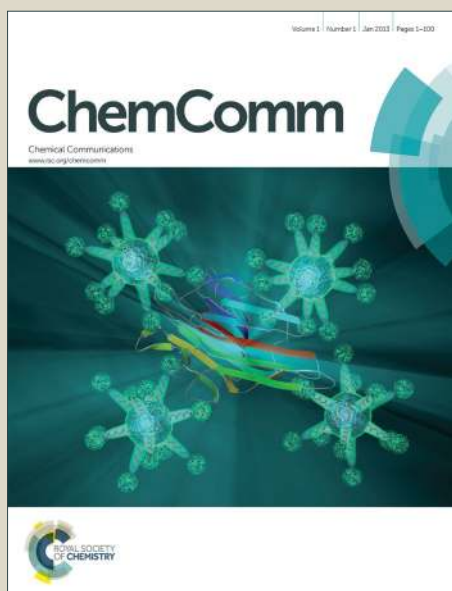


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Extending the chemistry of carbenes: P-N bond cleavage via an S_N2' -like mechanism

Received 00th January 20xx,
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DOI: 10.1039/x0xx00000x

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Reactivity of nucleophilic carbodiphosphorane ($C(PPh_3)_2$, **1**) and carbodicarbene ($C(C(NMe)_2C_6H_4)_2$, **2**) towards various dichlorophosphines has been explored. In most cases the expected carbene-for-chloride ligand exchange was observed. However, the use of $MeN(PCl_2)_2$ resulted in a unique P-N bond cleavage that, according to computational studies, occurred via an S_N2' -like mechanism.

Carbene molecules, also known as bent allenes, have been known for over 50 years but their chemistry has not been greatly explored until the last few years.^{1,2} Recent renaissance could arguably be attributed to a series of theoretical studies performed by Frenking and co-workers highlighting that the central carbon atom in these compounds not only existed in the formal oxidation state of zero but it also contained two lone pairs available for bonding (**A**, Fig. 1).³⁻⁵ It was then not surprising that these exceptionally nucleophilic species were used not only as reducing agents⁶ but also as ligands for the preparation of several highly electron deficient main group species.⁷

One of our achievements in this field was manifested by the synthesis and unusual reactivity of a two-coordinate phosphonium dication (**B**, Fig. 1) stabilized by carbodiphosphorane ($(PPh_3)_2C$, **1**).^{7c-e} The preparation of this dication is a two-step process that first required mixing of **1** with excess iPr_2NPCl_2 to form monocationic precursor $[^iPr_2NPC(PPh_3)_2Cl][Cl]$, $[1-PCl(N^iPr_2)][Cl]$, followed by chloride abstraction.^{7c} As both of these steps seemed to be quite straight forward we wondered whether it would be possible to prepare a molecule that would contain two such phosphonium cations to generate a tetracation (**C**, Figure 1). However, during the attempted synthesis we observed unusual P-N bond cleavage that,

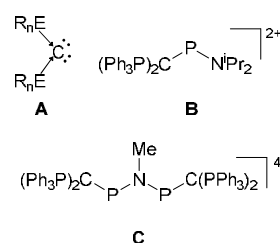


Fig. 1 General structure for carbenes (**A**), recently prepared P-dication (**B**) and targeted tetracation (**C**).

according to theoretical investigations, occurred via an S_N2' -like mechanism.

The initial step for the potential preparation of tetracation **C** involved the reaction between **1** and $MeN(PCl_2)_2$ to aim for the formation of expected product $[(Ph_3P)_2CPCl]NMe(PCl_2)[Cl]$, $[1-P_e][Cl]$. This product would then be subjected to additional carbene-for-chloride substitution at the second PCl_2 unit followed by the usual chloride abstraction. However, we were quite surprised that irrespective of substrate ratios used ($1:MeN(PCl_2)_2 = 1:1, 2:1$ or $1:2$) the formation of a different-than-expected phosphorus species, highlighted by a δ_p signal at ~ 173 ppm was always observed. After examining reported reactions involving **1** with Cl-containing phosphines we realized that this signal was a close match for already reported $[(PPh_3)_2CPCl_2][Cl]$, $[1-PCl_2][Cl]$ (Scheme 1).⁸ Indeed, after isolation of this species and addition of 1 equiv of $AlCl_3$ we managed to crystallographically elucidate $[1-PCl_2][AlCl_4]$ (Fig. 2).⁹ Considering the overall reaction stoichiometry, extrusion of a "MeNPCl" fragment by P-N bond cleavage, which might have dimerized/oligomerized followed by ring conversion in solution, has presumably occurred.¹⁰ Unfortunately, attempts to trap this fragment using 2,3-dimethylbutadiene were unsuccessful.

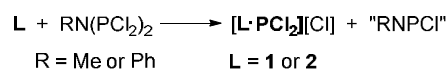
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Electronic Supplementary Information (ESI) available: Detailed experimental procedures, summary of single crystal X-ray and computational analyses. See DOI: 10.1039/x0xx00000x



Scheme 1 Observed P-N bond cleavage.

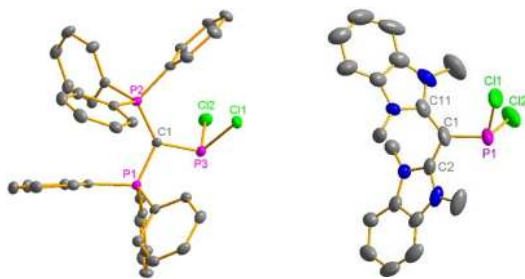
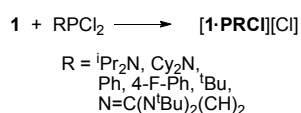


Fig. 2 Molecular structures for **[1-PCl₂][AlCl₄]** (left) and **[2-PCl₂][SbF₆]** (right) with the ellipsoids drawn at the 50% probability level. All hydrogen atoms as well as the counterions have been omitted for clarity.

These observations were quite unique considering that similar reactions involving several $\text{R}(\text{PCl}_2)_2$ precursors ($\text{R} = \text{}^i\text{Pr}_2\text{N}$, ${}^7\text{C}$ C_2N , 11a Ph , 11b 4-F-Ph , 11b $\text{N}=\text{C}(\text{N}^t\text{Bu})_2(\text{CH}_2)$, 7b ${}^t\text{Bu}$ (this work)) always yielded the expected products **[1-PRCl][Cl]**, i.e. the carbene-for-chloride exchange, (Scheme 2) suggesting that the presence of two PCl_2 units in $\text{MeN}(\text{PCl}_2)_2$ played a decisive role in the overall reaction mechanism. This assessment was confirmed by using (i) a slightly modified starting material ($\text{PhN}(\text{PCl}_2)_2$) and (ii) a carbene substituent ($\text{C}(\text{C}(\text{NMe})_2\text{C}_6\text{H}_4)_2$, **2**) that differed not only in steric but also electronic properties from **1**.^{3b} The reaction between **2** and $\text{MeN}(\text{PCl}_2)_2$ did not, once again, result in the expected carbene-for-chloride exchange but the observed P-N bond cleavage and formation of **[2-PCl₂][Cl]** occurred. Besides the ${}^{31}\text{P}$ NMR spectroscopy (δ_p , 162 ppm), the identity of this latest compound was also established by single crystal X-ray diffraction once the Cl counterion was replaced with SbF_6^- (Fig. 2). Furthermore, the formation of **[1-PCl₂][Cl]**, as the major phosphorus containing species, was noted when **1** was reacted with $\text{PhN}(\text{PCl}_2)_2$. Therefore, the nature of the bis(dichlorophosphino)amine seemed to be crucial for the observed P-N bond cleavage.

It was initially hypothesized that the ligand replacement and the formation of the expected products **[L-P_e][Cl]** ($\text{L} = \mathbf{1}$ or $\mathbf{2}$) might have been the first step in the overall reaction mechanism which would have been followed by, for example, a 1,3-chloride shift to yield the observed products **[L-PCl₂][Cl]** and “ RNPCl ” ($\text{R} = \text{Me}$, Ph). Indeed, preliminary theoretical investigations (using the Gaussian 09 package at the B3LYP/6-31G(d) level) revealed that the formation of the observed products was more thermodynamically favoured than **[L-P_e][Cl]** by about 93 and 50 kJ/mol for **1** and **2**, respectively.¹² However, after numerous attempts no low energy pathway could be identified that would transform **[L-P_e][Cl]** into **[L-PCl₂][Cl]** and “ MeNPCl ” suggesting that the initial ligand exchange was not the first step in the formation of the observed products.

Subsequently, using computational methods, we examined structural changes as the central carbon atom (C_A) of **1** or **2** was

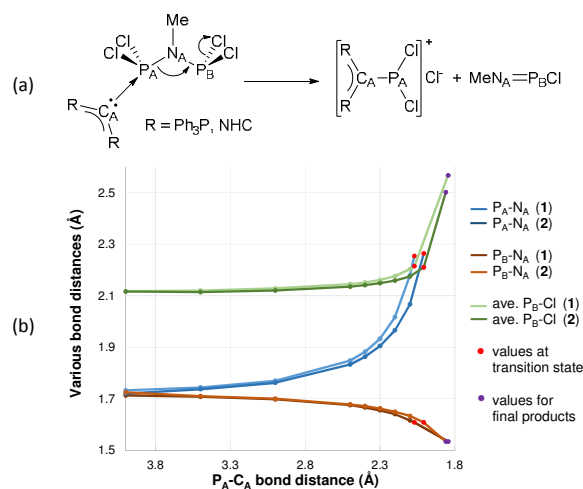


Scheme 2 Carbene-for-chloride exchange.

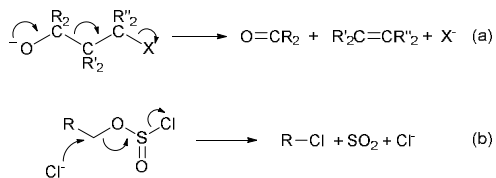
approaching and interacting with one of the phosphorus atoms (P_A) of $\text{MeN}(\text{PCl}_2)_2$ (Scheme 3a).¹³ The most significant changes were detected for the $\text{P}_A\text{-N}_A$, $\text{P}_B\text{-N}_A$ and average $\text{P}_B\text{-Cl}$ ¹⁴ bond distances. As the $\text{P}_A\text{-C}_A$ distance was systematically reduced the $\text{P}_A\text{-N}_A$ and $\text{P}_B\text{-Cl}_{(\text{ave})}$ bonds elongated while the $\text{P}_B\text{-N}_A$ bond contracted (Scheme 3b). This pattern was continued throughout the transition state resulting in the complete cleavage of the $\text{P}_A\text{-N}_A$ and one of the $\text{P}_B\text{-Cl}$ bonds while creating a doubly bonded $\text{P}_B\text{-N}_A$ fragment. This is consistent with the experimentally observed formation of **[L-PCl₂][Cl]** and presumably MeNPCl . It is also noteworthy that throughout the approach C_A interacted with P_A exclusively *trans* to N_A i.e. the $\text{C}_A\text{-P}_A\text{-N}_A$ angle was very close to the linearity along the entire process.¹⁵ This would allow the C_A to interact with the σ^* orbital of the $\text{P}_A\text{-N}_A$ bond causing its weakening/elongation and subsequent cleavage.

These observations are consistent with a concerted $\text{S}_{\text{N}}2'$ mechanism established for well-known nucleophilic allylic substitutions manifested by allylic rearrangement.¹⁶ Intramolecular Grob fragmentation (Scheme 4a)¹⁷ and certainly the last step in alcohol conversion to alkyl chlorides using SOCl_2 , in the presence of a base (Scheme 4b)¹⁸, are actually more reminiscent mechanisms as they also involve a σ -bond cleavage and formation of a π -bond. In fact, the last step of the latter mechanism seems to be virtually identical to the mechanism described in Scheme 3a. However, this type of mechanism does not appear to be reported for P-N bond activation induced by hydrolysis,^{19a-d} acidolysis,^{19e-f} alcoholysis,^{19f-h} Fe-Fe oxidative bond cleavage²⁰ and small molecule (e.g. CO_2 , CS_2 , aldehydes, isocyanates, etc.) insertions.²¹ Therefore, this report has established a new approach for P-N bond cleavage involving nucleophilic substitution of the N-fragment without preceding N-protonation or P-oxidation. It also showed that carbene molecules could induce P-N bond fragmentation through an $\text{S}_{\text{N}}2'$ -like mechanism.

In summary, the reaction between a carbene (**1** or **2**) and $\text{RN}(\text{PCl}_2)_2$ ($\text{R} = \text{Me}$ or Ph) did not result in the typical ligand exchange observed for similar phosphorus substrates. In this instance, P-N bond cleavage was detected and according to the computational analysis resembled an $\text{S}_{\text{N}}2'$ mechanism. This



Scheme 3 (a) Proposed mechanism. (b) Computationally determined bond distance changes as **1** or **2** is approaching P_A of $\text{MeN}(\text{PCl}_2)_2$.



Scheme 4 Mechanisms describing (a) intramolecular Grob fragmentation and (b) the last step in alcohol conversion to alkyl chlorides.

represents a unique reactivity mode not only of carbene molecules but also of bis(dichlorophosphino)amines.

This work was financially supported by the A*STAR-MSHE grant (DV, # 1220703062) and by the Ministry of Education, Science, and Technological Development of the Republic of Serbia within the framework of the project 172040 (MP). Numerical simulations were run 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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- For the computational studies the formation of the monomeric MeNPCI was always used. The use of, for example, the dimer form does not affect the conclusions.
- The P_A-C_A was fixed at a certain distance (the x-axis for the graph in Scheme 3) but the rest of the system was optimized.
- As (i) the optimized structures for $[\text{L}-\text{P}(\text{Cl})_2][\text{Cl}]$ ($L = \mathbf{1}, \mathbf{2}$) contain two Cl atoms at approximately equal distance from the central P and (ii) both P-Cl bonds showed elongation during the mechanism it was then appropriate to use the average value for the two P-Cl bonds to construct the graph.
- We have tried to initially place C_A *trans* to one of the Cl atoms of $\text{MeN}(\text{P}(\text{Cl})_2)_2$ but partial optimization would always orient C_A *trans* to N_A .
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