FULL PAPER

The reactivity of *cyclo*- $(P_5{}^tBu_4)^-$ towards group 13, 14 and 15 metal chlorides: complexation and formation of cyclooligophosphanes, $\{cyclo-(P_5{}^tBu_4)\}_2$ and $\{cyclo-(P_4{}^tBu_3)P{}^tBu\}_2$, by reductive elimination

Andrea Schisler,^a Peter Lönnecke,^a Thomas Gelbrich^b and Evamarie Hey-Hawkins^{*a}

^a Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany. E-mail: hey@rz.uni-leipzig.de; Fax: +(0049)3419739319; Tel: +(0049)3419736151

^b EPSRC National Crystallography Service, University Southampton, Dept. of Chemistry, Highfield, Southhampton, UK SO17 1BJ

Received 21st May 2004, Accepted 3rd August 2004 First published as an Advance Article on the web 20th August 2004

 $[Na(THF)_4][cyclo-(P_5'Bu_4)] (1) \text{ reacts with Et}_2AlCl and GeCl_4 to give Et_2Al{cyclo-(P_5'Bu_4)}(THF) (2) and, in low yield, GeCl_3{cyclo-(P_5'Bu_4)}, respectively, while the reaction of 1 with SnCl_2, PbCl_2 or BiCl_3 results in the formation of the structural isomers {cyclo-(P_5'Bu_4)}_2 (3) and {cyclo-(P_4'Bu_3)P'Bu}_2 (4) (besides other cyclic phosphanes) and elemental metal.$

Introduction

Cyclooligophosphanes¹ *cyclo*-(PR)_n, which are isolobal to cycloalkanes, have long attracted the interest of chemists. While the first example of this class of compounds, *cyclo*-(PPh)₅, was synthesised as early as 1877,² the number of bicyclic compounds obtained in pure form, mainly by Baudler *et al.*, is still small,³⁻⁶ and only three structurally characterised examples are known to date: {*cyclo*-(P₃R₂)}₂ (R = 'Bu, Cp)⁴ and {*cyclo*-(P₄'Bu₃)}₂.⁶ Theoretical studies performed on oligocyclic P_n molecules and clusters (*n* = 2, 4, 6,..., 28) indicate that these compounds should be thermodynamically stable at low temperatures.⁷

Bicyclic oligophosphanes should be accessible by oxidative coupling of cyclooligophosphanide anions *cyclo*-($P_n R_{n-1}$)^{-, 8-10} and this method was already employed in the preparation of {*cyclo*-($P_n R_{2}$)}₂ ($R = {}^{B}$ Bu, Cp).⁴ The first cyclooligophosphanide anions *cyclo*-($P_n R_{n-1}$)⁻ were reported in 1987,^{8,9,11,12} and even today, the number of readily accessible, pure compounds is still small.¹⁰ Most compounds were only obtained in inseparable mixtures and characterised by ³¹P NMR spectroscopy. Recently, we reported the targeted high-yield synthesis of Na[*cyclo*-(P_5 'Bu₄)] and preliminary results on its use in coordination chemistry.¹³

Although linear and cyclic oligophosphanides are of interest as ligands in main group and transition metal chemistry, there are only few reports of the use of linear oligophosphanide ligands $(P_nR_n)^{2-}$ in main group metal and coordination chemistry. Examples of the former include the synthesis of the germatetraphospholanes¹⁴ *cyclo*- $(P_4'Bu_4GeR_2)$ (R = Et, Ph) and *cyclo*- $\{P_4'Bu_4Ge(\eta^2-P_2'Bu_2)\}$ and the stannatetraphospholanes¹⁵ *cyclo*- $(P_4'Bu_4SnR_2)$ (R = 'Bu, "Bu, Ph) and *cyclo*- $\{P_4'Bu_4Sn(Cl)^*Bu_4\}$. In addition, we have shown that the cyclic oligophosphanide anion *cyclo*- $(P_5'Bu_4)^-$ exhibits a rich and unprecedented transition metal chemistry.^{13,16}

However, in main group metal chemistry, redox reactions play an important role besides salt-elimination reactions. We now report the reaction of $[Na(THF)_4][cyclo-(P_5'Bu_4)]$ (1) with Et₂AlCl and GeCl₄, which give Et₂Al{ $cyclo-(P_5'Bu_4)$ }(THF) (2) and, in low yield, GeCl₃{ $cyclo-(P_5'Bu_4)$ }, respectively, while the reaction of 1 with SnCl₂, PbCl₂ or BiCl₃ results in the formation of the structural isomers { $cyclo-(P_5'Bu_4)$ }₂ (3) and { $cyclo-(P_4'Bu_3)P'Bu$ }₂ (4) (besides other cyclic phosphanes) and elemental metal.

Experimental

General

DOI: 10.1039/b407736

All manipulations were carried out under an inert atmosphere. NMR spectra: AVANCE DRX 400 (Bruker), standards: ³¹P NMR (161 MHz): external 85% H₃PO₄; ¹H NMR (400 MHz): internal TMS; ¹³C NMR (100 MHz): internal TMS. The IR spectra were recorded as Nujol mulls on a Perkin-Elmer Spektrum 2000 spectrometer in the range 400–4000 cm⁻¹. The FAB mass spectra were obtained on a ZAB-HSQ-VG Analytical Manchester. The coupling constants of the ³¹P{¹H} NMR spectra were calculated with the program SPINWORKS.¹⁷

Preparations

Reaction of 1 with Et₂AlCl. A solution of 0.29 g (2.39 mmol) Et₂AlCl in 10 ml *n*-pentane was added to a vigorously stirred solution of 0.97 g (2.39 mmol) **1** in 20 ml *n*-pentane. A colour change from yellow–orange to light yellow was observed. After 30 min the solution was filtered and the solvent evaporated *in vacuo*. The pale yellow oily residue consists of Et₂Al{*cyclo*-(P₅/Bu₄)}(THF) (**2**) (72%) and *cyclo*-(P₅/Bu₄H)¹⁸ (28%) (by ³¹P NMR spectroscopy). **2** could not be obtained in pure form; traces of *cyclo*-(P₅/Bu₄H) were always present.

¹H NMR (C₆D₆): δ 0.18 (q, ³J_{HH} = 8.3 Hz, 4H, CH₂), 1.27–1.53 (m, 46H, 'Bu, CH₃ and THF), 3.49 (s, 4H, THF). ¹³C NMR (C₆D₆): δ 0.36 (br, CH₂), 8.67 (qt, ¹J_{CH} = 124.5 Hz, ²J_{CH} = 5.0 Hz, CH₃), 24.34 (t, ¹J_{CH} = 134.8 Hz, THF), 30.58–32.82 (m, ¹Bu), 71.08 (t, ${}^{1}J_{CH} = 153.0$ Hz, THF). ${}^{27}A1$ NMR (C₆D₆): δ 68.4 (br, W = 3040 Hz). ³¹P{¹H} NMR (C₆D₆): ABB'CC' spin system, δ_A –110.6(1) ${}^{1}J_{AB} = -324.9(1)$ Hz = ${}^{1}J_{AB'}$, ${}^{2}J_{AC} = +13.3(1)$ Hz = ${}^{2}J_{AC'}$), (m, $\delta_{B,B'}$ +47.1(1) (m, ${}^{1}J_{BC}$ = -298.3(2) Hz = ${}^{1}J_{B'C'}$, ${}^{2}J_{BB'}$ = -15.9(2) Hz), $\delta_{C,C'}$ +51.7(1) (m, ${}^{1}J_{CC'}$ = -311.4(1) Hz, ${}^{2}J_{BC'}$ = -6.2(1) Hz = ${}^{2}J_{B'C}$). FAB-MS, THF-free 2 (matrix: 3-NBA, m/z (%)): 469.5 (2.9) $[M^+ + H]$, 383.4 (2.1) $[M^+ - Al - 2Et = P_5'Bu_4]$, 352.2 (10.1) $[M^+Al - P - 2Et = P_4 Bu_4], 351.1 (24.9) [M^+ - Al - P - 2Et - H],$ 239.5 (6.4) $[M^+ - 4^tBu = Et_2AlP_5]$, 235.7 (5.8) $[M^+ - 2P - 3^tBu]$, 233.8 (100.0) [M⁺ - 4'Bu - 6H], 210.3 (19.4) [M⁺ - 4'Bu - Et], 209.3 (2.3) $[M^+ - P - 4^t Bu = Et_2 AlP_4],$ 204.5 (13.6) $[M^+ - 3P - 3^{t}Bu], 178.0(2.6)[M^+ - 2P - 4^{t}Bu = Et_2AlP_3], 177.0(10.0)$ $[M^+ - 2P - 3'Bu - 2Et], 155.4 (3.8) [M^+ - Al - 4'Bu - 2Et = P_5],$ 150.7 (16.7) [M⁺ - P - 4'Bu - 2Et], 147.7 (24.8) [M⁺ - 3P - $4'Bu = Et_2AlP_2$], 120.4 (5.5) [M⁺ - 2P - 4'Bu - 2Et], 116.4 (15.5) $[M^+ - 4P - 4^tBu = Et_2AIP].$

Reaction of 1 with GeCl₄. A solution of 0.13 g (0.62 mmol) GeCl₄ in 10 ml petroleum ether (bp 45–70 °C) was added slowly to a solution of 0.5 g (1.23 mmol) **1** in 10 ml petroleum ether (bp 45–70 °C) at -70 °C. A colour change from colourless to light yellow and finally orange was observed. After 3 h at r.t. the solution was filtered and concentrated. The ³¹P NMR spectrum (C₆D₆) of

Dalton

this inseparable mixture showed the presence of the following Pcontaining compounds:

 $cyclo-(P_4^tBu_4)^{19}$ (7.6%)

cyclo-(P₃'Bu₃)²⁰ (14.9%): $\delta_{\rm A}$ -108.4 (t, ${}^{1}J_{\rm A,B}$ = ±201.5 Hz), $\delta_{\rm B}$ -70.0

cyclo-(P₅'Bu₄H)¹⁸ (43.7%): δ_A -56.3 (m), δ_B +67.9 (m), δ_C +39.0 (m), δ_D +60.3 (m), δ_E +80.2 (m); ¹*J*_{AB} = -317.5 Hz, ¹*J*_{AC} = -270.1 Hz, ¹*J*_{BD} = -279.4 Hz, ¹*J*_{CE} = -325.7 Hz, ¹*J*_{DE} = -305.2 Hz, ²*J*_{AE} = +0.1 Hz, ²*J*_{AD} = -11.7 Hz, ²*J*_{BC} = +0.2 Hz, ²*J*_{BE} = -11.3 Hz, ²*J*_{CD} = -12.2 Hz

cyclo-(P₄'Bu₃)P'BuH²¹⁻²³ (5.1%): δ_{A} –5.3 (m, ¹ J_{AE} = ±219.3 Hz, ² J_{AB} = ±44.5 Hz), δ_{B} –31.9 (m, ¹ J_{BC} = ±154.1 Hz, ² J_{AD} = ±207.4 Hz), δ_{C} –42.3 (m, ¹ J_{BE} = ±142.2 Hz, ² J_{BD} = ±14.8 Hz), δ_{D} –46.1 (m, ¹ J_{CD} = ±148.1 Hz, ² J_{CE} = ±8.9 Hz), δ_{E} –143.2 (m, ¹ J_{DE} = ±106.7 Hz, ³ J_{AC} = ±8.9 Hz)

GeCl₃{*cyclo*-(P₄/Bu₃)}²⁴ (2.4%): $\delta_A - 14.6$ (td, ${}^{1}J_{AM} = \pm 145.2$ Hz), $\delta_M - 57.6$ (dd, ${}^{1}J_{BM} = \pm 115.6$ Hz), $\delta_B - 93.3$ (td, ${}^{2}J_{AB} = \pm 20.7$ Hz) GeCl₃{*cyclo*-(P₃'Bu₄)} (5.3%): $\delta_A - 110.8$ (m), $\delta_{BB'} - 33.1$ (m),

Get₁₃{ $cyclo-(r_5 Bu_4)$ } (5.5%). $\delta_A = 110.8$ (iii), $\delta_{BB'} = 55.1$ (i) $\delta_{CC'} = 28.2$ (m).

Reaction of 1 with SnCl₂. A suspension of 0.17 g (0.94 mmol) SnCl₂ in 10 ml *n*-pentane was added to a solution of 0.76 g (1.87 mmol) **1** in 20 ml *n*-pentane at -50 °C. A grey solid (Sn and NaCl) formed immediately. The colour of the solution (yellow) did not change. The solution was filtered and concentrated. At room temperature yellow cubes of {*cyclo*-(P₅'Bu₄)}₂ (**3**) were obtained. Yield: 0.3 g, 42%.

³¹P{¹H} NMR (C₆D₆): AA'BB'CC'DD'EE' spin system, $\delta_{A,A'}$ +28.8 (m), $\delta_{B,B'}$ -27.2 (m), $\delta_{C,C'}$ -1.0 (m), $\delta_{D,D'}$ -4.7 (m), $\delta_{\text{E},\text{E}'}$ -33.9 (m). FAB-MS (matrix 3-NBA; m/z (%)): 766.1 (23.0) $[M^+]$, 709.0 (21.1) $[M^+ - {}^{t}Bu]$, 652.0 (10.6) $[M^+ - 2{}^{t}Bu]$, 595.0 (2.8) $[M^+ - 3'Bu]$, 538.0 (7.0) $[M^+ - 4'Bu]$, 507.0 (3.3) $[M^+ - P - 4'Bu]$, 481.1 (4.5) $[M^+ - 5'Bu]$, 476.0 (3.3) $[M^+ - 2P - 4'Bu]$, 445.1 (7.1) $[M^+ - 3P - 4^iBu]$, 424.0 (9.2) $[M^+ - 6^iBu]$, 414.1 (10.3) $[M^+ - 4P - 4'Bu]$, 383.1 (13.2) $[M^+ - 5P - 4'Bu = M^+/2]$, 367.1 (6.7) $[M^+ - 7^iBu]$, 352.8 (6.8) $[M^+ - 6P - 4^iBu = P_4^iBu_4]$, 310.1 (10.4) $[M^+ - 8'Bu = P_{10}]$, 295.1 (10.2) $[M^+ - 6P - 5'Bu]$, 279.1 (100.0) $[M^+ - 1P - 8'Bu = P_9]$, 248.1 (7.3) $[M^+ - 2P - 8'Bu = P_8]$, 238.1 (10.2) $[M^+ - 6P - 6'Bu]$, 207.0 (13.6) $[M^+ - 7P - 6'Bu]$, 217.1 (13.7) $[M^+ - 3P - 8'Bu = P_7]$. IR (KBr, cm⁻¹): 2934s, 2888s, 2854s, 2704w, 1468m, 1457s, 1386m, 1358s, 1261s, 1167s, 1097s, 1019s, 934w, 866m, 804s, 701w, 669w, 601w, 566w, 527w, 467w, 418w, 403w.

A ³¹P NMR spectrum (C_6D_6) of the reaction mixture showed the presence of the following P-containing compounds besides **3**: *cyclo*-(P_5 /Bu₄H)¹⁸ (24.9%), *cyclo*-(P_4 /Bu₃)P/BuH²¹⁻²³ (3.7%), {*cyclo*-(P_4 /Bu₃)P/Bu $_2$ (**4**) (15.1%), *cyclo*-(P_4 /Bu₄)¹⁹ (3.9%).

Reaction of 1 with PbCl₂. A suspension of 0.09 g (0.35 mmol) PbCl₂ in 10 ml *n*-pentane was added to a solution of 0.28 g (0.70 mmol) **1** in 10 ml *n*-pentane at r.t. A grey solid (Pb and NaCl) formed immediately. The colour of the solution changed from yellow to green–yellow. The solution was stirred at r.t. for 3 h and filtered. The ³¹P NMR spectrum (C₆D₆) of this solution showed the presence of the following P-containing compounds:

 $cyclo-(P_5'Bu_4H)^{18}$ (32.4%), { $cyclo-(P_5'Bu_4)$ }₂ (3) (55.2%) and { $cyclo-(P_4'Bu_3)P'Bu$ }₂ (4) (11.4%).

Reaction of 1 with BiCl₃. A suspension of 0.33 g (1.06 mmol) BiCl₃ in 10 ml petroleum ether (bp 45–70 °C) was added slowly to a solution of 0.43 g (1.06 mmol) **1** in 10 ml petroleum ether (bp 45–70 °C) at r.t. A black solid (Bi and NaCl) formed slowly. The colour of the solution changed from yellow to dark green. The solution was filtered and the solvent evaporated *in vacuo*. The dark green solid was studied by ³¹P NMR spectroscopy (C₆D₆), which showed the presence of *cyclo*-(P₄/Bu₄)¹⁹ (11.5%), *cyclo*-(P₃/Bu₃)²⁰

(11.7%), cyclo-($P_5'Bu_4H$)¹⁸ (13.0%), cyclo-($P_4'Bu_3$) $P'BuH^{21-23}$ (19.7%), {cyclo-($P_5'Bu_4$)}₂ (**3**) (29.6%) and {cyclo-($P_4'Bu_3$)P'Bu}₂ (**4**) (14.5%).

X-Ray data collection, structure determination, and refinement crystallography. Crystal data²⁵ for $C_{32}H_{72}P_{10}$ {*cyclo*-(P₅'Bu₄)}₂ (3): M = 766.60, orthorhombic, space group *Aba2*, $a = 13.1781(8), b = 12.5258(7), c = 26.3187(11), V = 4344.3(4) Å^3$, T = -153 °C; Z = 4, $D_c = 1.172$ g cm⁻³; μ (Mo-K α) = 0.416 mm⁻¹; 11341 reflections measured of which 3598 were independent. Final R = 0.1225, $R_w = 0.2311$ for 1184 reflections with $F^2 > 2\sigma(F^2)$.

Intensity data were recorded using a Nonius Kappa CCD areadetector diffractometer mounted at the window of a rotating-anode FR591 generator with a molybdenum anode ($\lambda = 0.71073$ Å). φ and ω scans were carried out to fill the Ewald sphere. An empirical absorption correction was applied using SORTAV. The structure was solved by direct methods and refined on F^2 by full-matrix leastsquares refinements.²⁶ Disorder over two positions of the atoms P3 and P4 is imposed by the two-fold axis parallel to the *c* axis.

Crystal data for $C_{32}H_{72}P_{10}$ (4); M = 766.60, monoclinic, space group C2/c, a = 22.763(5), b = 14.679(3), c = 16.629(3) Å, $\beta = 126.54(3)^\circ$, V = 4464(1) Å³, T = -73 °C; Z = 4, $D_c = 1.141$ g cm⁻³; μ (Mo-K α) = 0.404 mm⁻¹; 5291 independent reflections. Final R = 0.0433 and $R_w = 0.1104$ for reflections with $F^2 \ge 2\sigma(I)$ and R = 0.0543 and $R_w = 0.1161$ for all reflections. X-Ray diffraction data were obtained with a Stoe IPDS using ϕ scan rotation. The structures were solved by direct methods using SHELXS-97 and SHELXL-97 for structure refinement.²⁶ Anisotropic refinement of all non-hydrogen and isotropic refinement of the hydrogen atoms.

CCDC reference numbers 237083 and 238064.

See http://www.rsc.org/suppdata/dt/b4/b407736a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Our attempts to obtain main group metal complexes of the cyclooligophosphanide anion *cyclo*- $(P_5'Bu_4)^-$ starting from Na[*cyclo*- $(P_5'Bu_4)$] (1) and Et₂AlCl, GeCl₄, SnCl₂, PbCl₂ or BiCl₃ were only successful in the case of Al and Ge, while the last three reactions failed regardless of the solvent (*n*-pentane, THF, diethyl ether, toluene) or temperature employed. In these cases the formation of elemental metal (Sn, Pb, or Bi) was observed even at low temperature.

Aluminium and germanium cyclopentaphosphanides

More successful was the reaction of Na[*cyclo*-(P₅'Bu₄)] (1) with Et₂AlCl, which gave Et₂Al{*cyclo*-(P₅'Bu₄)}(THF) (2) and *cyclo*-(P₅'Bu₄H)¹⁸ (28%); the latter is probably formed by protolysis of **1**. In the ³¹P NMR spectrum (in C₆D₆) **2** exhibits signals of an ABB'CC' spin system (ratio 1:2:2). The nuclei P_{B,B'} and P_{C,C'} fulfill the requirement for a higher order spectrum, $|v_B - v_C|/J_{BC} < 10.^{3.4}$ The chemical shifts of P_B, P_{B'}, P_C, P_{C'} are in the range of *tert*-butyl-substituted cyclopentaphosphanes;⁵ however, compared to **1**, high-field shifts ($\Delta \delta = 35.6$ (P_B, P_B'), 23.3 (P_C, P_C'), 5.0 (P_A)) are observed in **2**.



Coordination of the *cyclo*- $(P_5'Bu_4)^-$ anion *via* the phosphorus atom P_A to Al results in smaller ${}^1J_{AB}$ and ${}^1J_{AB'}$ (-324.9(1) Hz; *cf.* 1: 379.2(1) Hz) and similar ${}^1J_{BC}$, ${}^1J_{B'C'}$ and ${}^1J_{CC'}$ coupling constants.

In the ²⁷Al NMR spectrum (C_6D_6) a signal at 68.4 ppm (W = 3040 Hz) is observed for **2**.

The mass spectrum (FAB-MS) of THF-free **2** shows the molecular ion peak at m/z = 469.5 (2.9%; [M⁺ + H]) as well as the expected fragmentation products.

The reaction of **1** with GeCl₄ in petroleum ether at -70 °C in a ratio of 2:1 gave numerous products, which could only be identified by ³¹P NMR spectroscopy, but not isolated and purified. These include *cyclo*-(P₄/Bu₄),¹⁹ *cyclo*-(P₃/Bu₃),²⁰ *cyclo*-(P₅/Bu₄H),¹⁸ *cyclo*-(P₄/Bu₃)P'BuH,^{21,22,23} *cyclo*-(P₄/Bu₃)P'BuCl,^{9,18} GeCl₃{*cyclo*-(P₄/Bu₃)}²⁴ and GeCl₃{*cyclo*-(P₅/Bu₄)}. The last-named is formed in only 5.3% yield. Signals at δ +88.7 and +57.6 could not be assigned.

When an excess of GeCl₄ was employed, only one Ge-containing product was obtained, which we assume to be GeCl₃{*cyclo*-(P₅'Bu₄)} (by ³¹P{¹H} NMR spectroscopy). Three multiplets are observed for the complicated higher-order ABB'CC' spin system (ratio 1 : 2 : 2; -110.8 (P_A), -33.1 and -28.2 ppm; the last two correspond to P_B, P_{B'}, P_C and P_{C'}, which bear *tert*-butyl groups). However, this product could not be obtained in pure form.

The structural isomers $\{cyclo-(P_5'Bu_4)\}_2$ (3) and $\{cyclo-(P_4'Bu_3)P'Bu\}_2$ (4)

In the reactions of $Na[cyclo-(P_5'Bu_4)]$ (1) with $SnCl_2$ (2:1), $PbCl_2$ (2:1) or $BiCl_3$ (1:1) the formation of elemental metal (Sn, Pb, or Bi) was observed even at low temperature.

³¹P NMR spectroscopy showed the formation of the dimer $\{cyclo-(P_5'Bu_4)\}_2$ (**3**) as the main product (*ca.* 50% for SnCl₂ and PbCl₂, *ca.* 30% for BiCl₃) as well as of $\{cyclo-(P_4'Bu_3)P'Bu\}_2$ (**4**) (*ca.* 11–15%). Other P-containing products are $cyclo-(P_5'Bu_4H)$,¹⁸ $cyclo-(P_4'Bu_3)P'BuH^{21,22,23}$ and $cyclo-(P_4'Bu_4)$.¹⁹ As these compounds show similar solubility in all common solvents, separation was only achieved by fractional crystallisation of **3** and **4**.

We assume that the corresponding $[M{cyclo-(P_5'Bu_4)}_x]$ are formed initially, which, however, are unstable even at low temperature and decompose with formation of different cyclic phosphorus products. Scheme 1(a) shows the proposed decomposition pathway for the reaction of 1 with SnCl₂.



Scheme 1

Elimination of 'BuCl, which reacts with **1** with formation of *cyclo*-(P_5 'Bu₄H) and isobutene (Scheme 1(b)),¹³ was already observed in the reaction of **1** with [NiCl₂(PEt₃)₂].²⁷ In a comparable reaction, K₂(P_4 'Bu₄) reacts with *tert*-butyl chloride with elimination of KCl and isobutene and formation of H₂P₄'Bu₄.²⁸ The reaction of **1** with SnCl₂ was also carried out in deuterated THF to prove that the formation of *cyclo*-(P_5 'Bu₄H) is not due to ether cleavage. No *cyclo*-(P_5 'Bu₄D) was observed in the ³¹P NMR spectrum.

The formation of the structural isomers $\{cyclo-(P_5'Bu_4)\}_2$ (**3**) and $\{cyclo-(P_4'Bu_3)P'Bu\}_2$ (**4**) occurs *via* reductive elimination from the corresponding Sn complexes. The formation of elemental Sn (and NaCl) was shown by powder diffraction and elemental analysis (no P present, which rules out the formation of tin phosphides, Sn_xP_y). $\{cyclo-(P_4'Bu_3)P'Bu\}_2$ (**4**) was previously obtained by dehalogenating 'BuPCl₂ with magnesium in the presence of P₄, purified by HPLC (30 mg starting from 0.33 mol 'BuPCl₂) and characterised by ³¹P NMR spectroscopy.⁴

The structural isomer **3** was characterised by IR, NMR spectroscopy, MS (FAB) and by X-ray structure determination.

In the ³¹P NMR spectrum at room temperature (in C₆D₆) compound **3** showed a complicated higher order AA'BB'CC'DD'EE' spin system consisting of five signals at δ +28.8, -1.0, -4.7, -27.2 and -33.9 (ratio 1:1:1:1). A two-dimensional ³¹P³¹P spectrum yielded the constitution of the P₁₀ framework, showing a direct linkage between P_A and P_B, P_A and P_E, P_B and P_C, P_D and P_E, as well as between P_C and P_D. The proton-coupled ³¹P NMR spectrum showed that P_A bears no *tert*-butyl group. The dimeric nature of **3** is also apparent from the mass spectrum and the X-ray structure determination.

In the mass spectrum, a molecular ion peak is observed for **3** at m/z = 766.1 (23.0%) as well as the fragment *cyclo*-(P₅'Bu₄) (M⁺/2) at m/z = 383.1 (13.2%). Interestingly, a signal for the 'Bu-free molecule P₁₀ is also observed at m/z = 310.1 (10.4%). Theoretical studies performed on oligocyclic P_n molecules and clusters showed them to be thermodynamically stable at low temperatures.⁷ Thus, compound **3** could be a suitable precursor for such a novel P_n (n = 10) modification.

Molecular structures of $\{cyclo-(P_5'Bu_4)\}_2$ (3) and $\{cyclo-(P_4'Bu_3)P'Bu\}_2$ (4)

Crystals of **3** suitable for X-ray diffraction were obtained from a saturated *n*-pentane solution. The crystals were rather small and systematically twinned; thus, the observed cubes were in fact intergrown platelets, which could, however, not be separated mechanically due to their small size. The diffraction pattern was thus contaminated by the signals of at least one other individuum, with apparent overlap of signals at low diffraction angles. This problem was also apparent during the structure refinement. The molecule is disordered statistically with the atoms P3 and P4 occupying alternative positions (Fig. 1). This disorder generates a twofold symmetry for the crystal structure. Compound **3** crystallises in the orthorhombic space group *Aba2* with four molecules in the unit cell.

The two non-planar chiral ring systems have envelope conformations in which the atoms P3 and P4 deviate from the plane formed by P2'-P1'-P1-P2 and P5'-P6'-P6-P5, respectively. The P2-P3



Fig. 1 ORTEP plot of the molecular structure of compound 3; H atoms are omitted for clarity.

and P4-P5 bond lengths (213.7(6) and 211.4(6) pm) are smaller than the other P-P bond lengths (219.9(6)-226.5(6) pm), which are in the typical range for single bonds. Similarly, one of the P-P'Bu distances in 1 is shorter (213.2(1) pm) than the other P-P bonds (220.4(1)-222.9(1) pm).16

 $\{cyclo-(P_4'Bu_3)P'Bu\}_2$ (4) crystallises in the monoclinic space group C2/c with four molecules in the unit cell. The centre of the P5-P5' bond coincides with a twofold axis (Fig. 2).



Fig. 2 ORTEP plot of the molecular structure of compound 4; H atoms are omitted for clarity.

The molecule consists of two cyclotetraphosphanes, which have a butterfly conformation, with one exocyclic P'Bu group. The dihedral angle between the planes P1-P2-P4 and P2-P3-P4 is 40.59(4)°. The P-P distances range from 220.39(8) to 224.29(9) pm and are typical for P-P single bonds.²⁹ The P₄ chain P1-P5-P5'-P1 has a svn arrangement. The torsion angle between the planes P1-P5-P5' and P1'-P5'-P5 is only 4.9(1)°.

Conclusion

While the reaction of $[Na(THF)_4][cyclo-(P_5'Bu_4)](1)$ with Et₂AlCl or GeCl₄ gives the substitution products, $Et_2Al\{cyclo-(P_5Bu_4)\}$ (THF) (2) and $GeCl_3\{cyclo-(P_5'Bu_4)\}$, 1 reacts with $SnCl_2$, $PbCl_2$ or $BiCl_3$ with formation of the structural isomers $\{cyclo-(P_5'Bu_4)\}_2$ (3) and $\{cyclo-(P_4'Bu_3)P'Bu\}_2$ (4) (besides other cyclic phosphanes) and elemental metal.

Acknowledgements

A. S. thanks the Saxonian Ministry of Science and Art for a PhD grant.

References

- 1 M. Baudler and K. Glinka, Chem. Rev., 1993, 93, 1623
- 2 H. Köhler and A. Michaelis, Ber. Dtsch. Chem. Ges., 1877, 10, 807.
- 3 (a) M. Baudler, C. Wiaterek and K. Kazmierczak, Z. Anorg. Allg Chem., 1989, 579, 7; (b) M. Baudler, L. De Riese-Meyer and C. Wiaterek, Z. Naturforsch., Teil B, 1989, 44, 375; (c) M. Baudler and L. De Riese-Meyer, Z. Naturforsch., Teil B, 1986, 41, 399; (d) M. Baudler and B. Makowka, Angew. Chem., 1984, 96, 976; M. Baudler and B. Makowka, Angew. Chem., Int. Ed. Engl., 1984, 23, 987; (e) M. Baudler and V. Arndt, Z. Naturforsch., Teil B, 1984, 39, 275; (f) M. Baudler and H. Tschaebunin, Z. Anorg. Allg. Chem., 1992, 617, 31; (g) M. Baudler and M. Schnalke, Z. Anorg. Allg. Chem., 1990, 585, 18; (h) M. Baudler, M. Schnalke, C. Wiaterek, S. Opiela and J. Hahn,

Z. Anorg. Allg. Chem., 1989, 578, 7; (i) M. Baudler, J. Hellmann, P. Bachmann, K. F. Tebbe, R. Fröhlich and M. Feher, Angew. Chem., 1981, 93, 415; M. Baudler, J. Hellmann, P. Bachmann, K. F. Tebbe, R. Fröhlich and M. Feher, Angew. Chem., Int. Ed. Engl., 1981, 20, 406; (j) M. Baudler and H. Jachow, Z. Naturforsch., Teil B, 1994, 49, 1755; (k) M. Baudler, M. Michels, J. Hahn and M. Pieroth, Angew. Chem., 1985, 97, 514; M. Baudler, M. Michels, J. Hahn and M. Pieroth, Angew. Chem., Int. Ed. Engl., 1985, 24, 504.

- 4 M. Baudler, M. Schnalke and Ch. Wiaterek, Z. Anorg. Allg. Chem., 1990. 585, 7
- 5 N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, D. Fenske, G. Baum, A. Dransfeld and P. von Rague Schleyer, Eur. J. Inorg. Chem., 1998, 6, 833
- 6 M. Feher, R. Fröhlich and K. F. Tebbe, Z. Kristallogr., 1982, 158, 241.
- 7 (a) M. Häser and O. Treutler, J. Chem. Phys., 1995, 102, 3703; (b) M. Marco, U. Schneider and R. Ahlrichs, J. Amer. Chem. Soc., 1992, 114 9551
- 8 M. Baudler, Ch. Gruner, G. Fürstenberg, B. Kloth, F. Saykowski and U. Özer, Z. Anorg. Allg. Chem., 1978, 446, 169.
- 9 M. Baudler and B. Makowka, Z. Anorg. Allg. Chem., 1985, 528, 7.
- 10 A. Schmidpeter and G. Burget, Phosphorus Sulfur, 1985, 22, 323.
- G. Fritz and K. Stoll, Z. Anorg. Allg. Chem., 1986, 538, 78.
 G. Fritz, R. Biastoch, K. Stoll, T. Vaahs, D. Hanke and H. W. Schneider, Phosphorus Sulfur, 1987, 30, 385.
- 13 A. Schisler, U. Huniar, P. Lönnecke, R. Ahlrichs and E. Hey-Hawkins, Angew. Chem., 2001, 113, 4345; A. Schisler, U. Huniar, P. Lönnecke, R. Ahlrichs and E. Hey-Hawkins, Angew. Chem., Int. Ed., 2001, 40, 4217
- 14 (a) M. Baudler and H. Suchomel, Z. Anorg. Allg. Chem., 1983, 503, 7; (b) H. Binder, B. Schuster, W. Schwarz and K. W. Klinkhammer, Z. Anorg. Allg. Chem., 1999, 625, 699; (c) M. Baudler, L. Riese-Meyer and U. Schings, Z. Anorg. Allg. Chem., 1984, 519, 24.
- 15 (a) M. Baudler and H. Suchomel, Z. Anorg. Allg. Chem., 1983, 505, 39; (b) D. Bongert, G. Heckmann, W. Schwarz, H.-D. Hausen and H. Binder, Z. Anorg. Allg. Chem., 1995, 621, 1358; (c) D. Bongert, H.-D. Hausen, W. Schwarz, G. Heckmann and H. Binder, Z. Anorg. Allg. Chem., 1996, 622, 1167.
- 16 A. Schisler, Dissertation, Leipzig, 2003; A. Schisler, P. Lönnecke and E. Hey-Hawkins, Dalton Trans.; to be submitted; A. Schisler, P. Lönnecke and E. Hey-Hawkins, Inorg. Chem., to be submitted; A. Schisler, P. Lönnecke and E. Hey-Hawkins, Chem. Eur. J., to be submitted.
- 17 A negative sign was generally used for the coupling constants ${}^{1}J_{PP}$ and the remaining signs and coupling constants were calculated with the program SPINWORKS (K. Marat, SPINWORKS, version 2000 05 10, University of Manitoba).
- 18 A. Schisler, Diplomarbeit, Leipzig, 1999.
- 19 K. Issleib and M. Hoffmann, Chem. Ber., 1966, 99, 1320
- 20 M. Baudler, J. Hahn, H. Dietsch and G. Fürstenberg, Z. Naturforsch., Teil B, 1976, 31, 1305.
- M. Baudler and H. Tschäbunin, Z. Anorg. Allg. Chem., 1984, 511, 77. 21
- 22 M. Baudler and Ch. Gruner, Chem. Ber., 1982, 115, 1739.
- 23 M. Baudler, J. Hellman and T. Schmidt, Z. Naturforsch., Teil B, 1983, 38, 537.
- 24 M. Karnop, W.-W. du Mont, P. G. Jones and J. Jeske, Chem. Ber., 1997, 130, 1611.
- 25 Data collection and cell refinement: D. Z. Otwinowski and W. Minor, Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, 1997, p. 307. Absorption correction: SORTAV: R. H. Blessing, Acta Crystallogr., Sect. A, 1995, 51, 33; R. H. Blessing, J. Appl. Crystallogr., 1997, 30, 421.
- 26 Structure solution and refinement: SHELXS and SHELXL97: G. M. Sheldrick 1997, University of Göttingen, Germany.
- K. A. Jensen, Z. Anorg. Allg. Chem., 1936, 229, 265.
- 28 M. Baudler, G. Reuschenbach, J. Hellmann and J. Hahn, Z. Anorg. Allg. Chem., 1983, 499, 89.
- 29 D. E. C. Corbridge, The Structural Chemistry of Phosphorus, Elsevier, Amsterdam, 1974.