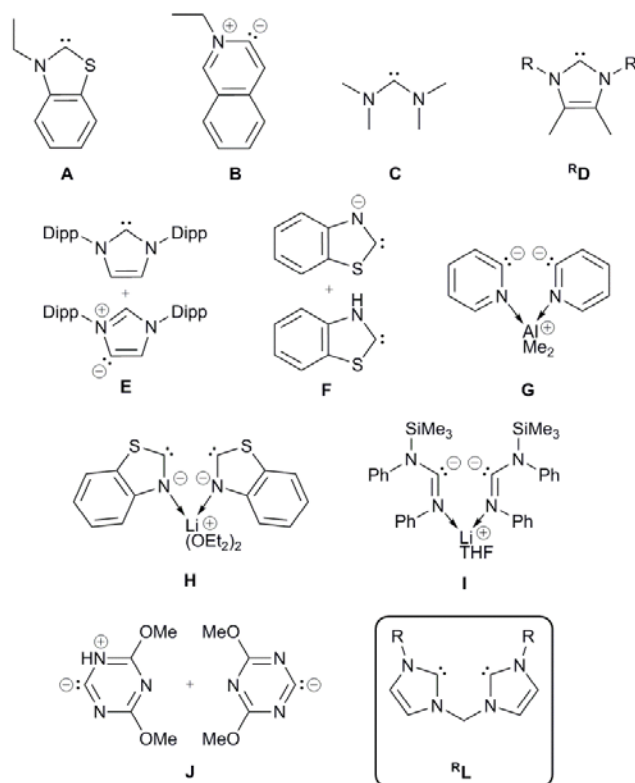
The <sup>31</sup>P NMR spectra of the [<sup>R</sup>LP][Br] salts each feature a singlet between -81 and -83 ppm, which is considerably less shielded than those of comparable acyclic variants (-112 to -127 ppm). The decreased shielding of the P atom is consistent with the increased  $\pi$ -character of the P-C bond.<sup>19</sup> The similarity of the chemical shifts for

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**Table 1** Selected metrical parameters for structurally characterized phosphamethine cyanines and related compounds.

[(Carbene)P][A]	P-C bonds (Å)	C-P-C angle (°)	Carb <sub>p</sub> -CPC <sub>p</sub> angles (°)*	Ref.
[A <sub>2</sub> P][ClO <sub>4</sub> ]	1.75(4), 1.75(7)	104.6	2.66, 4.39	3,4
[B <sub>2</sub> P][ClO <sub>4</sub> ]	1.77, 1.81	100.4	24.78, 38.84	20
[C <sub>2</sub> P][ClO <sub>4</sub> ]	1.796(4) [avg]	103.6(2)	32.02, 33.78	21
[ <sup>Me</sup> D <sub>2</sub> P][Br]·MeCN	1.807(6), 1.809(7)	99.2(3)	42.77, 38.75	13
[ <sup>Et</sup> D <sub>2</sub> P][Br]·MeCN	1.8345(2), 1.8358(3)	96.99(2)	55.49, 57.14	13
[ <sup>iPr</sup> D <sub>2</sub> P][Cl]·Tol	1.824(2), 1.823(2)	97.35(9)	51.71, 60.17	10
[EP][OTf]·DCM	1.773(3), 1.818(3)	109.2(1)	10.02, 11.77	14
FP	1.784(5), 1.778(4)	98.7(2)	3.772, 6.770	5
GP	1.786(2), 1.782(2)	106.60(7)	15.58, 16.68	7
HP	1.779(2)	104.2(1)	3.604, 4.870	22
IP	1.783, 1.784	106.91	6.227, 15.177	23
JP	1.745(3), 1.794(3)	103.4(1)	0.00, 0.00	6
3[ <sup>Me</sup> LP][Br]·MeCN	1.778(3) to 1.795(2)	91.43(10) to 93.13(11)	15.77 to 25.38	This work
[ <sup>Me</sup> LP][OTf]	1.7810(14), 1.7813(15)	92.07(6)	18.83, 19.10	This work
[ <sup>Bn</sup> LP][Br]	1.793(2)	91.87(11)	25.02, 25.47	This work
[ <sup>Bn</sup> LP][BPh <sub>4</sub> ]·THF	1.7797(16), 1.7811(16)	92.51(7)	18.74, 19.51	This work
[ <sup>Bn</sup> LP][BPh <sub>4</sub> ]·DCM	1.782(2), 1.790(2)	92.08(9)	21.67, 22.36	This work

\*These values are the angles (°) between the C-P-C plane and the respective N-C-X planes of the two heterocycles, where X is N, S, or C.



**Fig. 2** Ligands on phosphorus in structurally-characterized phosphamethine cyanines depicted in their “carbenic” proligand form. The ligand system investigated in this work is boxed.

all three cations suggests that the substitution at N does not result in substantial structural or electronic differences. Likewise, the <sup>1</sup>J-couplings of phosphorus to the carbenic carbons are all similar (ca.

75 Hz) and are marginally smaller than those of comparable acyclic variants (80–100 Hz).

Two of the [<sup>R</sup>LP][Br] salts crystallize readily from the evaporation of acetonitrile solutions and single-crystal XRD provides valuable structural information. As anticipated, the short methylene bridge restricts twisting of the NHC fragment relative to the P-C bonds and results in cations with butterfly conformations (Fig. 3) similar to the isovalent germanium(0) species reported by Driess.<sup>24</sup> The C-P-C angles are very small (91.3° to 92.9°) compared to other related 2-phosphaallylic compounds almost certainly as a result of the constraints imposed by the chelating ligand. The P-C distances are longer than those of phosphalkene P=C double bonds (1.61–1.71 Å) but shorter than P-C single bonds (1.85 Å),<sup>25</sup> and are thus consistent with some degree of π-bonding.

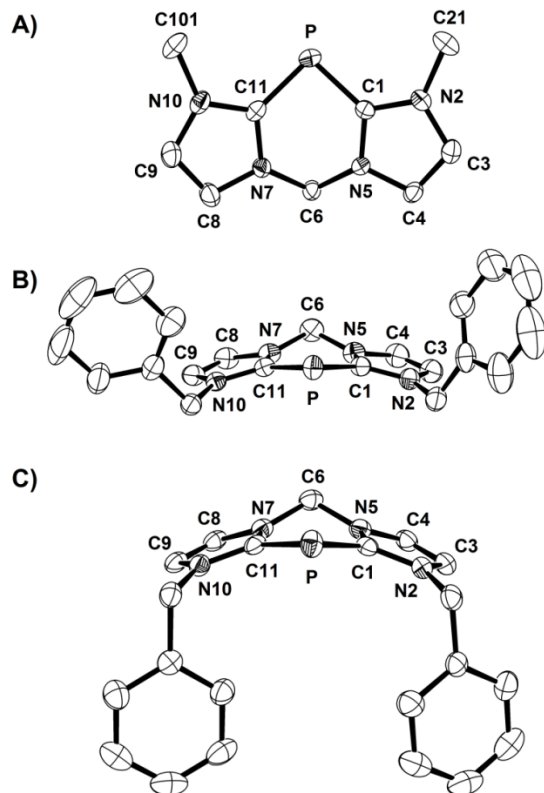
The salt [<sup>Me</sup>LP][Br], which crystallizes in the space group *P*–1, features three crystallographically unique cations in the asymmetric unit. The values observed for the P-C distances, C-P-C angles, and C-P-C-N torsion angles within each cation exhibit significant variation (> 3-esd) and illustrates that the 6-membered ring containing the 2-phosphaallylic fragment is flexible. In fact, the angle between the two NHC planes within each cation varies from 142.7° to 156.2°.

Density functional theory (DFT) calculations on models of [<sup>Me</sup>LP]<sup>+</sup> and the acyclic analogue [(<sup>Me</sup>NHC<sup>H</sup>)<sub>2</sub>P]<sup>+</sup> were performed in order to rationalize any differences in the bonding between the related species. The geometry optimizations reproduce the features of the experimental structures of both ions very accurately and attest to the quality of the method used.<sup>†</sup> Natural Bond Orbital (NBO) analyses<sup>26</sup> suggest that both cations are best considered as P<sup>I</sup> species, in which the phosphorus atom bears two non-bonding pairs of electrons. The P<sup>I</sup> assignment is perhaps surprising given that the much more co-planar structure of [<sup>Me</sup>LP]<sup>+</sup> might have yielded a P<sup>III</sup> structure (as is found for the related acyclic thiazolium model).<sup>†</sup> Importantly, the stabilization resulting from hyperconjugation of the π-type lone pair on P to the NHC fragments is much larger (96.53

vs. 67.68 kcal mol<sup>-1</sup>) in the model of [MeLP]<sup>+</sup> with respect to the acyclic model which is consistent with more effective  $\pi$ -bonding in the constrained cyclic cations. Furthermore, TD-DFT calculations reveal that all of the allowed transitions in [MeLP]<sup>+</sup> are shifted to higher energy with respect to those in the acyclic analogue, which is also consistent with the “lone pair” becoming more  $\pi$ -bond-like.

In order to probe reactivity of the cations, metathesis reactions were done to provide salts with counter-anions better suited for further chemistry – in particular, less nucleophilic anions should facilitate investigation of the coordination chemistry of the cations. Thus, treatment of [BnLP][Br] with sodium tetraphenyl borate or trimethylsilyl triflate results in anion exchange to yield [BnLP][BPh<sub>4</sub>] and [BnLP][OTf], respectively. The most significant spectroscopic change observed upon anion exchange is the increased shielding of the <sup>1</sup>H NMR signal of the methylene bridge protons. The increased shielding (from ca. 6 ppm to ca. 4 ppm) is most prominent for the more weakly coordinating tetraphenyl borate anion.

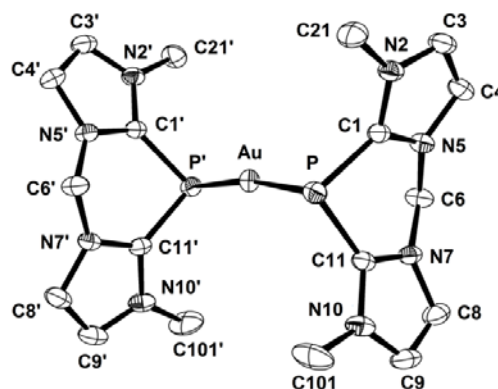
The *N*-benzyl salt [BnLP][BPh<sub>4</sub>] recrystallizes readily by slow evaporation of either THF or dichloromethane solutions. While the metrical parameters for the core of the cation remain similar to those of the bromide salt, the orientation of the benzyl groups changes significantly (Fig. 3; B vs. C), almost certainly as a consequence of differing non-covalent interactions in the solid state.



**Fig. 3** A) Top-down view of the [MeLP][OTf] cation. B) Side-on view of [BnLP][BPh<sub>4</sub>] and C) [BnLP][Br]. Ellipsoids are drawn with 50% probability surface. Hydrogen atoms and anions are omitted for clarity. Selected distances and angles are summarized in Table 1.

Extensive investigations of further reactivity of the [R<sup>1</sup>LP]<sup>+</sup> salts is currently underway and complete results will be presented later in a full paper. However, in light of the recent results of Weigand *et al.* for related NHC stabilized P<sup>I</sup> ligands,<sup>14</sup> we do wish to note one interesting result. Whereas they found that the phosphorus atom in a single [EP]<sup>+</sup> cation (Table 1) can function as a ligand for either one or two gold(I) chloride fragments, we find very different chemistry

for the cations in this report. In particular, the reaction of [MeLP][OTf] with equimolar amounts of AuCl generates a mixture of two products (as assessed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy) but exhibiting only a single peak at -86 ppm in the <sup>31</sup>P NMR spectrum. The phosphorus-containing product of the reaction was successfully characterized by XRD as the salt [Au(MeLP)<sub>2</sub>][OTf]<sub>2</sub>[Cl]: the C<sub>2</sub>-symmetric cation (Fig. 4) consists of a gold(I) ion ligated by two [MeLP]<sup>+</sup> cations and there are two non-coordinated triflate anions and a non-coordinated chloride anion in the formula unit. The tricationic fragment adopts a transoid geometry with Au-P bonds of 2.3329(9) Å, and a P-Au-P angle of 170.71(4)°. The P-C distances within the [MeLP]<sup>+</sup> ligands lengthen considerably upon coordination, which is consistent with decreased hyperconjugation as the  $\pi$ -type lone pair on P binds the metal. Otherwise, the overall ligand geometry remains relatively unchanged upon coordination and it is likely that the considerably smaller size of [MeLP]<sup>+</sup> with respect to [EP]<sup>+</sup> allows for the simultaneous attachment of two ligands to a single metal site. It is perhaps worth noting that although there are a large number of related bis-phosphine gold(I) ions in the Cambridge Structural Database, there are only a handful of known bis-phosphanides; the Au-P distances and angles in [Au(MeLP)<sub>2</sub>] are consistent with those of comparable gold(I) phosphanides.<sup>28</sup> Attempts to assess the donor ability of [R<sup>1</sup>LP]<sup>+</sup> experimentally using [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> are complicated by rapid evolution of CO from the mixture and lability. FT-IR spectroscopy and ligand exchange reactions of the resultant complexes suggest that the cations are comparable to some phosphites or  $\alpha$ -mono-cationic phosphine ligands.<sup>29</sup> Moreover, computational models suggest that [MeLP]<sup>+</sup> is a donor comparable to PH<sub>3</sub> and corroborate that assessment.<sup>†</sup>



**Fig. 4** Thermal ellipsoid plot of [Au(MeLP)<sub>2</sub>][OTf]<sub>2</sub>[Cl] (50% probability surface). Hydrogen atoms and anions are omitted for clarity. Selected distances (Å) and angles (°): Au-P, 2.3329(9); P-Au-P, 170.71(4); P-C1, 1.817(3); P-C11, 1.818(4); C1-P-C11, 92.08(15).

In summary, we report a convenient synthetic approach to fused tricyclic 2-phosphaallylic cations and demonstrate that the constraints of the cyclic system do indeed increase the  $\pi$ -delocalization within the compounds with respect to acyclic phosphamethine cyanine dye analogues. Most importantly, the resultant molecules exhibit remarkable stability toward air and moisture that will finally allow for the practical application of these functional dyes. Calculations confirm that these species are still best considered as carbene-ligated P<sup>I</sup> ions in spite of their more planar structures. The bromide salts are suitable for metathesis reactions and preliminary results from coordination chemistry demonstrate different behaviour than any other analogues. Further investigations of the photophysical and chemical properties of these and related species are underway.

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## Notes and references

<sup>a</sup> Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada.

† Electronic Supplementary Information (ESI) available: Crystallographic information; details of synthesis and characterization; details of calculations. See DOI: 10.1039/c000000x/

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