



Communication

An unusual reaction of cyclopropenylphosphonium bromide with sodium polyphosphides – A novel approach to sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide

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ARTICLE INFO

Article history:

Received 17 June 2008

Received in revised form 23 July 2008

Accepted 4 August 2008

Available online 11 August 2008

Keywords:

Triphenylcyclopropenyl bromide

Phosphonium salt

Sodium polyphosphides

1,2-Diphosphacyclopentadienide anion

ABSTRACT

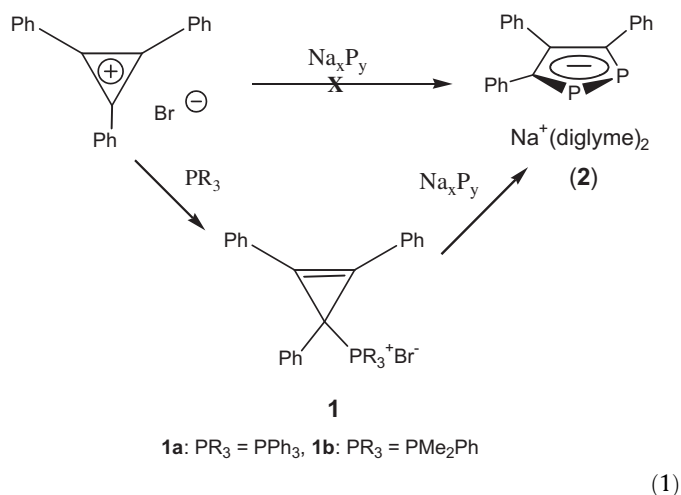
1,2,3-Triphenylcyclopropenylphosphonium bromide reacts with sodium polyphosphides to give sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide in high yield.

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1. Introduction

Phosphonium salts are useful reagents in organic synthesis [1] and have found broad application for the preparation of a variety of Wittig reagents, which are widely used for the conversion of ketones and aldehydes to alkenes [2]. Furthermore, cyclopropenylphosphonium cations react with different nucleophiles to give cyclic compounds such as furans [3] and cyclopentenones [4] due to intermolecular Wittig reactions. Ring-opening reactions of cyclopropene also take place in reactions with different amines [5,6], aryl magnesium bromides [7], and phosphites [8]. We are interested in the reactivity of phosphonium salts of cyclopropenes toward sodium polyphosphides as a possible route to sodium 1,2-diphosphacyclopentadienide [9], which was recently obtained by reaction of cyclopropenyl nickel complexes with different polyphosphides such as NaP₅ [10] and Na₃P₇ [11].

We have found that triphenylcyclopropenyl bromide reacts with tertiary phosphines to form novel phosphonium salts **1** in high yield (Eq. (1))



The structure of **1** was confirmed by NMR spectroscopy, and additionally by X-ray analysis for **1b** (see Fig. 1). To the best of our knowledge, **1b** is the first structurally characterized cyclopropenylphosphonium salt. The cyclopropenyl ring and the two phenyl rings at the C–C double bond of the cyclopropenyl ring are almost coplanar. The P1–C1 bond length (1.824(4) Å) is slightly longer than a P–C single bond. The C–C distances of the cyclopropenyl ring in **1b** differ: one bond is short (C=C, C2–C3 1.315(5) Å) and two are

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long (C1–C3, 1.526(5) and C1–C2 1.517(5) Å), in contrast to [cyclo-(CPh)₃]ClO₄ [12] and [cyclo-(CNMe₂)₃]ClO₄ [13], in which all three C–C bonds are equivalent (1.373(5) and 1.363(7), respectively).

No aromaticity of cyclopropene ring of **1** was found in solution, as is apparent from the ¹³C NMR spectrum, which exhibits a doublet at ca. 31 ppm for C¹, characteristic for an sp³-hybridized carbon atom.

Phosphonium salts **1a** and **1b** were treated with mixture of polyphosphides, obtained *in situ* from sodium and white phosphorus and containing mainly NaP₅ and Na₃P₇ [14]. Only the signals of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide (**2**) and the tertiary phosphine were detected in the ³¹P NMR spectrum of the reaction mixture after refluxing for 3 h (Eq. (1)).

Compound **2** can easily be isolated from the reaction mixture by filtration. After washing with *n*-hexane **2** is obtained in good purity and can be used for following reactions without further purification.

So reaction of phosphonium salts **1** with sodium polyphosphides affords a new convenient method for preparation of **2**. In contrast, no sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide **2** was formed in reaction of 1,2,3-triphenylcyclopropenyl bromide with sodium polyphosphides without tertiary phosphines or at presence of catalytic amount tertiary phosphines. Recently we have proposed that the first stage of formation of sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide in reaction of cyclopropenyl complexes of nickel with sodium polyphosphides is a nucleophilic attack polyphosphide-anion to one of carbon of C₃-ring [11,15]. The absence of aromaticity of cyclopropene ring of **1** allow to explain the difference of reactivity of 1,2,3-triphenylcyclopropenyl bromide and phosphonium salts **1** towards sodium polyphosphides – the positive charged carbon atom C¹ facilitates the nucleophilic attack of polyphosphide-anion to one of carbon of cyclopropenilium ring.

In summary we have found that 1,2,3-triphenylcyclopropenyl-phosphonium salts react cleanly with sodium polyphosphides to give sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide in good yield.

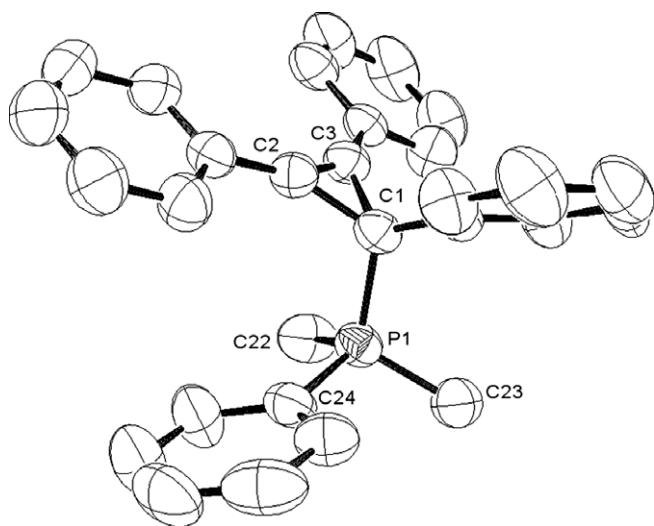


Fig. 1. Molecular structure of **1b**. Hydrogen atoms, bromide anion, and solvent omitted for clarity; thermal ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): C1–C2 1.517(5), C1–C3 1.526(5), C2–C3 1.315(5), P1–C1 1.824(4), P1–C22 1.777(4), P1–C23 1.774(4), P1–C24 1.793(4); C2–C1–C4 121.3(3), C3–C1–C4 121.9(3), C2–C1–C3 51.2(2), C3–C2–C1 64.8(3), C1–C3–C2 64.0(3), C1–P1–C23 112.48(18), C1–P1–C22 108.6(2), C1–P1–C24 108.8(2).

2. Experimental

All reactions and manipulations were carried out under dry pure N₂ 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 AVANCE DRX 400 or an MSL-400 (¹H 400 MHz, ³¹P 121.7 MHz, ¹³C 100.6 MHz). SiMe₄ was used as internal reference for ¹H and ¹³C NMR chemical shifts, and 85% H₃PO₄ as external reference for ³¹P. PMe₂Ph [16] and [C₃Ph₃]Br [17] were prepared according to literature procedures.

2.1. (1,2,3-Triphenylcyclopropenyl)triphenylphosphonium bromide (**1a**)

A mixture of triphenylcyclopropenyl bromide (0.34 g, 0.01 mmol) and PPh₃ (0.26 g, 0.01 mmol) in THF (20 mL) was refluxed for 3 h. The precipitate was collected by filtration and washed with cold THF to give 1,2,3-triphenylcyclopropenyl/triphenylphosphonium bromide (**1a**) as white crystals (0.54 g, 90%). M.p.: 169 °C.

¹H NMR ([D₆]DMSO): δ = 7.38 (d, 6H, Ph, ³J_{HH} = 6.82 Hz), 7.3 (d, 2H, Ph, ³J_{HH} = 6.9 Hz), 7.42–7.54 (m, 8H, Ph), 7.62 (t, 2 H, Ph, ³J_{HH} = 7.02 Hz), 7.69 (t, 2H, Ph, ³J_{HH} = 7.34 Hz), 7.79 (t, 2H, Ph, ³J_{HH} = 7.34 Hz), 7.94 (d, 8H, Ph, ³J_{HH} = 6.82 Hz). ³¹P NMR ([D₆]DMSO): δ = 30.4 (s). ¹³C NMR ([D₆]DMSO): δ = 30.04 (d, C1, ¹J_{PC} = 74.5 Hz), 112.33 (C=C), 121.24 (*p*-C, Ph-C1), 121.69 (*p*-C, Ph-P), 123.55 (d, *m*-C, Ph-P, ³J_{CP} = 2.4 Hz), 127.23 (*p*-C, Ph), 127.64 (*p*-C, Ph), 128.46 (*m*-C, Ph-C1), 129.04 (*m*-C, Ph), 129.11 (*m*-C, Ph), 129.13 (*o*-C, Ph-C1), 129.53 (*o*-C, Ph), 129.56 (*o*-C, Ph), 130.33 (*ipso*-C, Ph), 131.55 (*ipso*-C, Ph), 131.61 (d, *o*-C, Ph-P, ²J_{CP} = 9.61 Hz), 133.5 (*ipso*-C, Ph-C1), 133.45 (d, *ipso*-C, Ph-P, ¹J_{CP} = 25.2 Hz). Anal. Calc. for C₃₉H₃₀BrP (609.54): C, 76.85; H, 4.96; P, 5.08. Found: C, 76.62; H, 4.86; P, 5.19%.

2.2. (1,2,3-Triphenylcyclopropenyl)dimethylphenylphosphonium bromide (**1b**)

Compound (**1b**) was prepared in a similar manner to **1a** and was obtained as white crystals in 85% yield. M.p.: 144 °C. Crystals suitable for X-ray analysis were growth from a saturated solution of **1b** in CHCl₃ at –30 °C.

¹H NMR ([D₆]DMSO): δ = 2.39 (d, 6H, Me, ²J_{HP} = 13.5 Hz), 7.34 (d, 3H, Ph, ³J_{HH} = 7.0 Hz), 7.46 (d, 2H, Ph, ³J_{HH} = 6.9 Hz), 7.49–7.58 (m, 8H, Ph), 7.69 (t, 1 H, Ph, ³J_{HH} = 7.15 Hz), 7.75 (t, 1H, Ph, ³J_{HH} = 7.52 Hz), 7.77 (t, 1H, Ph, ³J_{HH} = 7.15 Hz), 7.82 (d, 4H, Ph, ³J_{HH} = 6.60 Hz). ³¹P NMR ([D₆]DMSO): δ = 29.8 (s). ¹³C NMR ([D₆]DMSO) δ = 8.02 (d, Me, ¹J_{CP} = 52.9 Hz), 31.04 (d, C1, ¹J_{CP} = 74.5 Hz), 112.46 (C=C), 121.27 (*p*-C, Ph-C1), 121.8 (*p*-C, Ph-P), 124.59 (d, *m*-C, Ph-P, ³J_{CP} = 2.4 Hz), 128.35 (*p*-C, Ph), 128.46 (*p*-C, Ph), 128.94 (*m*-C, Ph-C1), 129.25 (*m*-C, Ph), 129.35 (*m*-C, Ph), 129.54 (*o*-C, Ph-C1), 129.64 (*o*-C, Ph), 129.97 (*o*-C, Ph), 130.83 (*ipso*-C, Ph), 131.21 (*ipso*-C, Ph), 131.79 (d, *o*-C, Ph-P, ²J_{CP} = 9.61 Hz), 134.1 (*ipso*-C, Ph-C1), 136.56 (d, *ipso*-C, Ph-P, ¹J_{CP} = 25.2 Hz). Anal. Calc. for C₂₉H₂₆BrP (485.40): C, 71.76, H, 5.40, P, 6.38. Found: C, 71.10, H, 5.24, P, 6.57%.

2.3. Sodium bis(diglyme) 1,2-diphospha-3,4,5-triphenylcyclopentadienide (**2**)

A mixture of Na (0.46 g, 2 mmol) and P₄ (1.24 g, 1 mmol) in diglyme (40 mL) was refluxed for 6 h to give a mixture of sodium polyphosphides. The reaction mixture was cooled to RT, **1a** (0.6 g, 1 mmol) was added, and the mixture was refluxed for an additional 3 h. The reaction mixture was filtered, and the solid was washed twice with diglyme. The solvent was evaporated in vacuum and

the remaining residue was washed three times with *n*-hexane (20 mL) to give **2** (0.4 g, 65%) as a brown powder. M.p.: 125 °C (decomp).

¹H NMR ([D₈]thf): δ = 3.15 (s, 12H, MeO), 3.30 (t, 8H, ³J_{HH} = 5.1 Hz, OCH₂), 3.38 (t, 8H, ³J_{HH} = 5.1 Hz, OCH₂), 6.63 (t, 2H, ³J_{HH} = 7.3 Hz, *p*-CH in Ph), 6.75 (br s, 9H, Ph), 6.93 (br d, 4H, ³J_{HH} = 7.3 Hz, *o*-CH in Ph). ¹³C NMR ([D₈]thf): δ = 58.07 (s, MeO), 69.69 (s, OCH₂), 71.39 (s, OCH₂), 121.77 (s, *m*-C, Ph), 122.96 (s, *m*-C, Ph), 125.91 (s, *p*-C, Ph), 126.20 (s, *p*-C, Ph), 129.73 (t, ²J_{CP} = 4.9 Hz, *ipso*-C, Ph), 131.93 (s, *ipso*-C, Ph), 143.88 (s, *o*-C, Ph), 144.27 (s, *o*-C, Ph), 147.02 (t, ²J_{CP} = 8.9 Hz, C-Ph), 161.61 (ps.t, ¹J_{CP} + ²J_{CP} = 28.5 Hz, C-Ph). ³¹P NMR ([D₈]thf): δ = 190.0 (s). Anal. Calc. for C₃₃H₄₃NaO₆P₂ (620.60): C, 63.86; H, 6.98; P, 9.98. Found: C, 64.10; H, 7.04; P, 9.57%.

2.4. X-ray analysis

Data were collected on a Bruker Smart Apex II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. C₂₉H₂₆BrP · 2 CHCl₃; *M* = 724.11; colorless prism; crystal size 0.30 × 0.30 × 0.30 mm; *T* = 273 K; triclinic; space group *P*1̄; *a* = 9.549(2) pm, *b* = 12.301(4) pm, *c* = 14.997(7) pm, α = 104.28 (3)°, β = 92.65(3)°, γ = 93.28(3)°; *V* = 1701.0(10) nm³; *Z* = 2; ρ_{calcd} = 1.414 mg/m³; *F*(000) = 732; *q* range for data collection 2.65–26.29°; 0 ≤ *h* ≤ 11; −15 ≤ *k* ≤ 15; −18 ≤ *l* ≤ 18; 6796 reflections collected; 6404 independent reflections [*R*_(int) = 0.0236]; *F*₂ = 0.961; final *R* indices [*I* > 2σ(*I*)]: *R*₁ = 0.0609; *wR*₂ = 0.0795; *R* indices (all data) *R*₁ = 0.1261; *wR*₂ = 0.0956; largest difference peak/hole: 3 0.436/−0.380 e Å. Data were corrected for absorption using SADABS [18] program (μ(Mo Kα) = 1.749 mm^{−1}). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms. Data collection images were indexed, integrated, and scaled using the APEX2 data reduction package [19]. Structure solution and refinement with SIR [20], SHELXL97 [21], WINGX [22] program. Pictures were generated with ORTEP3 for Windows [23]. One of the two molecules of trichloromethane solvent is disordered in the crystal and was refined as two equivalent molecules with the same occupancy value of 0.5.

Supplementary material

CCDC 666891 contains the supplementary crystallographic data for **1b**. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft and RFBR (07-03-91556) for financial support of this work.

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