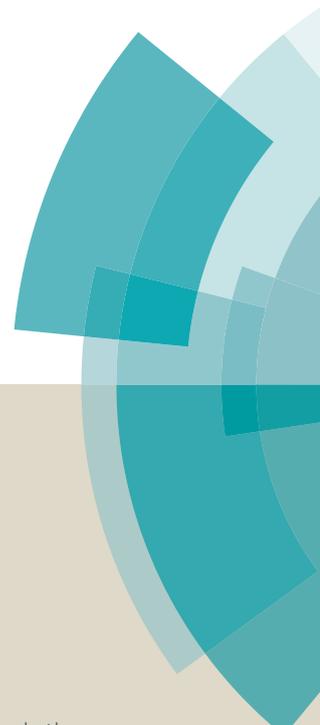
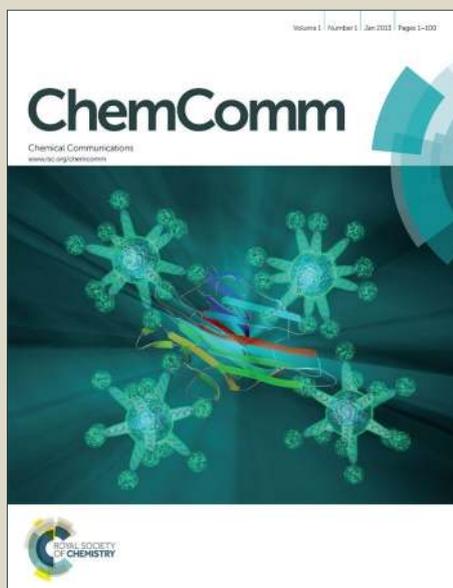


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Bis(carbodicarbene)phosphenium trication: A case against hypervalency

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

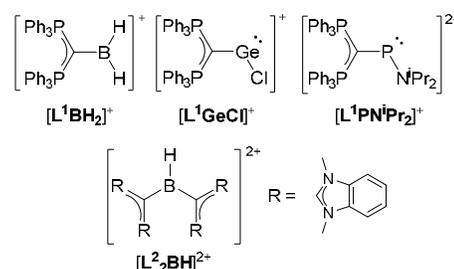
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The first example of a phosphenium trication has been prepared by using exceptional nucleophilic properties of a carbodicarbene ligand. According to the theoretical investigations the trication contains quite polarized P-C bonds suggesting a substantial contribution from the dative bond model. As one of the resonance forms for the title compound depicted a hypervalent phosphoranide we also showed that phosphoranides, in general, do not contain a hypervalent P centre.

Carbones are proving to be quite versatile ligands in stabilizing electron deficient main group species due to their ability to act as both σ - and π -donor substituent.^{1,2,3} For example, BH_2^+ and GeCl^+ cations^{2a,b} have been stabilized by carbodiphosphorane ($\text{C}(\text{PPh}_3)_2$, L^1 , Figure 1),^{3a} while dicationic hydridoborenium ion^{2c} was stabilized by two carbodicarbene ($\text{C}(\text{C}(\text{NMe})_2\text{-C}_6\text{H}_4)_2$, L^2 , Figure 1) ligands.^{3b} We have also shown that the electronic properties of L^1 were sufficient enough for isolation of two-coordinate phosphenium dications (e.g. $[\text{L}^1\text{PN}^+\text{Pr}_2]^{2+}$, Figure 1).^{2d,e} In this work we wish to report the preparation of a bis(carbodicarbene)phosphenium trication whose P-C bonds contain a high degree of ionic character according to the Durrant's method⁴ for assessing covalency/hypervalency. We also used this method to demonstrate that phosphoranide molecules, which are considered hypervalent, also contain a high degree of ionic bonding and appear not to be hypervalent.

In view of the exceptional nucleophilic properties of carbene ligands¹⁻⁵ we were cautiously confident that two carbene ligands would be adequate to support the preparation of a phosphenium trication (e.g. $[\text{L}_2\text{P:}]^{3+}$). We then decided to use L^2 instead of L^1 because L^2 was not only predicted to be more

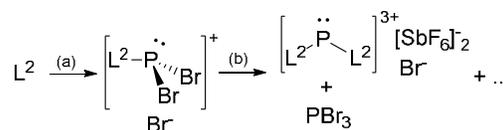
Fig 1 Examples of electron deficient main group species stabilized by carbene

ligands L^1 and L^2 .

nucleophilic^{4a} but it is also significantly less sterically demanding. The steric factors seem to be as important as the electronic properties due to the expected bent geometry of the target trication. Thus, it was difficult to envision that two L^1 ligands could be bound in a bent geometry around an atom considering that the only example of a molecule with two L^1 ligands ($[\text{L}^1\text{-Ag-L}^1]^+$) was linear.⁵ On the other hand, fitting two L^2 ligands in a non-linear geometry (e.g. $[\text{L}^2_2\text{BH}]^{2+}$, Figure 1) has already been reported.^{1c}

We attempted a step-wise synthesis hoping that sequential binding of two L^2 ligands to a P-containing fragment might be possible. The first ligand coordination, achieved by reacting L^2 and excess PBr_3 (Scheme 1), occurred smoothly to produce the expected monocation ($[\text{L}^2\text{PBr}_2]\text{Br}$) characterized by a δ_p signal at 163 ppm. The identity of this monocation was confirmed by

Scheme 1. General synthetic procedure. Reaction conditions: (a) Excess PBr_3 , benzene; (b) 2 equiv of AgSbF_6 , acetonitrile.



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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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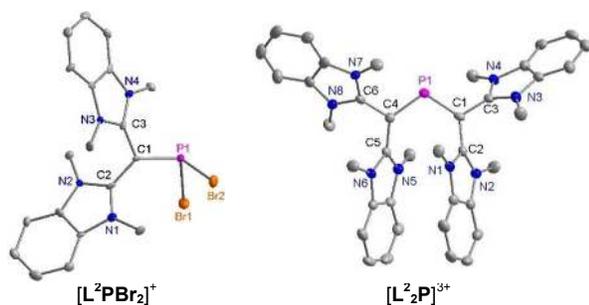
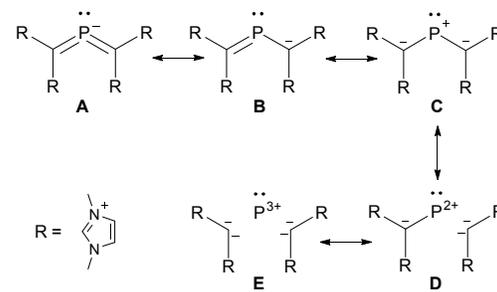


Fig 2 Molecular structures for $[\text{L}^2\text{PBr}_2]^+$ and $[\text{L}^2\text{P}][\text{SbF}_6]_2[\text{Br}]$ drawn at 50% probability. All H atoms as well as counterions have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): $[\text{L}^2\text{PBr}_2]^+$: P1-C1 1.748(8), P1-Br1 2.238(2) (2.228(2)), P1-Br2 2.341(2) (2.397(2)), C2-C1-C3 114.8(6) (115.3(7)); $[\text{L}^2\text{P}]^{3+}$: P1-C11.733(4), P1-C2 1.747(4), C1-P1-C4 111.0(2).

single crystal X-ray diffraction (Figure 2). However, the addition of one more equivalent of L^2 to $[\text{L}^2\text{PBr}_2]^+$ did not result in the formation of the target dication (e.g. $[\text{L}^2_2\text{PBr}]^{2+}$) but in the formation of several unidentified products.⁶ Interestingly, the attempted replacement of the non-coordinated bromide anion in $[\text{L}^2\text{PBr}_2]^+$, as this was our standard procedure for crystallizing similar monocations,⁷ by addition of 1 equiv of AgSbF_6 resulted in the formation of at least two new compounds as observed by ^{31}P NMR spectroscopy.⁶ Apart from the presence of the monocation (δ_{p} 163 ppm), it was possible to detect two new species as identified by δ_{p} signals at 302 (major) and 228 (minor) ppm. We postulated that the signal at δ_{p} 302 ppm might have been due to the formation of $[\text{L}^2\text{PBr}]^{2+}$ dication. This assessment was somewhat supported by the observation that the addition of two (or even three) equiv of AgSbF_6 to an acetonitrile solution containing $[\text{L}^2\text{PBr}_2]^+$ resulted in the complete disappearance of the signal assigned to the monocation.⁶ However, the compound characterized by the δ_{p} 228 ppm signal, most likely PBr_3 , has also become a major component of the reaction mixture suggesting a more complex reaction mechanism than a simple bromide abstraction. After layering this solution with Et_2O a few red crystals suitable for single crystal X-ray diffraction was obtained. The single crystal X-ray analysis revealed truly unexpected result as the compound identified by the δ_{p} signal at 302 ppm was in fact our target trication supported by two carbodicarbene (L^2) ligands (Figure 2). Although the correct mechanism is not known at the



moment it

Fig 3 Possible resonance forms for the central C-P-C fragment of $[\text{L}^2\text{P}]^{3+}$.

is reasonable to assume that one of the key mechanistic steps involved carbene-bromide substituent exchange which led to the formation of the trication and PBr_3 . P-substituent exchange is certainly not unprecedented in phosphorus chemistry as several reports have already described this phenomenon including a recent work which illustrated a carbene-chloride substituent exchange.^[8] It is also noteworthy that the trication appears to be quite reactive as numerous but unsuccessful attempts have been made to obtain it in pure form.

According to the dative bonding model the nature of $[\text{L}^2\text{P}]^{3+}$ could be described as a bis(carbene) capture of a P(III)^{3+} cation i.e. $\text{L}^2 \rightarrow \text{P}^{3+} \leftarrow \text{L}^2$.⁹ The values for the P1-C1 (1.733(4) Å) and P1-C4 (1.747(4) Å) suggest the presence of considerable double bond character (Frenking⁹ argues that dative bonds could be quite strong) generated by a substantial amount of electron density flow from L^2 ligands to the triply charged P(III) cation. The L^2 -to-P electron flow is further supported by the elongation of the average C1/C4-C bond distances upon the formation of the trication. The average value for these bonds increased from 1.343(2) Å for free L^2 to 1.448(6) Å for the trication implying electron density movement from the imidazolyl rings towards the center of the molecule. The ellipticity value of 0.31 for the P-C bonds obtained by computational means (Bader's Quantum Theory of Atoms in Molecules (QTAIM)¹⁰) using a model compound $[\text{L}^2_2\text{P}]^{3+}$ ($\text{L}^2 = \text{C}(\text{NMe})_2(\text{CH})_2$) also indicated the presence of a double bond character.⁶ Considering the above mentioned computational studies it is then not unexpected that the QTAIM partial charge (+1.45e) calculated for the central P for $[\text{L}^2_2\text{P}]^{3+}$ was quenched from the formal value of +3e and that around +0.7e has been delocalized on each imidazolyl moiety.⁶

When the covalent bonding model is considered numerous resonance forms could be generated for the entire trication.¹¹ If

Table 1. Calculated QTAIM partial charges and the valence equivalent parameter (γ) for the central P atom of several phosphoranide molecules. In each case the hypervalent form is only drawn.

	1	2	3	4	5	6	7
Partial Charge	+1.12	+0.88	+1.48	+1.12	+1.40	+1.52	+1.31
$\gamma(\text{P})$	5.76	6.24	5.04	5.78	5.2	4.96	5.38

the central C-P-C fragment is only considered several resonance forms as depicted in Figure 3 could be drawn.¹² Taking into account only the double bond character of the P-C bonds the trication could be described using the hypervalent form **A** or at least that the overall resonance depiction of the trication is substantially shifted towards form **A**. Conversely, the other extreme resonance form **E**, which is fully ionic, resembles the dative bond description already used for the trication. Lastly, the resonance form **B** is considered covalent as it obeys the eight electron rule while the other two forms **C** and **D** are partially ionic. In order to assess whether the central P is really hypervalent or the covalent form **B** is more appropriate or the P-C bonds contain significant ionic character we used the recently developed method by Durrant.³ The method only depends on atomic charges that, apart from experimental means, could be obtained using QTAIM as atomic charges obtained by this analysis have been shown to quite closely match the experimental values.^{3,13} In fact, the most important information is the charge on the central atom, again generated from appropriate experimental or theoretical investigations, from which a parameter called the valence electron equivalent (γ) for that particular atom can be calculated.³ If the γ parameter is 8 (or close to it) then the covalent form is the most appropriate description of the compound. If the parameter is larger than 8 then the central atom is hypervalent while the values for γ that are less than 8 indicate the presence of ionic bonding. It turns out that the $\gamma(P)$ value for the trication is dramatically lower than 8 as it was calculated to be 5.1. It is interesting that for calculating the $\gamma(P)$ parameter it is required to use only the two extreme resonance forms **A** and **E** with their respective distributions of 39% and 61% suggesting that the overall resonance depiction is shifted towards the ionic form(s). Additionally, depletion of electron density in the contact area of P and C atoms characterized by positive values of its Laplacian in the P-C bond critical points (+ 0.143 au) is also an indication of closed shell interactions i.e. ionic bonding.¹⁴ This would then imply the resonance forms **C**, **D** and **E** are major contributors to the overall covalent bonding depiction of the trication. As form **E** is the fully ionic form it also believed that using the dative bonding model ($L^2 \rightarrow P^{3+} \leftarrow L^2$) to describe the title compound is also valid i.e. the dative contribution to the overall portrayal is significant.

In the view of these findings and the fact that the resonance form **A** represents an example of a hypervalent phosphoranide molecule we wanted to investigate whether phosphoranide molecules, in general, are hypervalent as they have been described in the literature.¹⁵ The most commonly reported phosphoranides are four coordinate and they are designated as 10-P-4 phosphoranides (10 electrons around a four coordinate phosphorus center). We included a couple of simple examples (**1** and **2**, Table 1) as well as simplified versions of several recently published anionic (**3**),^{15c} neutral (**4**)^{15b} and cationic (**5**)^{15b1} phosphoranide molecules. Also, we have examined an example of a 10-P-3 phosphoranide (**6**)^{15a} as well as hypothetical bis(methylene)phosphoranide **7** (10-P-2) because it closely resembles the resonance form **A** of our

trication. The partial charges for these species have also been obtained by the QTAIM analysis. The calculated values for $\gamma(P)$ parameter for most of these species fall below 6 suggesting a high degree of ionic bonding concerning the central P atom. Thus, this particular evaluation disagrees with the idea that phosphoranides are hypervalent¹⁶ and that a better representation of, for example, simplest 10-P-4 phosphoranides would be $PX_3^+X^-$ or even $X^+PX_2^+X^-$ rather than PX_4^+ (X = Cl or Br). It is also worth noting that the relationship between $\gamma(P)$ and the partial charges on the P is linear allowing us to generating equation $y = -2.01x + 8.01$ ($R^2 = 0.9998$) from which the $\gamma(P)$ parameter (i.e. γ) for any phosphoranide could be calculated if the P partial charge (i.e. x) is known.

Conclusions

We succeeded in preparing the first example of a two-coordinate tricationic P(III)-based molecule by unusual ligand exchange. According to the computational investigations the bonding concerning the central C-P-C possesses a substantial amount of ionic character, which supports the presence of dative bonding in this compound. As one of the possible resonance forms for the trication would resemble a 10-P-2 phosphoranide we theoretically analyzed a representative sample of most common phosphoranide molecules and concluded that phosphoranides are not hypervalent because the bonding around the central P contains a high degree of ionic character.

Acknowledgements

We would like to thank A*STAR-PSF (DV, grant # 1321202066) and the Ministry of Education, Science, and Technological Development of the Republic of Serbia within the framework of the project (MP, 172040) for financial support. Computational analysis were performed on the PARADOX cluster at the Scientific Computing Laboratory of the Institute of Physics Belgrade, supported in part by the Ministry of Education, Science, and Technological Development of the Republic of Serbia under project No. ON171017 (MP).

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