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Protonation of sodium 1,2-diphospha-3,4,5-triphenylcyclopentadienide: the first example of [2 + 2] cycloaddition reaction for phosphacyclopentadiene

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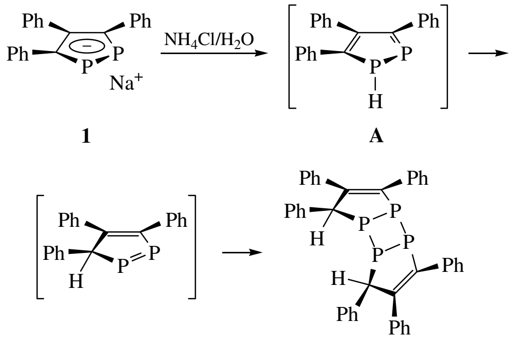
Protonation of sodium 1,2-diphospha-3,4,5-triphenylcyclopentadienide occurs with a [1,5]-proton shift and leads to rac-*trans*-1,2,6,7-tetraphosphatricyclo$[5.3.0.0^{2,6}]$-3,9-decadiene, the product of an unusual [2 + 2] cycloaddition reaction.

In phosphorus chemistry, alkali metal phosphacyclopentadienides are of special interest as these compounds are the examples of phosphorus anions for which the organometallic chemistry of the carbon analogue, the cyclopentadienide anion, is well known and thus allows the reactivity of the two compounds to be compared.[1] They can also be used as building blocks for the construction of various organometallic complexes and clusters, such as unusual one- and two-dimensional polymeric compounds and a unique fullerene-like molecule, which were obtained by Scheer and co-workers[2] from pentamethylpentaphosphaferrocene and copper(I) halides.

Recently, we reported a highly facile synthetic approach to sodium 1,2-diphospha-3,4,5-triphenylcyclopentadienide **1** by reaction of NaP_5 with the half-sandwich nickel complex [(cyclo-C_3Ph_3)Ni(PMe_2Ph)$_2$Br].[3] We studied the reactivity of this phosphorus analogue of a pyrazolyl anion, and we were especially interested in its protonation, which should give the corresponding 3,4,5-triphenyl-1,2-diphosphacyclopentadiene. However, it was previously observed[4] that the protonation of alkali metal phosphacyclopentadienides, *i.e.*, 1-phosphacyclopentadienide,[5] 1,3-diphosphacyclopentadienide[6] and 1,2,4-triphosphacyclopentadienide,[7] first gave the expected PH products, which subsequently underwent a [1,5]-proton shift followed by a [4 + 2] cycloaddition reaction. In the case of 1,2,4-triphosphacyclopentadienide, an additional [2 + 2] intramolecular cycloaddition reaction took place.[6] This reactivity is similar to that observed for cyclopentadiene and its derivatives, which usually undergo [4 + 2] cycloadditions, although [2 + 2] cycloadditions were also realised under photochemical conditions.[8,9]

Cycloaddition reactions are especially important for the construction of cyclic organic molecules and organoelement heterocycles. The basic principle enunciated is that reactions occur readily when there is congruence between the orbital symmetry characteristics of reactants and products, and only with difficulty when that congruence is absent, that is, orbital symmetry is conserved in concerted reactions.[10] Thus, new phosphorus cage compounds should be available through protonation of phosphacyclopentadienides.

The protonation of **1** was carried out in THF by addition of a few drops of a saturated aqueous NH_4Cl solution (Scheme 1).† The main product in the resulting reaction mixture was one diastereomer only, *i.e.*, the *R*,*R* and *S*,*S* isomers of *trans*-3,4,5,8,9,10-hexaphenyl-1,2,6,7-tetraphosphatricyclo[5.3.0.0^{2,6}]-3,9-decadiene **2**, which was isolated in high yield (82%). The formation of only one diastereomer can be explained by a very favourable anti-orientation of the lone electron pair at the phosphorus atoms and the CH proton.



Scheme 1

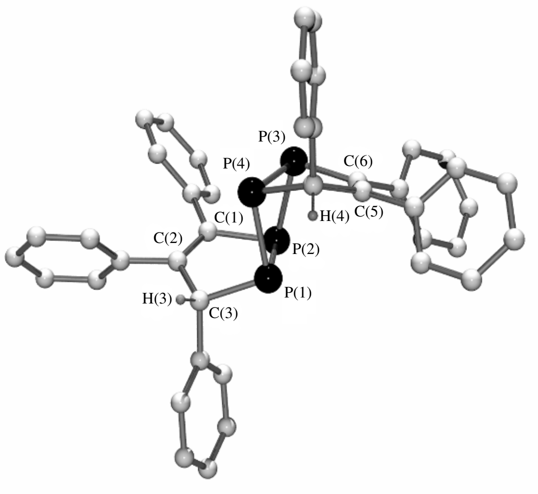


Figure 1 Molecular structure of (*R*,*R*)-*trans*-3,4,5,8,9,10-hexaphenyl-1,2,6,7-tetraphosphatricyclo[5.3.0.0^{2,6}]-3,9-decadiene **2**. Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.237(1), P(1)–P(4) 2.233(1), P(2)–P(3) 2.243(1), P(3)–P(4) 2.237(1), P(1)–C(3) 1.880(2), P(2)–C(1) 1.850(2), P(3)–C(6) 1.850(2), P(4)–C(4) 1.878(2), C(1)–C(2) 1.345(4), C(5)–C(6) 1.336(3); P(1)–P(2)–P(3) 87.50(3), P(1)–P(4)–P(3) 87.74(3), P(4)–P(1)–P(2) 87.83(3), P(4)–P(3)–P(2) 87.59(4), C(3)–P(1)–P(4) 99.03(8), C(4)–P(4)–P(1) 97.33(8).

As a possible pathway for the formation of **2**, protonation of the 1,2-diphosphacyclopentadienide anion to form PH diphosphole **A** is proposed as the first step. The formation of PH products was previously shown by low-temperature NMR investigations of protonation reactions of 1-phosphacyclopentadienide,[5] and several PH phospholes were stabilised by coordination to tungsten carbonyl derivatives.[6] The following [1,5]-proton shift results in the formation of CH diphosphole **B**, which can then undergo a [2 + 2] cycloaddition reaction to give **2**.

The formation of cyclotetraphosphanes with four P–P single bonds as the result of a dimerisation reaction of two P=P double bonds was also suggested in the formation of 3,7-diaza-1,2,4,5,6,8-hexaphosphatricyclo[4.2.0.0^{2,5}]octane[11] and *trans*-1,2,4,5-tetraphosphatricyclo[3.1.0.0^{2,4}]hexane.[12]

The structure of **2** was confirmed by NMR spectroscopy and X-ray analysis.‡ The molecule consists of two symmetrical diphosphacyclopentene fragments, which are connected by two phosphorus–phosphorus bonds (Figure 1). The P_4 fragment has a trapezoidal geometry [P–P 2.233(1) to 2.243(1) Å]. Both diphosphacyclopentene rings are non-planar, and as a result the central P_4 ring is also puckered. This is in contrast to a related compound, which was prepared by the dimerisation of the cyclo-1σ^4,3σ^2,4σ^2-triphosphapentadienyl radical.[13] A planar P_4 ring was also found for 3,7-diaza-1,2,4,5,6,8-hexaphosphatricyclo[4.2.0.0^{2,5}]octane[11] and *trans*-1,2,4,5-tetraphosphatricyclo[3.1.0.0^{2,4}]hexane.[12] In the crystal, the molecule is chiral with the lone pairs on P(1) and P(2) being on opposite sides to those on P(3) and P(4) and related by a C_2 axis in the idealised structure in which the phosphorus ring is planar. In the solid state, **2** forms columns along the *b* axis (Figure 2).

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† All reactions and manipulations were carried out under dry pure nitrogen in standard Schlenk apparatus. All solvents were distilled from sodium/benzophenone and stored under nitrogen before use. The NMR spectra were recorded on a Bruker MSL-400 instrument (^{1}H, 400 MHz; ^{13}C 100.6 MHz; ^{31}P 121.7 MHz). TMS was used as an internal reference for ^{1}H and ^{13}C NMR chemical shifts, and 85% H_3PO_4, as an external reference for ^{31}P NMR. Na(diglyme)$_2$[cyclo-1,2-$P_2C_3Ph_3$] was prepared according to the published procedure.[3]

*Synthesis of rac-*trans*-3,4,5,8,9,10-hexaphenyl-1,2,6,7-tetraphosphatricyclo[5.3.0.0^{2,6}]-3,9-decadiene* **2**. To a solution of 0.62 g (0.17 mmol) of sodium 1,2-diphospha-3,4,5-triphenylcyclopentadiene in 30 ml of THF was added 1 ml of a saturated aqueous NH_4Cl solution. The mixture was stirred at room temperature for 3 h. The solvent was evaporated and the residue dried *in vacuo* at 40 °C. This solid was recrystallised from toluene–hexane (3:1, 20 ml) to give 0.54 g (82%) of **2** as yellow crystals; mp 155 °C (decomp.).

^{1}H NMR ($CDCl_3$) δ: 5.27 (s, 2H), 7.05–7.33 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$) δ: 63.84 (m, CH), 126.54, 127.12, 127.92, 128.31, 129.02, 129.10, 129.27, 131.39, 138.26 (t, $^2J_{PC}$ 7.7 Hz), 139.11, 140.59, 141.06 (t, $^2J_{PC}$ 9.3 Hz), 144.55 (t, $^2J_{PC}$ 20.06 Hz), 147.37 (tt, $^1J_{PC}$ 6.62 Hz, $^1J_{PC}$ 1.45 Hz). ^{31}P NMR ($CDCl_3$) δ: AA′BB′ system, δ_A 12.7, δ_B 35.5, $^1J_{AA'}$ –161.0 Hz, $^1J_{BB'}$ –117.4 Hz, $^1J_{AB}$ –146.3 Hz, $^1J_{AB'}$ –8.6 Hz. Found (%): C, 76.24; H, 4.91; P, 19.07. Calc. for $C_{42}H_{32}P_4$ (%): C, 76.36; H, 4.88; P, 18.75.

‡ *Crystal data for* **2**: $C_{42}H_{32}P_4\cdot0.5PhMe$, *M* 706.62, monoclinic, space group *C*2/*c*, $Z = 8$, $a = 23.198(2)$, $b = 12.953(1)$ and $c = 27.172(3)$ Å, $\beta = 111.76(1)°$, $V = 7583(1)$ Å^3, μ(MoKα) = 0.231 mm^{-1}, $d_{calc} = 1.238$ g cm^{-3}, $T = 213(2)$ K. Data were collected on a Siemens SMART CCD diffractometer. Of a total of 27450 reflections 7306 were unique (R_{int} = = 0.0937). The structure was solved by direct methods[15] and refined by full-matrix least-squares procedures on F^2. Final $R_1 = 0.0493$ (wR_2 = = 0.1136) for [$I > 2\sigma(I)$] and $R_1 = 0.0763$ ($wR_2 = 0.1207$) for all data. The solvent molecule (toluene) was located disordered on a special position. All non-hydrogen atoms (except disordered toluene) were refined anisotropically. With the exception of toluene all hydrogen atoms were refined isotropically.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 298205. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2006.

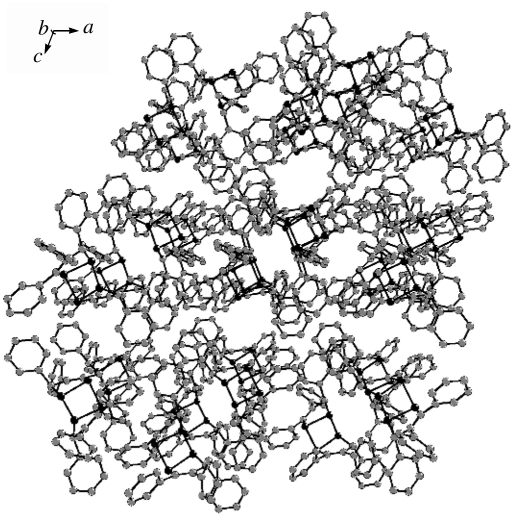

Figure 2 Crystal packing of rac-*trans*-3,4,5,8,9,10-hexaphenyl-1,2,6,7-tetraphosphatricyclo[5.3.0.0^{2,6}]-3,9-decadiene **2**.

The ^{31}P NMR spectrum of **2** shows the coupling pattern of an AA′BB′ system. The chemical shifts and coupling constants were obtained by simulation[14] of the experimental spectrum (δ_A 12.7 ppm, δ_B 35.5 ppm, $^1J_{AA'}$ –161.0 Hz, $^1J_{BB'}$ –117.4 Hz, $^1J_{AB}$ –146.3 Hz, $^1J_{AB'}$ –8.6 Hz).

In summary, we found that the protonation of sodium 1,2-diphospha-3,4,5-triphenylcyclopentadienide leads to an unusual [2 + 2] cycloaddition product, namely, rac-*trans*-3,4,5,8,9,10-hexaphenyl-1,2,6,7-tetraphosphatricyclo[5.3.0.0^{2,6}]-3,9-decadiene, which still contains a potentially reactive C=C double bond, as well as reactive lone electron pairs at phosphorus.

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