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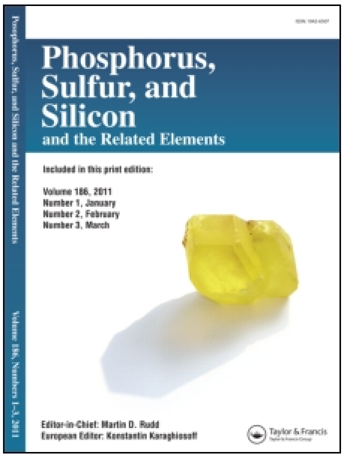

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis, Properties, Structure and Reactivity of Sodium 2,3,4,5-Tetra- tert -butylcyclopentaphosphanide

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SYNTHESIS, PROPERTIES, STRUCTURE AND REACTIVITY OF SODIUM 2,3,4,5-TETRA-*TERT*-BUTYLCYCLOPENTAPHOSPHANIDE

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*The reaction between Na, ^{t}BuPCl$_2$, and PCl$_3$ in thf gives Na[*cyclo-*(^{t}Bu$_4$P$_5$)] (**1**). **1** reacts with PCl$_3$ to yield (*cyclo-*^{t}Bu$_3$P$_4$)^{t}BuPCl (**2**), and with a proton source, such as HCl, NH$_4$Cl, or ^{t}BuCl, to give* cyclo-*^{t}Bu$_4$P$_5$H (**3**). The reaction of **1** with [MCl$_2$(PRR'$_2$)$_2$] (M = Ni; R = R' = Et; M = Pd, Pt, R = Ph, R' = Me) gives [Ni{*cyclo-*(^{t}Bu$_3$P$_5$)}(PEt$_3$)$_2$] (**4**), [Pd{*cyclo-*(^{t}Bu$_4$P$_5$)}$_2$] (**5**), and [PtCl{*cyclo-*(^{t}Bu$_3$P$_4$)^{t}BuP}(PPhMe$_2$)] (**6**). **1–6** were characterized by ^{31}P{^{1}H} NMR spectroscopy, and **1** and **4–6** were also characterized by X-ray crystallography.*

INTRODUCTION

In 1877, Köhler and Michaelis reported the isolation of the first cyclooligophosphane, which was thought to be the phosphorus analogue of azobenzene.[1] One-hundred years later, the first cyclooligophosphanide anions were described.[2,3] To date, only K[*cyclo*-(^{t}Bu$_2$P$_3$)], K[*cyclo*-(Ph$_4$P$_5$)], and Li[*cyclo*-(^{t}Bu$_{n-1}$P$_n$)] ($n = 3$–5) were characterized in inseparable mixtures by ^{31}P NMR spectroscopy.[2,4] We now report the synthesis of Na[*cyclo*-(^{t}Bu$_4$P$_5$)] (**1**) in high purity and good yield (56%).

DISCUSSION AND RESULTS

Na[*cyclo*-(^{t}Bu$_4$P$_5$)] (**1**) was obtained by the reaction of Na with ^{t}BuPCl$_2$ and PCl$_3$ in the ratio 12:4:1 in thf. In the ^{31}P NMR spectrum, **1** exhibits an ABB′CC′ spin system. Only one conformer is present in solution and in the solid state.[5]

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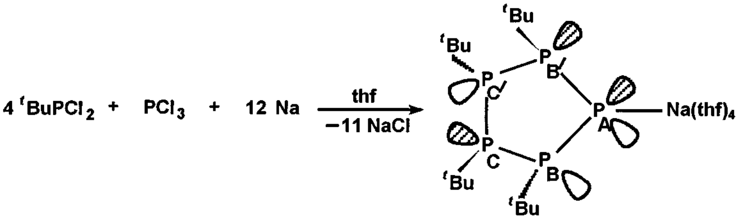
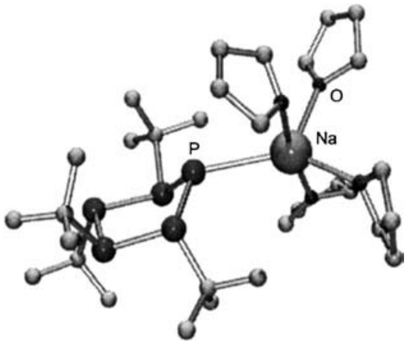
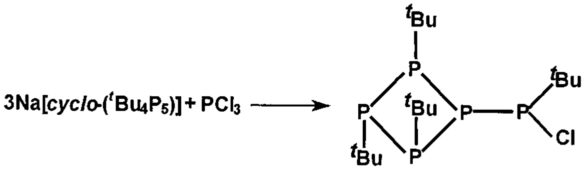


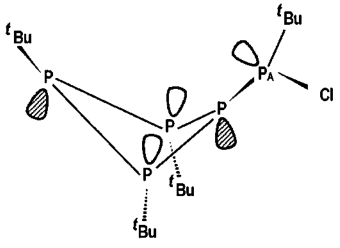
In the solid state, the P_5 ring has an envelope conformation. The P1—P5 bond (213.20(11) pm) is shorter than the other P—P bonds (220.35(12)–222.92(11) pm). The sodium atom has the unusual coordination number of 5.

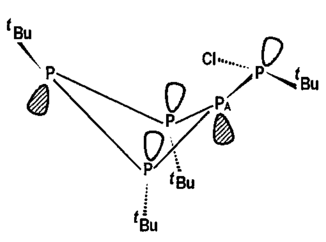


1 reacts with PCl_3 to give (*cyclo*-^{t}Bu$_3$P$_4$)^{t}BuPCl (**2**), which shows the coupling pattern of an ABCDE spin system in the ^{31}P NMR spectrum.



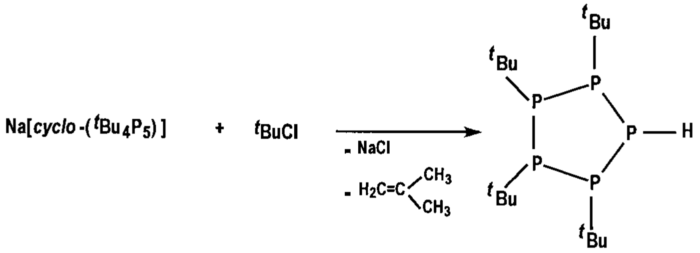
Two conformers are formed, of which the isomer is preferred in which the *tert*-butyl group on atom P_A has the maximum distance to the *tert*-butyl groups on the ring.



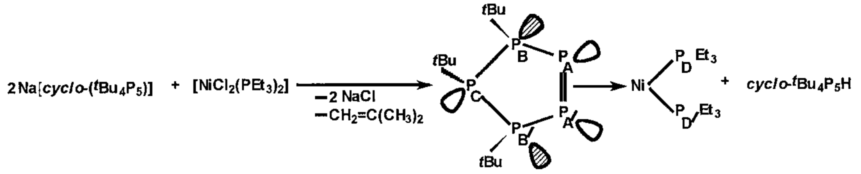


The reaction of **1** with a proton source, such as HCl, NH_4Cl, or ^{t}BuCl, results in the formation of *cyclo*-^{t}Bu$_4$P$_5$H (**3**).[6] In the

^{31}P NMR spectrum, **3** exhibits the coupling pattern of an ABCDE spin system.



The reaction of two equivalents of **1** with [NiCl$_2$(PEt$_3$)$_2$] in thf yields [Ni{*cyclo*-(^{t}Bu$_3$P$_5$)}(PEt$_3$)$_2$] (**4**).[5]



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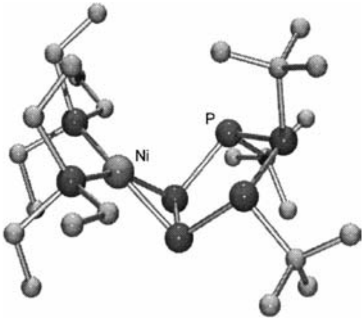
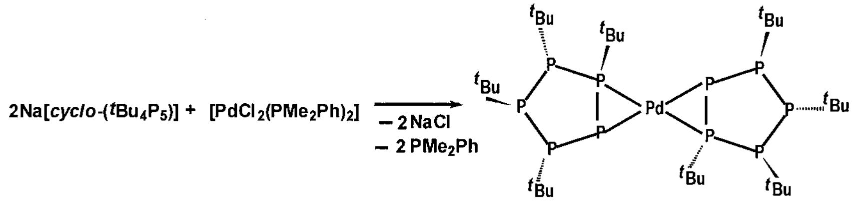
The ^{31}P NMR spectrum shows the coupling pattern of an AA′BB′CDD′ spin system. In the solid state, the P$_A$–P$_{A'}$ bond length of 211.83(11) pm indicates a double bond. In addition, the coupling constant $^1J_{AA'}$ is large (−434.6 Hz).



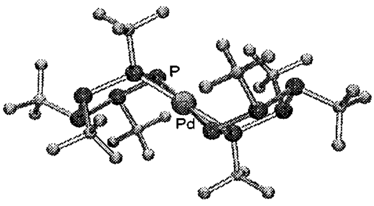
The reaction of **1** with [PdCl$_2$(PMe$_2$Ph)$_2$] gave **5**.



5

In **5**, the metal atom is located on a crystallographic center of inversion. The P1—P2 bond of the metal-coordinated P atoms (212.33(17) pm) is significantly shorter than expected for a normal P—P single bond.

The Pd complex exhibits the coupling pattern of an AA′BB′CC′DD′EE′ spin system in the ^{31}P NMR spectrum.



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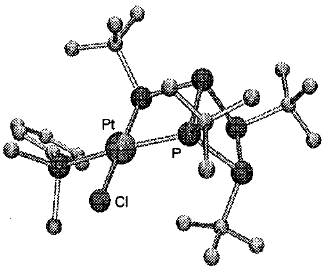
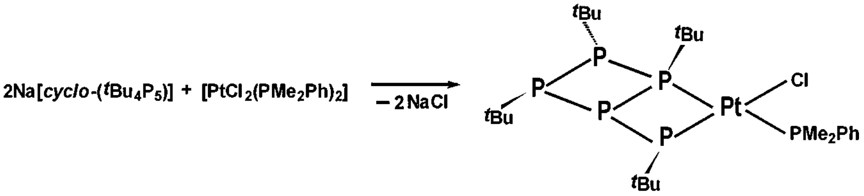


6

The reaction of **1** with [$PtCl_2(PMe_2Ph)_2$] (ratio 2:1) in thf yields [PtCl{*cyclo*-(^{t}Bu_3P_4)^{t}BuP}(PMe_2Ph)] (**6**).



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