Sodium Tetra-*tert*-butylcyclopentaphosphanide: Synthesis, Structure, and Unexpected Formation of a Nickel(0) Tri-*tert*-butylcyclopentaphosphene Complex**

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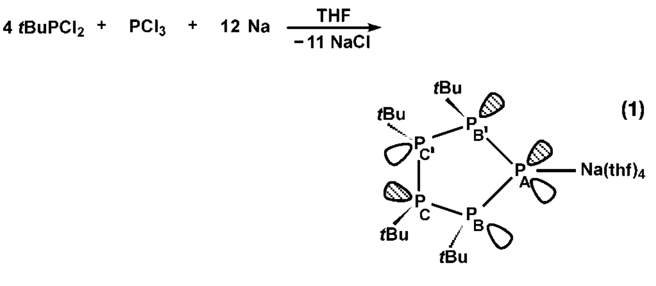
Dedicated to Professor Hans-Georg von Schnering on the occasion of his 70th birthday

While the first cyclooligophosphanes $(PR)_n$,[1] isolobal to cycloalkanes, were synthesized as early as 1877,[2] the first cyclooligophosphanide ions *cyclo*-$(P_nR_{n-1})^-$ were only described 100 years later,[3, 4] and today the number of such compounds that can be prepared in a targeted manner is still small.[5] The alkali metal compounds K[*cyclo*-(P_3tBu$_2$)],[3] K[*cyclo*-(P_5Ph_4)],[5] and Li[*cyclo*-(P_ntBu$_{n-1}$)] ($n = 3-5$)[6, 7] could not be isolated as pure compounds and were only characterized by ^{31}P NMR spectroscopy of an inseparable mixture; to date nothing is known about their coordination chemistry. A few complexes with linear oligophosphanide ligands $P_nR_n^{\,2-}$ are known: metallocene triphosphane-1,3-diyl complexes $[Cp_2M(P_3R_3)]$ (M = Ti, Zr, Hf; R = Me, Et, Ph, *t*Bu),[8] a nickel tetraphosphane-1,4-diyl complex [Ni(η^2-P_2tBu$_2$)(P_4tBu$_4$)],[9] and the stannatetraphospholanes (tBuP)$_4$SnR$_2$ (R = *t*Bu, *n*Bu, Ph) and (tBuP)$_4$Sn(Cl)*n*Bu.[10]

We have shown that the reaction of sodium with *t*BuPCl$_2$ and PCl$_3$ in the ratio 12:4:1 in THF gave a product mixture comprising Na[*cyclo*-(P_3tBu$_2$)],[3, 7] Na[*cyclo*-(P_4tBu$_3$)],[7] *cyclo*-(P_4tBu$_4$),[11] Na$_2$(P_4tBu$_4$),[3] and sodium tetra-*tert*-butylcyclopentaphosphanide Na[*cyclo*-(P_5tBu$_4$)] (**1a**). By a systematic variation of the reaction conditions we have now been able to optimize the synthesis of **1a**. Just by warming the reaction mixture to 80 °C for 8 h *cyclo*-(P_4tBu$_4$) ($\delta(^{31}P) = -58.4$) is formed as the main product; over five days this converts into **1a** and a small amount of the other sodium salts [Eq. (1)]. As *cyclo*-(P_4tBu$_4$) does not react with Na even on heating for several days in THF, **1a** is probably generated by the direct attack of Na$_3$P, formed from sodium and PCl$_3$.[12] As only **1a** and *cyclo*-(P_4tBu$_4$) are soluble in *n*-pentane, they can be readily separated from the by-products. The separation of *cyclo*-(P_4tBu$_4$) from **1a** is possible by sublimation; only pure **1a** remains (yield 56 %). Recrystallization from THF gives [Na(thf)$_4$][*cyclo*-(P_5tBu$_4$)] (**1b**). This compound is stable under an inert atmosphere at room temperature and is soluble in ethers and aliphatic and aromatic hydrocarbons.



1b

The ^{31}P{^{1}H} NMR spectrum of **1b** shows resonance signals corresponding to an ABB′CC′ spin system.[13] Only one conformational isomer is present. Of the four conformations that correspond to the spectral symmetry[3] and based on the steric requirements of the *tert*-butyl groups the all-*trans* isomer is preferred and this is supported by the coupling constants.[5, 14]

In agreement with the ^{31}P NMR spectrum, the X-ray crystal structure shows an all-*trans* configuration of the *tert*-butyl groups on the phosphorus atoms with an „envelope“ conformation[15] of the chiral P$_5$ ring system (Figure 1).[16] The P1–P5 bond (213.20(11) pm) is noticeably shorter than the other P–P bonds (220.35(12)–222.92(11) pm). The Na atom has an unusual five-coordinate geometry with four thf molecules and the P_5tBu$_4$ ring as ligands.[17] The Na–P1 bond of 293.82(15) pm is in the range typical for those reported for sodium phosphanides (277.8(2)–335.7(2) pm)[18] and the triphosphide [Na(thf)$_4$][1,3-(Si*t*Bu$_3$)$_2$P$_3$].[19]

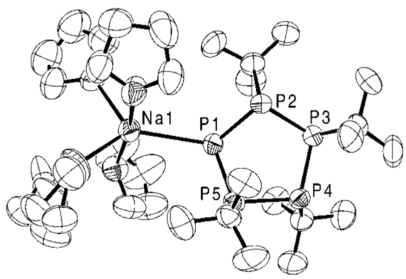
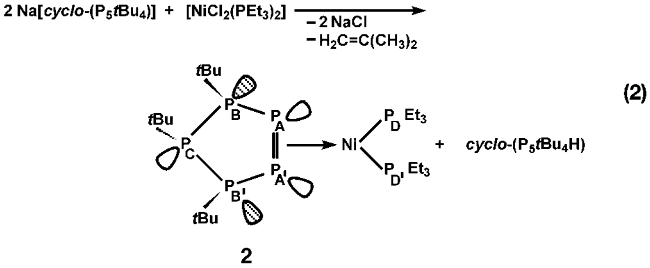


Figure 1. Molecular structure of **1b** (H atoms not shown). Selected bond lengths [pm] and angles [°]: Na-P1 293.82(15), P1-P5 213.20(11), P1-P2 220.35(12), P2-P3 222.92(11), P3-P4 220.81(11), P4-P5 221.11(12), Na-O 235.4(3), 236.6(3), 236.8(3), and 241.2(3); P5-P1-P2 103.74(4), P1-P2-P3 99.97(4), P4-P3-P2 102.56(4), P3-P4-P5 106.34(4), P1-P5-P4 104.99(4) (angle sum 517.6°).

Compound **1a** reacts readily with bis(triethylphosphane)nickel(II) chloride in polar or nonpolar solvents to give (η^2-3,4,5-tri-*tert*-butylcyclopentaphosphene)bis(triethylphosphane)nickel(0) (**2**) [Eq. (2)]; *cyclo*-(P_5tBu$_4$H) is formed as a by-product.[20] Noteworthy in the formation of **2** is the cleavage of



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a *t*Bu group from the anionic *cyclo*-(P$_5$*t*Bu$_4$) ring as *t*BuCl with the formation of the previously unknown cyclopentaphosphene ring; however, a few isolobal cyclopentene[21] and 1,2,3-triphospholene complexes[22] are known. Clearly *t*BuCl reacts immediately with **1b** to form *cyclo*-(P$_5$*t*Bu$_4$H) and isobutene, as was confirmed by an independent reaction.[23]

In the mass spectrum of [Ni{*cyclo*-(P$_5$*t*Bu$_3$)}(PEt$_3$)$_2$] (**2**), as well as the peak for the molecular ion there is also a peak corresponding to *cyclo*-(P$_5$*t*Bu$_3$). Detailed information concerning the structure of **2** is obtained from the ^{31}P{^{1}H} NMR spectrum, which shows the typical pattern for an AA′BB′CDD′ spin system.[13] The chemical shifts determined for the five phosphorus atoms (P$_A$, P$_{A'}$, P$_B$, P$_{B'}$, P$_C$) are in the range typical for *tert*-butyl-substituted cyclopentaphosphanes.[24] In this case, as for **1b**, the positions of the lone pairs can be derived from the ^1J and ^2J coupling constants.[5, 14] Thus, as for **1b**, the substituents on the P$_5$ ring are in an all-*trans* arrangement because of steric constraints. The (negative) coupling constant $^1J_{A,A'}$, which is large in comparison to the other ^1J ring coupling constants, arises from the presence of the multiple bond between the two phosphorus atoms. In good agreement with the NMR data, the X-ray structure of **2** (Figure 2)[16] shows an all-*trans* arrangement of the *t*Bu groups and an envelope conformation[25] of the P$_5$ ring. The nickel atom is in a distorted square-planar coordination environment, in which the atoms P7, P6, P1, P5 are coplanar and the nickel atom lies 17.73(5) pm out of this plane. At 211.83(11) pm the P1–P5 bond of the P$_5$ ring clearly has multiple-bond character.[9, 26] The remaining P–P bonds are in the range expected for single bonds.[27] The nickel diphosphene complexes [Ni{η^2-P$_2$(SiMe$_3$)$_2$}(PEt$_3$)$_2$],[28] [Ni(η^2-P$_2$Ph$_2$)L] (L = 2,3-bis(diphenylphosphanyl)-*N*-methylmaleinimide),[29] and [Ni(η^2-P$_2$*t*Bu$_2$)(P$_4$*t*Bu$_4$)][9] have Ni–P bonds (223.6(6) – 225.8(2) pm)[9, 28, 29] that are similar, and P–P bonds that are longer (ca. 214 pm),[28, 29] or of similar length (211.0(5) pm)[9] to those of **2**.

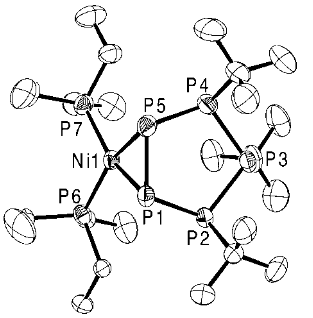

Figure 2. Molecular structure of **2** (H atoms not shown). Selected bond lengths [pm] and angles [°]: Ni1-P7 219.04(9), Ni1-P6 219.69(8), Ni1-P1 223.22(8), Ni1-P5 223.91(8), P1-P5 211.83(11), P1-P2 219.92(10), P2-P3 221.08(11), P3-P4 220.20(11), P4-P5 220.10(12); P6-Ni-P7 108.22(3), P1-Ni1-P5 56.55(3), P1-P5-Ni1 61.56(3), P5-P1-Ni1 61.89(3).

Experimental Section

All procedures were performed under an inert atmosphere of pure argon with the vigorous exclusion of air and moisture. The solvents were saturated with argon and stored over potassium mirrors. *t*BuPCl$_2$[30] and [NiCl$_2$(PEt$_3$)$_2$][31] were prepared by literature methods.

1a, **1b**: PCl$_3$ (8.29 g, 0.06 mol; 5.3 mL) and Na (17.3 g, 0.75 mol) were carefully added to *t*BuPCl$_2$ (38.4 g, 0.24 mol) in THF (300 mL). The mixture was heated under reflux for 5 days. After 6 h the initially colorless solution was yellow green, after 5 days, dark brown. The THF was then removed under reduced pressure and the dark brown residue extracted with *n*-pentane (450 mL). The solvent was removed under reduced pressure and the *cyclo*-(P$_4$*t*Bu$_4$) separated from **1a** by sublimation (120 °C/10^{-3} Torr). Crystallization from THF at −27 °C gave yellow cubic crystals of [Na(thf)$_4$][*cyclo*-(P$_5$*t*Bu$_4$)] (**1b**; m.p. 126.2 – 129.3 °C). On cellulose in air the compound spontaneously ignited. Yield 16.3 g (56 %); ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): $\delta = 1.51$ (d, ^3J(P,H) = 3.0 Hz, 18 H; *t*Bu), 1.58 (m, ^3J(P,H) = 3.0 Hz, 18 H; *t*Bu), 1.40 (m, thf), 3.60 (m, thf); ^{13}C{^{1}H,^{31}P} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): $\delta = 26.26$ (s, thf), 30.71 (s, *C*(CH$_3$)$_3$), 31.77 (s, C(*C*H$_3$)$_3$), 32.83 (s, *C*(CH$_3$)$_3$), 33.32 (s, C(*C*H$_3$)$_3$), 68.15 (s, thf); ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 25 °C): $\delta = 26.26$ (m, thf), 30.71 (m, *C*(CH$_3$)$_3$), 31.77 (q/m, ^1J(C,H) = 123.6 Hz; C(*C*H$_3$)$_3$), 32.83 (m, *C*(CH$_3$)$_3$), 33.32 (q/m, ^1J(C,H) = 126.1 Hz; C(*C*H$_3$)$_3$), 68.15 (m, thf); ^{31}P NMR (162 MHz, C$_6$D$_6$, 25 °C): $\delta_A = -105.6$, $\delta_B = \delta_{B'} = 82.7$, $\delta_C = \delta_{C'} = 75.0$; $^1J_{A,B} = {}^1J_{A,B'} = -379.2$, $^1J_{B,C} = {}^1J_{B',C'} = -317.3$, $^1J_{C,C'} = -309.4$, $^2J_{A,C} = {}^2J_{A,C'} = -0.1$, $^2J_{B,C'} = {}^2J_{B',C} = -5.4$, $^2J_{B,B'} = -17.2$ Hz.

2: A solution of **1a** (2.24 g, 5.51 mmol) in THF (20 mL) was added dropwise to a vigorously stirred solution of [NiCl$_2$(PEt$_3$)$_2$] (1.02 g, 2.79 mmol) in THF (20 mL) at −55 °C. The red solution immediately turned dark brown. After the addition was complete the mixture was stirred for a further 2 h at −55 °C then slowly warmed to room temperature. The solvent was removed under reduced pressure and the brown oily residue treated with *n*-pentane (10 mL) and the solution filtered by cannula. At −27 °C yellow rods of [Ni{*cyclo*-(P$_5$*t*Bu$_3$)}(PEt$_3$)$_2$] (**2**; m.p. 173.2 – 175.9 °C) crystallized, yield 0.92 g (53 %); **2** is soluble in toluene and sparingly soluble in *n*-pentane and *n*-hexane. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): $\delta = 0.95$ (dt, ^3J(H,H) = 7.6, ^3J(P,H) = 14.0 Hz, 18 H; CH$_3$), 1.46 (d, ^3J(P,H) = 12.0 Hz, 9 H; *t*Bu), 1.66 (br, 30 H; 2 *t*Bu, CH$_2$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 25 °C): $\delta = 9.32$ (t/d/m, ^1J(C,H) = 127.0, ^2J(C,H) = 4.1 Hz; CH$_3$), 19.45 (t/d/m, ^1J(C,H) = 126.8, ^2J(C,H) = 2.1, ^1J(C,P) = 21.7 Hz; CH$_2$), 32.13 (q/m, ^1J(C,H) = 124.8 Hz; CH$_3$ of *t*Bu), 32.97 (q/m, ^1J(C,H) = 123.1 Hz; CH$_3$ of *t*Bu), 33.16 (m; *C*(CH$_3$)$_3$ of *t*Bu; only one signal observed); ^{31}P NMR (162 MHz, C$_6$D$_6$, 25 °C): $\delta_A = \delta_{A'} = 56.6$, $\delta_B = \delta_{B'} = 128.0$, $\delta_C = 98.0$, $\delta_D = \delta_{D'} = 13.5$; $^1J_{A,A'} = -434.6$, $^1J_{A,B} = {}^1J_{A',B'} = -376.6$, $^1J_{B,C} = {}^1J_{B',C} = -332.4$, $^2J_{A,B'} = {}^2J_{A',B} = 18.6$, $^2J_{B,B'} = -26.7$, $^2J_{C,A} = {}^2J_{C,A'} = -11.9$, $^2J_{A,D} = 17.6$, $^2J_{A',D'} = 31.6$, $^2J_{D,D'} = 4.9$, $^3J_{B,D} = 6.3$, $^3J_{B',D'} = -9.9$, $^4J_{C,D} = 0.02$ Hz; MS (EI, 70 eV): *m*/*z* (%): 620.3 (3.4) [M^+], 590.2 (3.4) [M^+ − P], 533.0 (5.1) [M^+ − P*t*Bu], 502.0 (10.2) [M^+ − P$_2$*t*Bu], 445.0 (15.3) [M^+ − 2 P*t*Bu], 356.9 (5.1) [M^+ − 3 P*t*Bu], 327.0 (4.2) [M^+ − Ni − 2 PEt$_3$ = P$_5$*t*Bu$_3$$^+$], 294.1 (8.5) [$M^+$ − Ni − 2 PEt$_3$ − P = P$_4$*t*Bu$_3$$^+$], 264 (7.6) [$M^+$ − Ni − 2 PEt$_3$ − 2 P = P$_3$*t*Bu$_3$$^+$], 118.1 (44) [PEt$_3$$^+$] and its decomposition products; molecular ion: found: 620.3/621.3/622.0/623.0; calcd: 620.2/621.2/622.2/623.2; UV/Vis (*n*-pentane): $\lambda_{max}(\varepsilon) = 237$ (5809), 273 sh (2440), 338 (1074), 355 nm (1045).

Density functional calculations: the electronic structures of **1b** and **2** were investigated with the program package Turbomole[33] employing the Becke – Perdew functional B-P86.[32] The calculations for **1b** confirm the structural parameters given in Figure 1 with a P1–P5 bond that is 7 pm shorter than the other P–P bonds. The calculated structure of the free ion [P$_5$*t*Bu$_4$]$^-$ gives the same results. As **2** shows almost C_s symmetry (see Figure 2), this was also assumed in the calculation.[34] Starting from the all-*trans*-envelope form of P$_5$*t*Bu$_3$, which is energetically most favorable for the free molecule, the structure of **2** was optimized for different conformations of the PEt$_3$ groups. In the energetically most favorable structure the PEt$_3$ group has only C_1 symmetry as in Figure 2. The bond lengths of the different conformers differ by only 1 pm; they are up to 5 pm longer than those given in Figure 2 (Ni–P6, Ni–P7 219, Ni–P1, Ni–P5 227, P1–P2 215, remaining P–P bonds 225 pm), the angles given are retained to within 1°.

The electronic structure of **2** clearly shows a singlet wavefunction with formal d^{10} configuration for the Ni center: the Mulliken population analysis[35] gives the occupation Ni 3d$^{8.7}$4s$^{0.8}$4p$^{0.8}$, which is identical to that of [Ni(PEt$_3$)$_3$] with a trigonal-planar NiP$_3$ geometry. The Ni atom functions as an acceptor for the lone pairs of the two PEt$_3$ ligands and the bonding π molecular orbital (MO) of the P=P bond in P$_5$*t*Bu$_3$; it lies in an approximately trigonal-planar environment. This interpretation is in agreement with the P=P bond length and the angle of 97° between the planes Ni-P1-P5 and P1-P2-P4-P5.

The UV/Vis spectrum was calculated with time-dependent density functional theory (TDDFT).[36] In spite of the approximate character of this method the calculated spectrum is in good agreement with the measurements. The assignment of the individual peaks is difficult as the molecular orbitals are relatively highly delocalized. The bands all contain an electron transfer from the Ni to P centers.

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[15] The atom P1 lies −89.2(1) pm out of the P2-P3-P4-P5 plane; the dihedral angle between the planes P2-P1-P5 and P2-P3-P4-P5 is 41.83(4)°.

[16] Crystal structure data for **1b**: $C_{32}H_{68}NaO_4P_5$, $M_r = 694.70$, orthorhombic, space group *Pbca*, $a = 1790.1(2)$, $b = 2107.3(3)$, $c = 2227.9(3)$ pm; $V = 8.4044(19)$ nm^3, $Z = 8$, $\rho_{calcd} = 1.098$ Mg m^{-3}, $Mo_{K\alpha} = 71.073$ pm, $\mu = 0.258$ mm^{-1}, $2\theta_{max} = 52.8°$, $R = 0.0498$, $Rw = 0.1656$, 47959 measured, 8610 unique reflections, 419 refined parameters, max. residual electron density 0.34 e Å^{-3}. The atoms C25, C26, C27, C28, and O3 (a THF molecule) are disordered. Crystal structure data for **2**: $C_{24}H_{57}NiP_7$, $M_r = 621.20$, monoclinic, space group *C2/c*, $a = 4115.8(5)$, $b = 912.65(11)$, $c = 2082.8(3)$ pm, $\beta = 117.831(2)°$; $V = 6.9187(15)$ nm^3, $Z = 8$, $\rho_{calcd} = 1.193$ Mg m^{-3}, $Mo_{K\alpha} = 71.073$ pm, $\mu = 0.896$ mm^{-1}, $2\theta_{max} = 57.8°$, $R = 0.0389$, $Rw = 0.1063$, 21921 measured, 8290 unique reflections, 459 refined parameters, max. residual electron density 0.40 e Å^{-3}. The atoms C19–C24 (ethyl group on P6) are disordered. The data were collected with a Siemens SMART-CCD diffractometer ($T = 223$ K). The absorption correction was carried out with the program SADABS (G. M. Sheldrick, SADABS, Program for Scaling and Correction of Area-detector Data). Non-hydrogen atoms were localized by direct methods (SHELXS97: G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, Universität Göttingen, **1997**) and the parameters anisotropically refined with Fourier-Syntheses (SHELXL97: G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen, **1997**). The hydrogen atoms were calculated for **1b**; for **2** some of the hydrogen atoms could be located and isotropically refined. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166890 and -166891. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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