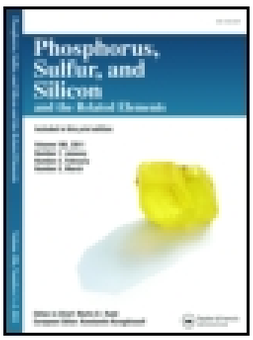

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[ClP(μ-PMes*)]$_2$ – A Versatile Reagent in Phosphorus Chemistry

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GRAPHICAL ABSTRACT

Abstract *The synthesis and some key reactions of the cyclotetraphosphane [ClP(μ-PMes*)]$_2$ (**2**, Mes* = 2,4,6-tri-tert-butylphenyl) with Lewis acids and reducing agents are discussed. All products were fully characterized, including single crystal X-ray diffraction, spectroscopic methods as well as computational studies.*

Keywords: *Ring systems; phosphorus chemistry; cyclo-phosphanes; ^{31}P NMR spectroscopy; DFT calculations*

INTRODUCTION

Ring systems composed of group 15 elements (pnictogens, Pn) are an interesting and widely investigated field of main group chemistry.[1–3] Especially, phosphorus based ring systems have received increasing attention,[4,5] since various types of mono- and polycyclic phosphanes were prepared by direct activation of white phosphorus (P_4).[6–13] However, selective functionalization of such ring systems was not studied in detail, which is why we set out to prepare a suitable functionalized P_4 precursor and investigate its reactivity. In analogy to the well explored chemistry of dichloro-*cyclo*-diphosphadiazanes,[1–3] the homologous dichloro-*cyclo*-tetraphosphanes seemed a worthwhile target for further chemistry. Known examples of such halogen substituted *cyclo*-tetraphosphanes comprised $[ClP(\mu\text{-}PSi(t\text{-}Bu)_3)]_2$ and $[ClP(\mu\text{-}PSi(t\text{-}Bu)_3)]_2$; yet we found their preparation unsuitable for synthetic scale.[14,15]

RESULTS AND DISCUSSION

Preparation of $[ClP(\mu\text{-}PMes^*)]_2$

In analogy to the synthesis of Mes*NPCl (Scheme 1, top; Mes* = 2,4,6-tri-*tert*-butyl-phenyl),[16] treatment of Mes^*PH_2 with PCl_3 in the presence of NEt_3 led to P–P coupling under elimination of $[HNEt_3]Cl$. In the first step, the tetraphosphene $Mes^*P{=}P{-}P(Mes^*)PCl_2$ (**1**) was formed, which underwent rearrangement to $[ClP(\mu\text{-}PMes^*)]_2$ (**2**) in polar solvents (Scheme 1, bottom).[17] After optimization of the reaction conditions, compound **2** could be prepared in 50–60 % yield (5 g scale), which facilitated the investigation of its reactivity.[18]

Compound **2** was characterized by an A_2X_2 spin system in the ^{31}P NMR spectrum (δ_{exptl} = −8.1, +131.1 ppm; δ_{calcd} = −1.6, 119.9 ppm). Its solid state structure was determined by single crystal X-ray diffraction. The four membered ring system adopts a puckered conformation, all substituents are arranged in the equatorial position (Figure 1). The experimental structural data correspond nicely with calculated structural parameters (PBE0/6-31g(d,p) level of theory).[17]

Reaction with $GaCl_3$

When **2** was treated with $GaCl_3$ at −80 °C, the intermediate formation of a highly reactive tetraphosphenium cation (**3**$^+$) could be detected by *in situ* ^{31}P NMR spectroscopy (Scheme 2).[18] Upon warming to −50 °C, a formal 1,2-Cl shift was observed, resulting in the formation of two isomers of an unprecedented bicyclic triphosphino-phosphonium cation (**4**$^+$; Figure 2, left).

In the ^{31}P NMR spectrum, both isomers of **4**$^+$ were characterized by A_2MX patterns (**4a**$^+$: δ_{exptl} = −214.5, −89.5, +51.2 ppm; δ_{calcd} = −220.3, −103.8, +24.6 ppm; **4b**$^+$: δ_{exptl} = −226.4, −123.6, +9.0 ppm; δ_{calcd} = −227.8, −135.7, −12.0 ppm). The molecular structure of **4a**[$GaCl_4$] was elucidated by single crystal X-ray diffraction.[18] The bicyclic P_4 scaffold adopts a butterfly conformation with a fold angle of 102°, which is comparable to other bicyclic tetraphosphanes.[13,19–25] According to NBO analysis,[26] the positive charge is mostly localized at the formal phosphonium centre (+0.76 *e*), while the whole P_4 scaffold bears a positive charge of +1.37 *e*.

The intermediate $\mathbf{3}^+$ could be trapped by a formal [4+2] cycloaddition reaction with dimethylbutadiene (dmb), resulting in a bicyclic tetraphosphaoctenium cation ($\mathbf{5}^+$; Figure 2, right), which is comparable to previously reported cyclic phosphino-phosphonium cations.[27–29]

Reduction reactions

Reduction of **2** with Mg selectively afforded the *exo-exo* isomer of the bicyclic tetraphosphane Mes*P_4Mes* (**6a**; Scheme 3, top) in good yields (73 %).[30] Compound **6** had previously been prepared by reacting a mixture of Mes*Br and Mes*Li with white phosphorus, though merely in low yields (5 %).[21,31] Intriguingly, the carbene promoted degradation of **2** gave rise to the elusive *endo-exo* isomer of Mes*P_4Mes* (**6b**; Scheme 3, bottom),[30] which had previously only been characterized spectroscopically.[32]

Both isomers of **6** were fully characterized. In the ^{31}P NMR spectrum, **6a** is characterized by an A_2X_2 pattern (δ_{exptl} = −273.2, −128.3 ppm; δ_{calcd} = −271.5, −138.0 ppm), while **6b** displays an A_2MX spin system (δ_{exptl} = −220.4, −94.8, −54.7 ppm; δ_{calcd} = −217.8, −100.2, −68.0 ppm). The molecular structure was determined by single crystal X-ray diffraction. In both isomers, the overall structure of the P_4 scaffold is rather similar. The fold angle of the bicyclus in the *endo-exo* isomer is significantly larger (108°) than in the *exo-exo* isomer (96°), presumably due to Pauli repulsion between the *endo*-Mes* substituent and the *ortho-t*-Bu groups of the *exo*-Mes* group (Figure 3).

In conclusion, the synthesis of the *cyclo*-phosphane **2** was newly developed and subsequently improved to make it readily available for synthetic use. The introduction of reactive P–Cl bonds directly at the ring system gave rise to fascinating follow-up chemistry by abstraction or reductive elimination of the Cl atoms, affording new preparative routes to known as well as unprecedented phosphorus ring systems. This nicely demonstrates the potential of our synthetic approach. To extend the product spectrum, the reactivity of **2** towards Lewis bases and transition metals is currently under investigation.

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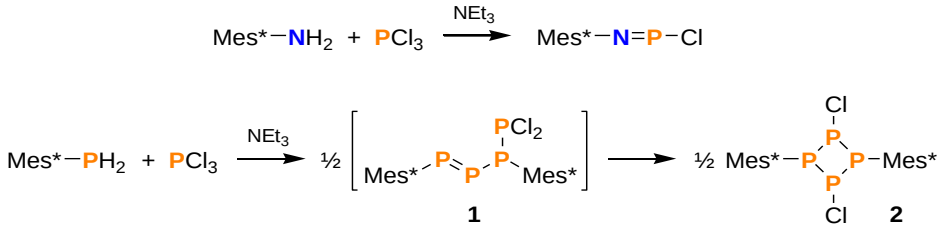
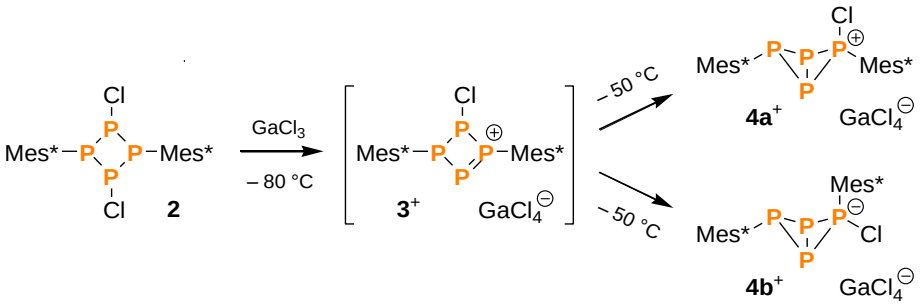
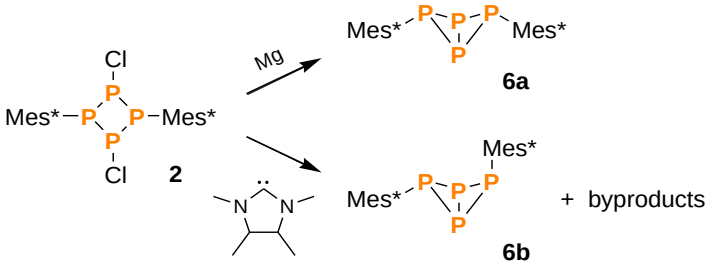


Scheme 1 Top: Synthesis of Mes*NPCl. Bottom: Synthesis of $[ClP(\mu\text{-}PMes^*)]_2$ (**2**)



Scheme 2 The reaction of **2** with $GaCl_3$ leads to the highly reactive intermediate $\mathbf{3}^+$, which rearranges to the bicyclic cation $\mathbf{4}^+$. The latter is observed as *exo-exo* ($\mathbf{4a}^+$) and *endo-exo* isomer ($\mathbf{4b}^+$)



Scheme 3 Starting from **2**, both isomers of the bicyclic tetraphosphane **6** can be obtained selectively

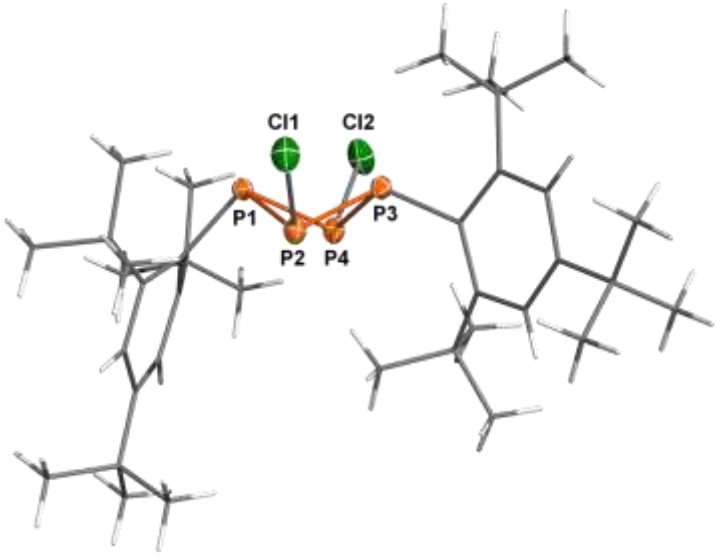


Figure 1 Molecular structure of **2** in the crystal ($P2_1/c$). Ellipsoids are set at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: P1–P2 2.2731(5), P1–P4 2.2596(5), P2–P3 2.1905(5), P2–Cl1 2.0967(5), P3–P4 2.2026(5), P4–Cl2 2.1061(6); P1–P2–P3 80.54(2), P1–P2–Cl1 106.45(2), P3–P2–Cl1 97.97(2), P2–P3–P4 84.65(2), P3–P4–P1 80.58(2), P3–P4–Cl2 97.32(2), P1–P4–Cl2 104.47(2); P1–P2–P4–P3 119.45(3), Cl1–P2–P4–Cl2 −1.06(5) C1–P1–P3–C19 −17.9(1)

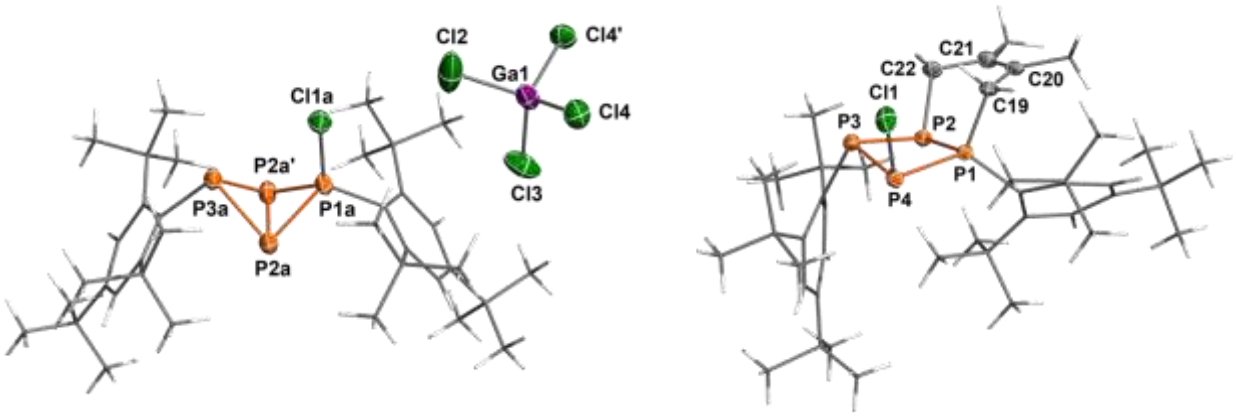


Figure 2 Molecular structure of **4**[$GaCl_4$] (left) and $\mathbf{5}^+$ (right) in the crystal. Ellipsoids are set at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: $\mathbf{4}^+$ P1a–P2a 2.150(2), P1a–Cl1a 2.009(2), P2a–P2a' 2.244(2), P2a–P3a 2.244(2); Cl1a–P1a–P2a 117.65(7), C1–P1a–Cl1a 118.7(2), P2a'–P1a–P2a 62.91(7), P1a–P2a–P2a' 58.55(3), P3a–P2a–P2a' 59.99(3), P1a–P2a–P3a 83.60(6), P2a'–P3a–P2a 60.02(7); P1a–P2a–P2a'–P3a −101.68(3); $\mathbf{5}^+$ P1–P2 2.195(1), P1–C19 1.846(3), C19–C20 1.514(4), C20–C21 1.334(4), C21–C22 1.500(4), P2–C22 1.871(3), P4–Cl1 2.068(1); P2–P1–P4 91.78(4), C19–P1–P2 102.3(1), C19–P1–P4 116.1(1); P1–P2–P4–P3 159.03(1)

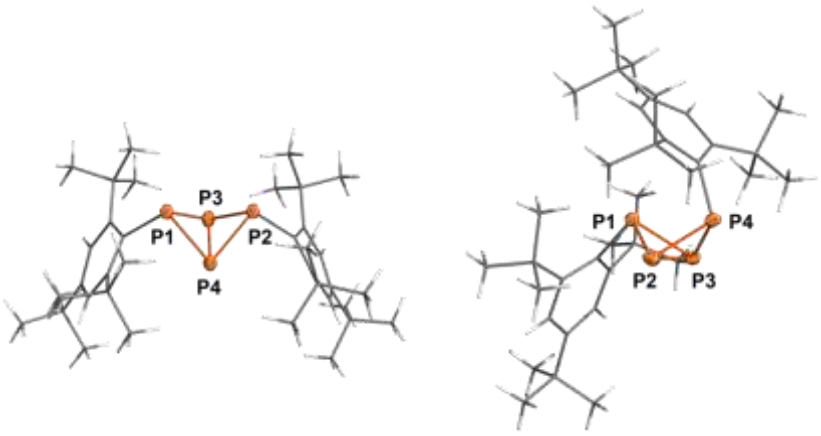


Figure 3 Molecular structures of **6a** (left) and **6b** (right) in the crystal. Ellipsoids are set at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: **6a** P1–P3 2.2310(7), P1–P4 2.2171(7), P2–P3 2.2294(7), P2–P4 2.2236(7), P3–P4 2.1634(8); P1–P3–P4–P2 −95.66(3); **6b** P1–P2 2.2244(7), P1–P3 2.2326(8), P2–P4 2.2131(8), P3–P4 2.2101(8), P2–P3 2.1773(8); P1–P2–P3–P4 107.78(3)