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Phosphorus Chemistry

A Tricyclic Hexaphosphane

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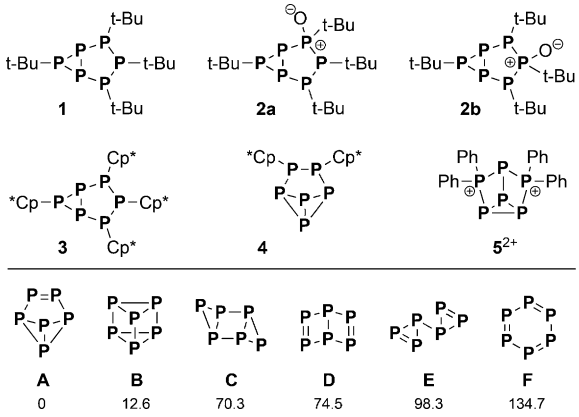
Dedicated to Prof. Dr. F. Ekkehardt Hahn on the occasion of his 60th birthday

Abstract: The reaction of the functionalized *cyclo*-tetraphosphane $[ClP(\mu\text{-}PMes^*)]_2$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) with different Lewis bases led to the formation of an unprecedented tricyclic hexaphosphane, Mes*P_6Mes*. The formation of this compound was investigated by spectroscopic and theoretical methods, revealing an unusual ring expansion reaction. The title compound was fully characterized by experimental and computational methods.

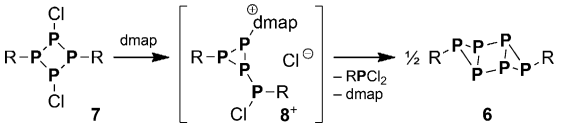
Phosphorus has fascinated chemists since its discovery by Henning Brand in 1669.[1] Especially since the development of modern day chemistry, various modifications of phosphorus have been identified,[2,3] and countless polyphosphorus systems with (organic) substituents have been reported that incorporate a plethora of different structural motifs.[2–5] The most prominent ones are possibly monocyclic ring systems with three to six phosphorus atoms, bicyclic tetra- or pentaphosphanes, derivatives of the heptaphosphatriide anion, as well as higher aggregates which resemble strands of violet phosphorus. Moreover, with the development of computational methods, a broad range of hypothetical P clusters was studied to identify possible minima on the potential energy surface.[6–13]

However, examples of polycyclic hexaphosphanes are still rare. Baudler and co-workers reported on $(t\text{Bu})_4P_6$ (**1**, Scheme 1) and the related oxide $(t\text{Bu})_4P_6O$ (**2**), which were derived from tBuPCl_2 and PCl_3 by reduction with Mg and subsequent oxidation by exposure to air.[14,15] As reported by the group of Jutzi, thermolysis of $(Cp^*P)_3$ yielded the structurally related bicyclic hexaphosphane $Cp^*_4P_6$ (**3**, Cp* = pentamethylcyclopentadienyl) as well as the tricyclic hexaphosphane $Cp^*_2P_6$ (**4**), which incorporates a benzvalene type P_6 scaffold (**A**).[16,17] Weigand and co-workers reported on the cationic compound $[Ph_4P_6]^{2+}$ (**5**), which can formally be derived from the prismane type structure (**B**) of P_6.[18] Additionally, a salt containing a bicyclic hexastibine scaffold similar to **1** and **3** was reported recently.[19]



Scheme 1. Top: Experimental examples of polycyclic hexaphosphanes. Bottom: Computed minimum structures on the potential energy surface of neutral P_6 (relative energies given in kJ mol^{-1}).[13]

Theoretical investigations revealed that the benzvalene type structure (**A**) of neutral P_6 is the most favorable isomer in the gas phase.[6–9,13] Nonetheless, other structures (**B**–**F**) were identified as local minima (Scheme 1),[13] which present desirable new structural motives in phosphorus chemistry. To date, no tricyclic hexaphosphanes that incorporate a P_6 scaffold of type **C** have been reported.[20] Therefore, we wish to present herein our results concerning the synthesis of the tricyclic hexaphosphane Mes*P_6Mes* (**6**, Mes* = 2,4,6-tri-*tert*-butylphenyl), which was derived from a P_4 precursor by an unusual ring expansion reaction (Scheme 2).



Scheme 2. Synthesis of the tricyclic hexaphosphane **6** (R = Mes*).

Recently, we reported on the synthesis of the cyclophosphane $[ClP(\mu\text{-}PMes^*)]_2$ (**7**),[21] which allows for selective functionalization of the P_4 ring system due to the chlorine substituents. Cyclophosphane **7** was synthesized from Mes*PH_2 and PCl_3 in the presence of NEt_3; thus, it can be regarded as a P_4 building block that was derived from P_1 units, as opposed to the commonly applied strategy to functionalize white phosphorus (P_4) directly using Lewis acids, (transition) metals, or singlet carbenes.[22–25] After investigating the reactivity of **7** to-

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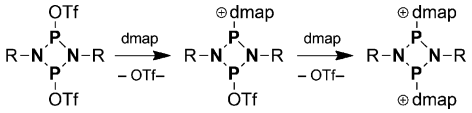
wards Lewis acids,[26] we aimed at nucleophilic substitution of the Cl atoms at the P_4 scaffold. Since 4-(*N*,*N*-dimethylamino)-pyridine (dmap) had previously been proven to be a good nucleophile and can effectively stabilize positive charges,[27–29] the reaction of **7** with dmap was investigated. In analogy to the reaction of $[TfOP(\mu\text{-}NDmp)]_2$ (Dmp = 2,6-dimethylphenyl) with dmap (Scheme 3),[28] the formation of a base-stabilized cyclophosphenium cation could be expected. In fact, in situ ^{31}P NMR spectroscopy revealed the formation of a P_4 species as indicated by an ABMX spin system (−99.3, −91.2, +9.7, and +79.3 ppm); however, the chemical shifts were indicative of a species containing a three- rather than a four-membered ring system (Figure 1).[21,30] Comprehensive DFT studies helped us assign the NMR signals to the intermediate [Mes*P_3(dmap)P(Cl)Mes*]Cl (**8**Cl, Scheme 2). The calculated NMR data agrees well with the experimental spectrum (Table S3, Supporting Information). With respect to the starting material, the formation of $\mathbf{8}^+$ can be understood in terms of a formal 1,2-Cl shift and rearrangement of one P–P bond.



Scheme 3. Reaction of a cyclodiphosphadiazane with dmap (R = Dmp).[28]

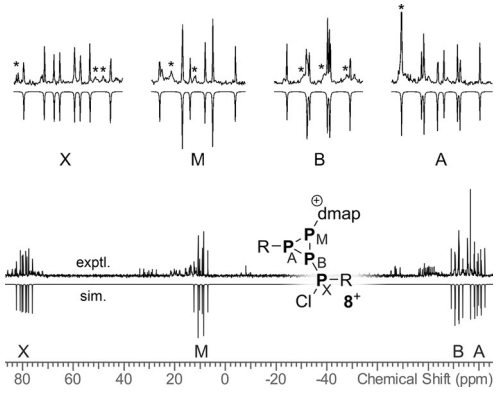


Figure 1. In situ ^{31}P NMR spectrum of the reaction mixture after 5 h. The main signals were attributed to the intermediate $\mathbf{8}^+$ (* denotes other species in solution).

Other signals in the in situ NMR spectrum were likely caused by different (configurational or rotational) isomers of $\mathbf{8}^+$. However, due to low intensity of the resonances, these could not be assigned unambiguously.

All attempts to crystallize the intermediate **8**Cl failed. Instead, colorless crystals of the novel tricyclic hexaphosphane **6** were obtained (yield: 58%). According to ^{31}P NMR spectroscopy, compound **6** and Mes*PCl_2 were in fact the only products after a total reaction time of about two days. Based on NMR integrals, the ratio of Mes*PCl_2 and **6** was found to be 2:1; thus, the formation of **6** can be rationalized in terms of formal Mes*PCl_2 extrusion and subsequent dimerization of the three-membered ring system. Comparable three-membered intermediates have been discussed previously in P_4 activation routes.[2,3,31]

The molecular structure of the tricyclic hexaphosphane **6** was determined by single-crystal X-ray diffraction (Figure 2).[32]

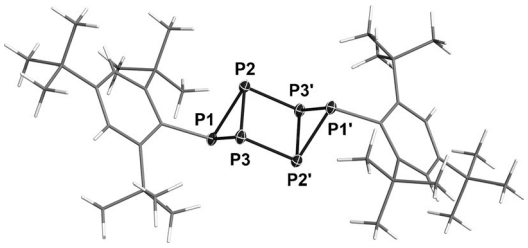


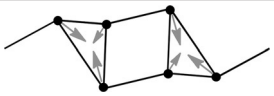
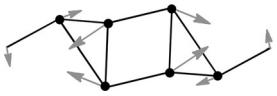
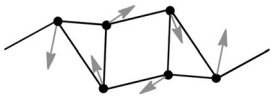
Figure 2. Molecular structure of **6**. Ellipsoids are set at 50% probability (123 K). Selected bond lengths [Å] and angles [°]: P1–C1 1.876(1), P1–P2 2.2189(5), P1–P3 2.2151(5), P2–P3 2.2373(5), P2–P3′ 2.2368(5); P3-P1-P2 60.61(2), P1-P2-P3 59.61(2), P1-P3-P2 59.78(2), P1-P2-P3′ 92.87(2), P2′-P3-P2 90.01(2); P1-P2-P3-P2′ 93.33(2).

The molecule is located on a crystallographic inversion center, hence the central P_4 ring system is perfectly planar. All bond angles within the four-membered ring system are close to 90°, the bond angles within the three-membered rings are close to 60°. The six-membered ring molecule adopts a chair conformation with two transannular P–P bonds. The P1–P2 and P1–P3 bonds are slightly shorter (average 2.217 Å) than the P2–P3 and P2–P3′ bonds (average 2.237 Å). Therefore, the central P_4 scaffold adopts an almost square geometry, while the three-membered rings correspond to isosceles triangles. All P–P bond lengths correspond to typical single bonds (Σr_{cov} = 2.22 Å).[33] The angle between the least-squares planes of the three- and four-membered ring systems is 93.3°, which compares to to those of other polycyclic phosphanes, such as bicyclic tetraphosphanes (≈ 100°)[22,34–36] or the aforementioned bicyclic hexaphosphanes **1** and **3** (89.8° and 99.2°, respectively).[14,17]

In the solid-state Raman spectrum, the P_6 scaffold can be identified by three characteristic bands at 414, 442, and 537 cm^{-1}, which were assigned on the basis of computed vibrational data (Table 1, for more details see Figure S5 in the Supporting Information)

In the ^{31}P NMR spectrum, the tricyclic hexaphosphane **6** is characterized by an AA′BB′B″B‴ spin system (−107.7 and −96.1 ppm; Figure 3). Due to dynamic rotation of the *t*Bu groups in solution, all four P atoms of the central P_4 scaffold become equivalent, resulting in apparent C_{2h} symmetry. The chemical shifts are similar to the NMR shifts of the P_3 unit of the structurally related compounds **1** and **3**,[14,17] but also comparable to either cyclotriphosphanes[21,30] or the bridging P atoms in bicyclic tetraphosphanes.[22,34–36] The experimental NMR data are in good agreement with calculated NMR shifts and coupling constants (Table 2).

Table 1. Characteristic Raman vibrations of **6**.

Vibration mode (● = P)	Main contribution	Frequency [cm^{-1}]
	in-phase P_3 ring mode	537
	out-of-phase P_4 ring mode	442
	out-of-phase P_3 ring mode	414

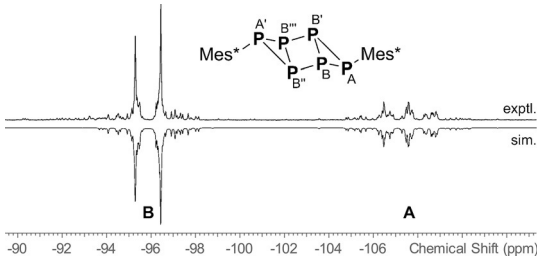


Figure 3. Experimental (top) and simulated (bottom) ^{31}P NMR spectrum of **6**.

Table 2. ^{31}P NMR data of **6**. Calculated values [PBE0/6-31G(d,p), GIAO method] are given in brackets.

	δ [ppm]	J [Hz]	
P_A	−107.7 (−126.2)	$J_{AA'} = -45$ (−56)	
P_B	−96.1 (−88.8)	$J_{AB} = J_{AB'} = -191$ (−158) $J_{AB''} = J_{AB'''} = +54$ (+35)	$J_{BB'} = -111$ (−78) $J_{BB''} = -146$ (−90 $J_{BB'''} = -30$ (−45)

To investigate the bonding situation within the P_6 scaffold, DFT calculations were performed.[37] As expected, natural bond orbital (NBO)[38] analysis revealed eight P–P single bonds, of which six are considerably bent out of the line of nuclear centers due to the small bonding angles within the three-membered rings. This effect is also reflected in the symmetry and shape of the Kohn–Sham orbitals and can be nicely visualized by the electron localization function (ELF, Figure 4), where the local maxima are located beside the bond axes. Hence, the bonding within the P_3 units is comparable to that of tetrahedral P_4.[39] To evaluate the stability of compound **6**, the corresponding *cis*-tricycle, which can formally be derived from the prismane-type structure (**B**) of P_6, as well as the benzvalene type isomer (**A**) were calculated (Figure 5). These were found to be 40.2 or 72.6 kJ mol^{-1} higher in energy (ΔG_{298}) than the experimental structure, respectively. However, in case of the smaller Cp* compound (**4**) or *t*Bu substituents (**9**), the benzvalene type isomers (**A**) were found to be the most stable ones, in accordance with the findings for neutral P_6 and experimental evidence.[16] Thus, the unusual tricyclic structure of type **C** is stabilized by the bulky Mes* moiety.

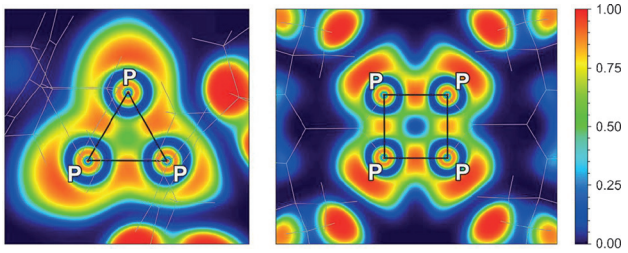


Figure 4. Depiction of the electron localization function, showing the P–P bonding system and the lone pairs at the P atoms; left: three-membered ring plane; right: four-membered ring plane.

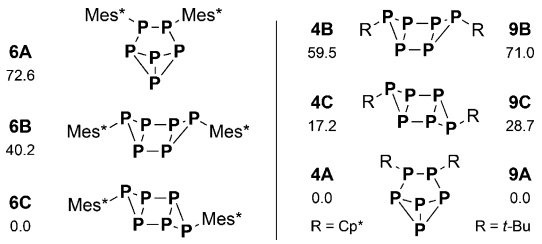


Figure 5. Relative stabilities of R_2P_6 isomers (ΔG_{298} in kJ mol^{-1}).

The tricyclic hexaphosphane **6** is poorly soluble in common organic solvents. It decomposes at 212 °C under inert conditions. Intriguingly, it was found to be stable in air. Even upon adding water to solution of **6** in CD_2Cl_2, 60% of the substance (by mole fraction) remained intact over a period of ten days at ambient temperature. This prompted us to develop an alternate synthetic protocol: starting from Mes*PH_2 and PCl_3, the precursor **7** was generated in situ by base-assisted HCl elimination. After removal of the hydrochloride, the crude product was treated with dmap without further purification. This led to precipitation of the tricyclic hexaphosphane, which was subsequently washed with water and acetone to remove all polar and nonpolar impurities. In this vein, compound **6** could be synthesized in 47% yield (based on Mes*PH_2), which is a significant improvement over the synthesis from pure **7** (combined yield based on Mes*PH_2: 26%).

When treating the cyclophosphane **7** with other Lewis bases, such as PPh_3 or tetramethylethylenediamine (TMEDA), practically no reaction was observed. Slow consumption of the starting material could only be detected after prolonged stirring, and a mixture of different products was observed in the ^{31}P NMR spectrum. In the case of PPh_3, trace amounts of **6** were identified in the NMR spectrum after nine days. On the other hand, the reaction of **7** with tetramethylimidazolylidene led to degradation of the P_4 ring system; the main products were identified as the *endo–exo* isomer of the bicyclic phosphane Mes*P_4Mes*, the diphosphene Mes*PPMes*, and the primary phosphane Mes*PCl_2 (5:1:7 ratio).[40] Accordingly, the unusual reactivity of the cyclophosphane **7** towards dmap cannot be generalized to other Lewis basic systems.

In conclusion, the first [3.1.0.0^{2,4}]-tricyclic hexaphosphane, Mes*P_6Mes* (**6**), could be prepared starting from a P_4 precursor molecule by formal ring expansion. Due to its symmetry, compound **6** displayed an unusual AA′BB′B″B‴ spin system in the ^{31}P NMR spectrum. The P_6 scaffold could be well discerned in the solid-state Raman spectrum due to three characteristic bands. Furthermore, DFT calculations showed that the structural motif is stabilized by the bulky Mes* substituents; in case of smaller moieties, such as Cp* or *t*Bu, a benzvalene type structure of the P_6 scaffold is preferred. This demonstrates the advantages of bulky substituents for the stabilization of unusual bonding patterns.

Experimental Section

All manipulations were carried out under an inert atmosphere of argon. A mixture of [{ClP(μ-PMes*)}$_2$] (350 mg, 0.51 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (dmap, 69 mg, 0.56 mmol) was dissolved in CH_2Cl_2 (3 mL) and stirred at ambient temperature for 2.5 days. Subsequently, the solution was slowly cooled to 5 °C, whereupon crystallization of colorless crystals was observed. The yellowish supernatant was removed by syringe and the crystals were washed with cold CH_2Cl_2 (0.5 mL) to remove adhering impurities. Drying in vacuo yielded a colorless product (100 mg, 0.15 mmol, 58%): m.p. 212 °C (decomposition); elemental analysis calcd (%) : C 63.90, H 8.64; found: C 63.75, H 8.82; ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): $\delta = -107.7$ (m, $^1J_{AB} = -191.3$ Hz, $^2J_{AB'} = +54.3$ Hz, $^3J_{AA'} = -44.8$ Hz, 2 P, (Mes**P*)$_2$P$_4$), −96.1 (m, $^1J_{AB} = -191.3$ Hz, $^1J_{BB'} = -110.5$ Hz, $^1J_{BB''} = -146.1$ Hz, $^2J_{BB'''} = -29.7$ Hz, $^2J_{AB'} = +54.3$ Hz, 4 P, (Mes*P)$_2$*P*$_4$); MS (CI positive, *iso*-butane): *m*/*z* (%): 677 [*M*]$^+$. Further experimental details can be found in the Supporting Information.

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Keywords: Lewis base · 4-(*N*,*N*-dimethylamino)pyridine · NMR spectroscopy · phosphorus compounds · polycyclic phosphanes · structure elucidation

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