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Extending the chemistry of carbones: P-N bond cleavage via an S\textsubscript{N}2\textsuperscript{Z'}-like mechanism

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Reactivity of nucleophilic carbodiphosphorane (C(PPh\textsubscript{3})\textsubscript{2}, 1) and carbodicycarbene (C(C(NMe\textsubscript{2})\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{2}, 2) towards various dichlorophosphines has been explored. In most cases the expected carbone-for-chloride ligand exchange was observed. However, the use of MeN(PCl\textsubscript{3})\textsubscript{2} resulted in a unique P-N bond cleavage that, according to computational studies, occurred via an S\textsubscript{N}2\textsuperscript{Z'}-like mechanism.

Carbone 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.\textsuperscript{1-3} 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 exists within the formal oxidation state of zero but it also contained two lone pairs available for bonding (A, Fig. 1).\textsuperscript{1,3} It was then not surprising that these exceptionally nucleophilic species were used not only as reducing agents\textsuperscript{6} but also as ligands for the preparation of several highly electron deficient main group species.\textsuperscript{7}

One of our achievements in this field was manifested by the synthesis and unusual reactivity of a two-coordinate phosphenium dication (B, Fig. 1) stabilized by carbodiphosphorane (PPh\textsubscript{3})\textsubscript{2}C, \textsuperscript{1,7} The preparation of this dication is a two-step process that first required mixing of 1 with excess Pr\textsubscript{2}NPCL\textsubscript{2} to form monocationic precursor [Pr\textsubscript{2}NPCL\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}Cl][Cl], \textsuperscript{7c} followed by chloride abstraction.\textsuperscript{7c} As both of these steps seemed to be quite straightforward, we wondered whether it would be possible to prepare a molecule that would contain two such phosphonium cations to generate a tetracation (C, Fig. 1). However, during the attempted synthesis we observed unusual P-N bond cleavage that, according to theoretical investigations, occurred via an S\textsubscript{N}2\textsuperscript{Z'}-like mechanism.

The initial step for the potential preparation of tetracation C involved the reaction between 1 and MeN(PCL\textsubscript{3})\textsubscript{2} to aim for the formation of expected product \{(PPh\textsubscript{3})\textsubscript{2}CPCl\}NMe(PCL\textsubscript{3})\textsubscript{2}[Cl], \textsubscript{1-Pe}[Cl]. This product would then be subjected to additional carbone-for-chloride substitution at the second PCl\textsubscript{2} unit followed by the usual chloride abstraction. However, we were quite surprised that irrespective of substrate ratios used (1:MeN(PCL\textsubscript{3})\textsubscript{2} = 1:1, 2:1 or 1:2) the formation of a different-than-expected phosphorus species, highlighted by a \textdelta\textsubscript{N} signal at \textsim 173 ppm was always observed. After examining reactions involving 1 with Cl-containing phosphines we realized that this signal was a close match for already reported [(PPh\textsubscript{3})\textsubscript{2}CPCl][Cl], \textsubscript{1-PCl}[Cl] (Scheme 1).\textsuperscript{8} Indeed, after isolation of this species and addition of 1 equiv of AlCl\textsubscript{3} we managed to crystallographically elucidate [1-PCl][AlCl\textsubscript{4}] (Fig. 2).\textsuperscript{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.\textsuperscript{10} Unfortunately, attempts to trap this fragment using 2,3-dimethylbutadiene were unsuccessful.

Scheme 1 Observed P-N bond cleavage.
These observations were quite unique considering that similar reactions involving several RPCl₂ precursors (R = Pr₂N, Cy₂N, Ph, 4-F-Ph, N=C(NBu)₂(CH₂)₂Bu (this work)) always yielded the expected products [1-P(Cl)] and, i.e. the carbone-for-chloride exchange, (Scheme 2) suggesting that the presence of two PCI units in MeN(PCl)₂ played a decisive role in the overall reaction mechanism. This assessment was confirmed by using (i) a slightly modified starting material (PhN(PCl₂)) and (ii) a carbone substituent (C(C(NMe)₂)₂(C₂H₅)₂) that differed not only in steric but also electronic properties from 1. The reaction between 2 and MeN(PCl)₂ did not, once again, result in the expected carbone-for-chloride exchange but the observed P-N bond cleavage and formation of [2-P(Cl)] occurred. Besides the ³¹P NMR spectroscopy (δₚ 162 ppm), the identity of this latest compound was also established by single crystal X-ray diffraction once the Cl counterion was replaced with SbF₅ (Fig. 2). Furthermore, the formation of [1-P(Cl)], as the major phosphorus containing species, was noted when 1 was reacted with PhN(PCl₂). 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(Cl)] (L = 1 or 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-P(Cl)] and “RNPCI” (R = 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(Cl)] by about 93 and 50 kJ/mol for 1 and 2, respectively. However, after numerous attempts no low energy pathway could be identified that would transform [L-P(Cl)] into [L-P(Cl)] and “MeNPCI” 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 (Cₖ₆) of 1 or 2 was

\[
\begin{align*}
1 + \text{RPCl}_2 & \rightarrow [1\text{-P(Cl)]}\quad R = \text{Pr}_2\text{N}, \text{Cy}_2\text{N}, \\
& \text{Ph}, 4\text{-F-Ph}, \text{N}=[\text{C(NBu)}_2\text{C}]=\text{Bu}
\end{align*}
\]

Scheme 2 Carbone-for-chloride exchange.

According and interacting with one of the phosphorus atoms (PA) of MeN(PCl₂) (Scheme 3a). The most significant changes were detected for PA-N₃, PA-N₄ and average PA-Cl bond distances. As the PA-Cₖ₆ distance was systematically reduced the PA-N₃ and PA-Cl bonds elongated while the PA-N₄ bond contracted (Scheme 3b). This pattern was continued throughout the transition state resulting in the complete cleavage of the PA-N₃ and one of the PA-Cl bonds while creating a doubly bonded PA-N₄ fragment. This is consistent with the experimentally observed formation of [L-P(Cl)] and presumably MeNPCI. It is also noteworthy that throughout the approach Cₖ interacted with PA exclusively trans to N₃, i.e. the Cₖ-PA-N₃ angle was very close to the linearity along the entire process. This would allow the Cₖ to interact with the σ* orbital of the PA-N₄ bond causing its weakening/elongation and subsequent cleavage.

These observations are consistent with a concerted Sn₂’ mechanism established for well-known nucleophilic allylic substitutions manifested by allylic rearrangement. Intramolecular Grob fragmentation (Scheme 4a) and certainly the last step in alcohol conversion to alkyl chlorides using SOCl₂, in the presence of a base (Scheme 4b), 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, acidolysis, alcoholysis, Fe-Fe oxidative bond cleavage and small molecule (e.g. CO₂, C₂H₂, aldehydes, isocyanates, etc.) insertions.

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 carbone molecules could induce P-N bond fragmentation through an Sn₂’-like mechanism.

In summary, the reaction between a carbene (1 or 2) and RN(PCl₂) (R = 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 Sn₂’ mechanism. This
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Notes and references


For the computational studies the formation of the monomeric MeNPCl was always used. The use of, for example, the dimer form does not affect the conclusions.

14. The $P_0-C_0$ was fixed at a certain distance (the $x$-axis for the graph in Scheme 3) but the rest of the system was optimized.

15. As (f) the optimized structures for [L-PCl$_2$]$(C_l = 1, 2)$ 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.

16. We have tried to initially place $C_0$ trans to one of the Cl atoms of MeP(Cl)$_2$ but partial optimization would always orient $C_0$ trans to $N_0$.