# Synthesis and Molecular Structure of Heterocycles Containing two Phosphorus(V) Centers Bridged by Two-Coordinate Phosphorus and Arsenic

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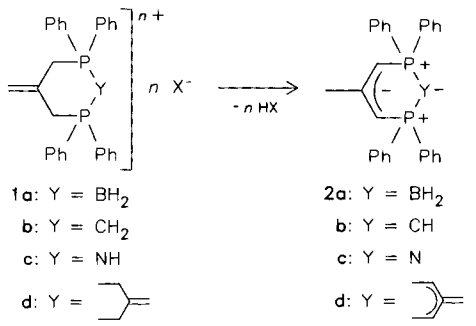
1,1-Bis[(diphenylphosphanyl)methyl]ethene (**3**) reacts with $PCl_3$ or $AsCl_3$ in the presence of $SnCl_2$ as a reducing agent to form cationic heterocycles in which the two newly generated phosphonium centers are bridged by two-coordinate, negatively charged phosphorus (**4a**) or arsenic (**4b**) centers. Hexachlorostannate(IV) dianions function as counterions to these heterocycles, in which the exocyclic methylene group is retained. By treatment of **4a** with a base a rearrangement is induced which includes a proton migration from an endo- to the exocyclic $CH_2$ group to give 5-methyl-1,1,3,3-tetraphenyl-1$\lambda^5$,2$\lambda^3$,3$\lambda^5$-triphosphinine (**5**), a novel 1,2,3-triphosphabenzene species. The reaction of the arsenic compound **4b** with base did not yield the corresponding arsa-diphosphabenzene, but gave only decomposition products. Compound **4b** · 0.5 $CH_3CN$ has been studied by X-ray crystallography. The six-membered heterocycle shows a chair conformation with an arsenic atom solely coordinated by two phosphorus atoms at roughly equal distances with a sharp angle P – As – P of only 93.0(1)°.

Recent studies of rearrangements of cyclic multi-ylides have provided a new synthetic approach to di-$\lambda^5$-phosphacyclic compounds, including 1,3-diphosphabenzenes, -diphosphazines, and -diphosphaborinanes[1]. In two-step syntheses cyclic phosphonium salts (**1a–d**) are prepared, which contain an exocyclic olefinic unit. Single deprotonation at one of the two endocyclic $CH_2$ groups induces an isomerization reaction including a 1,3-proton shift from the second $P-CH_2$ group to the exocyclic $CH_2$ function with concomitant formation of a methallylic $\pi$ system (Scheme 1). Analogous synthetic pathways have been found for the corresponding (2-hetero)-1,3-diphosphinines (**2a–c**), and also for the first 1$\lambda^5$,5$\lambda^5$-diphosphocine (**2d**), where two methallylic systems bridge the two phosphonium centers in 1,5-position.

Scheme 1




1a: Y = $BH_2$ 2a: Y = $BH_2$
b: Y = $CH_2$ b: Y = CH
c: Y = NH c: Y = N
d: Y = d: Y =

In these di-$\lambda^5$-phosphacyclic compounds the tetracoordinate phosphorus centers are acting as efficient conjugation barriers to the $\pi$ systems owing to the nodal planes of the $\sigma$ or $\pi$ wave functions. The methallylic parts with their formal negative charge are electrostatically well balanced, however, by the positively charged phosphonium centers to give fairly stable heterocyclic compounds. In full agreement with this description, recent work on transition metal complexes of the 1$\lambda^5$,3$\lambda^5$-diphosphinines[2] has shown that in fact the methallylic parts of these heterocycles are the electron-donating domains where four-electron acceptors become $\eta^3$-bound. For **2b**, but not for **2a** or **2c**, the PYP bridging atom Y may also be engaged in coordination.

We now report on the synthesis of the first 1$\lambda^5$,2$\lambda^3$,3$\lambda^5$-triphosphinine, the phosphorus analog of the diphosphazine **2c**, and the corresponding onium precursor. For the latter, the arsenic-containing analog could also be generated and structurally characterized by single crystal X-ray diffraction studies, but attempts to convert it into the deprotonated heterocycle (rearranged by 1,3-prototropy) have been unsuccesful.

## Results and Discussion

Work of Schmidpeter et al.[3–6] on the synthesis of open-chain triphosphenium cations $R_3PPPR_3^+$ has provided a good basis also for investigations aiming at the preparation of cyclic (2-hetero)-1,3-diphophinines with second and third row group V elements in position 2 of the heterocycles. Experiments using the procedures established for the preparation of the $R_3PPPR_3^+$ cations have immediately been successful.

Treatment of 1,1-bis[(diphenylphosphanyl)methyl]ethene (**3**) with equimolar quantities of $PCl_3$ in the presence of $SnCl_2$ affords the cyclic triphosphenium salt **4a** in good yield. The reducing agent $SnCl_2$ is oxidized to $SnCl_4$ which acts as a $Cl^-$ acceptor to give the $SnCl^{2-}$ counterions.

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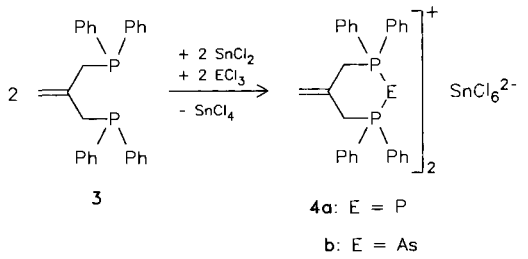
Scheme 2




With only one doublet resonance for the two P(V) atoms the $^{31}P\{^1H\}$-NMR spectrum of **4a** suggests idealized mirror or $C_2$ symmetry for the cation in acetonitrile solution. The chemical shift of this resonance ($\delta$ = 22.98) is in the same region as for the related cations in **1a–d**. The triplet signal of the two-coordinate phosphorus atom appears at very high field ($\delta$ = −213.44), quite typical of resonances of the central phosphorus atoms in related triphosphonium cations[3–6]. The coupling constant $J$(PP) = 431.4 Hz indicates direct (one-bond) coupling.

The $^1H$- and $^{13}C\{^1H\}$-NMR spectra are also in good agreement with those found for related singly charged phosphonium salts. NMR signals with second-order splittings can be assigned as pseudodoublets and -triplets, respectively, following established patterns of $A_nXX'$ or $A_nXX'A_n'$ spin systems, for which the spacing of the high-intensity lines is known to be $N = J(AX) + J(AX')$. The composition of the product is further confirmed by elemental analysis and field desorption mass spectrometry (see Experimental).

Similar to the preparation of compound **4a**, treatment of $AsCl_3$ with equimolar quantities of the bis(phosphane) **3** and $SnCl_2$ results in the formation of the arsenic analog **4b**. The cation of this product is a novel type of molecule in that it contains a two-coordinate arsenic atom between two phosphorus(V) centers.

Compound **4b** is soluble without decomposition only in acetonitrile. The solutions show a single resonance line in the $^{31}P\{^1H\}$-NMR spectrum. The chemical shift for this resonance ($\delta$ = 18.33) and the pattern of the signals found in the $^1H$- and $^{13}C\{^1H\}$-NMR spectra are in perfect agreement with the proposed formula and with the data found for **4a** where applicable.

On cooling of the acetonitrile solution to 0°C, yellow crystals separate which contain solvent of crystallization according to the results of an X-ray crystal structure investigation.

Crystals of **4b** · 0.5 $CH_3CN$ are monoclinic, space group *I2/a* (Nr. 15), with one complete heterocyclic cation, half a hexachlorostannate(IV) dianion, and half a molecule of solvent in the asymmetric unit.

The tin atom (at 0.25, *y*, 0.5) and the central carbon atom of the solvent molecule (at 0.25, *y*, 0.0) lie on a crystallographic twofold axis, indicating disorder for this molecule. The idealized mirror symmetry (point group $C_s$) of the heterocyclic ring (Figure 1) is reduced to point group $C_1$ mainly by the non-systematic orientation of the four phenyl rings. The six-membered ring of the cation adopts a chair conformation with the interplane angles P1/As/P2–P1/C1/C3/P2 = 143.7° and C1/C2/C3/C4–P1/C1/C3/P2 = 120.63°. The arsenic atom is only coordinated to the two phosphorus atoms and has no close contacts to the counterion or the solvent molecule. The valence angle at arsenic is quite sharp [P1–As–P2 = 93.0(1)°], and the phosphorus arsenic distances are almost equal [As–P1 = 2.250(1), As–P2 = 2.244(1) Å]. For other details see the caption to Figure 1.

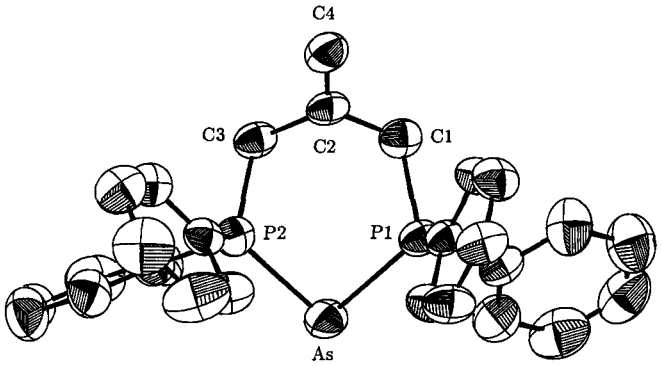
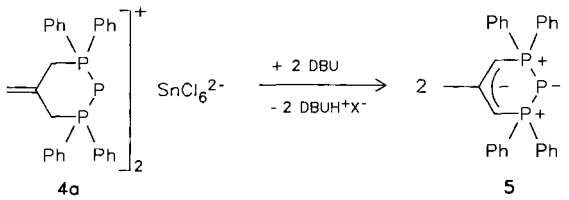



Figure 1. Molecular structure of the cation of compound **4b** · 0.5 $CH_3CN$ with atomic numbering scheme (ORTEP, 50% probability ellipsoids; hydrogen atoms have been omitted for clarity). Selected bond distances [Å] and angles [°] with standard deviations in parentheses: As–P1 2.250(1), As–P2 2.244(1), P1–C1 1.841(4), P2–C3 1.817(4), P1–C11 1.813(4), P2–C21 1.803(4), P1–C12 1.806(4), P2–C22 1.801(4), C1–C2 1.488(5), C2–C3 1.510(5), C2–C4 1.340(5); P1–As–P2 93.0(1), C1–C2–C3 117.0(3), As–P1–C1 114.2(1), As–P2–C3 113.6(1), C2–C1–P1 114.6(3), C2–C3–P2 114.4(3), C1–C2–C4 122.0(4), C3–C2–C4 120.9(4)

Experiments to accomplish base-induced deprotonation and isomerization of the cationic precursors **4a**, **4b** to give neutral phosphinines (2-hetero-1,3-diphosphabenzenes) have only been successful for compound **4a** (Scheme 3).

Scheme 3




The reaction of compound **4a** with one equivalent of the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[7] in a two-phase system of acetonitrile and hexane at ambient temperature leads to a yellow color of the slurry, indicating rapid ylide formation. After separation of the hexane phase and removal of the solvent, the pure product (**5**) is obtained in moderate yield as a yellow, air-sensitive, microcrystalline solid.

The composition of **5** is confirmed by a detailed NMR and elemental analysis. Benzene solutions of **5** show the expected doublet/triplet pattern in the $^{31}P\{^1H\}$-NMR spectrum with an upfield shift of 7 ppm for the phosphorus(V) centers and a downfield shift of ca. 20 ppm for the two-coordinate phosphorus atom as compared to the precursor

cation in **4a**. The chemical shifts and coupling constants in the $^1$H- and $^{13}C\{^1H\}$-NMR spectra are as expected for a methallylic fragment with $sp^2$-hybridized carbon atoms bearing a partial negative charge, and for phenyl groups at phosphonium centers. The conversion of the exo-methylene group into an exo-methyl group is obvious from the high-field shift of the corresponding H and C signals as well as from the multiplicity of the resonances (see Experimental).

No crystals of compound **5** large enough for single-crystal X-ray studies could be grown. The attempts are being continued, and studies of chemical reactions and complex formation of **5** are in progress. With this compound **5** being an unprecedented cyclic $R_2\overline{P-P-PR_2}$ species, analogous to cyclic carbodiphosphoranes $R_2\overline{P=C=PR_2}$[8] and diphosphiminium $R_2\overline{P-N-PR_2}^+$ cations[9], the results will be of a quite general interest.

This work has been generously supported by *Deutsche Forschungsgemeinschaft* (Leibniz-Programm), by *Fonds der Chemischen Industrie*, and by *Hoechst AG*. Prof. *W. Hiller* is thanked for establishing the crystallographic data set.

## Experimental

All experiments were carried out under pure nitrogen. Glassware and solvents were purified, dried, and kept under nitrogen accordingly. – NMR: Phosphoric acid and deuterated solvents as reference compounds (Jeol GX 400 spectrometer, 25°C). – MS: Varian MAT 112 S and MAT 311.

*Compound* **4a**: A solution of 1,1-bis[(diphenylphosphanyl)methyl]-ethene (**3**) (2.12 g, 5.0 mmol) and $SnCl_2$ (0.95 g, 5.0 mmol) in 25 ml of dichloromethane was treated at room temp. with a solution of $PCl_3$ (0.44 ml, 0.68 g, 5.0 mmol) in dichloromethane (25 ml). After stirring for 12 h the pale yellow precipitate was separated by filtration. Treatment of the colorless filtrate with diethyl ether (10 ml) gave a white precipitate of the product, which was separated and dried in vacuo; yield 1.6 g (52%) of a white powder, m.p. 184°C (dec.). – $^1$H NMR ($CD_3CN$): δ = 3.90 ["d", $^2J$(PH) = 17.4 Hz, 4H, $H_2C-P$], 5.29 (br. s, 2H, $H_2C=C$), 7.49–7.52 (m, 8H, *m*-H), 7.60–7.64 (m, 4H, *p*-H), 7.72–7.77 (m, 8H, *o*-H). – $^{13}C\{^1H\}$ NMR ($CD_3CN$): δ = 35.8 ("t", *N* = 21.0 Hz, $H_2C-P$), 124.03 ("t", *N* = 10.5 Hz, $H_2C=C$), 126.20 ("dd", AXX', *ipso*-C), 130.50 ("t", AXX', *m*-C), 131.08 ["dt", $^3J$(PC) = 7.8, $^4J$(PC) = 2.4 Hz, $C=CH_2$], 133.18 (m, *o*-C), 134.45 (s, *p*-C). – $^{31}P\{^1H\}$ NMR ($CD_3CN$): δ = 22.98 [d, $^1J$(PP) = 431.4 Hz, $P_2P$], –213.44 [t, $^1J$(PP) = 431.4 Hz, $PP_2$]. – MS (FD, $CH_2Cl_2$), *m/z* (%): 455 (100) [$M^+$].

$C_{56}H_{52}Cl_6P_6Sn$ (1242.5) Calcd. C 54.14 H 4.22 Cl 17.1
Found C 53.60 H 3.97 Cl 16.1

*Compound* **4b**: A solution of **3** (2.12 g, 5.0 mmol) and $SnCl_2$ (0.95 g, 5.0 mmol) in 25 ml of dichloromethane was treated at room temp. with a solution of $AsCl_3$ (0.91 g, 5.0 mmol) in 20 ml of dichloromethane. After stirring for 12 h the brown precipitate was separated by filtration and the yellow filtrate treated with 14 ml of diethyl ether until crystallization started. The product was collected and dried in vacuo; yield 1.06 g (32%), yellow powder, m.p. 144°C (dec.). – $^1$H NMR ($CD_3CN$): δ = 4.00 ["d", $^2J$(PH) = 17.8 Hz, 4H, $H_2C-P$], 5.14 ["t", $^4J$(PH) = 4.10 Hz, 2H, $H_2C=C$], 7.50–7.54 (m, 8H, *m*-H), 7.59–7.62 (m, 4H, *p*-H), 7.72–7.77 (m, 8H, *o*-H). – $^{13}C\{^1H\}$ NMR ($CD_3CN$): δ = 36.22 ("t", *N* = 19.1 Hz, $H_2C-P$), 124.48 [t, $^3J$(PC) = 10.68 Hz, $H_2C=C$], 125.80 (m, AXX', N = 67.9 Hz, *ipso*-C), 130.52 ("t", *N* = 5.3 Hz, *o*-C), 131.18 [t, $^2J$(PC) = 7.2 Hz, $C=CH_2$], 133.41 ("t", AXX', *N* = 5.3 Hz, *o*-C), 134.38 ("t", *n* = 1.5 Hz, p-C). – $^{31}P\{^1H\}$ NMR ($CD_3CN$): δ = 18.33 (s).

*5-Methyl-1,1,3,3-tetraphenyl-1λ$^5$,2λ$^3$,3λ$^5$-triphosphinine* (**5**): In a two-phase system of 250 ml of hexane and 15 ml of acetonitrile compound **4a** (0.67 g, 0.54 mmol) was treated at room temp. with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 25 ml of hexane. After stirring for 1 h the bright yellow hexane phase was separated and the solvent removed in vacuo; yield 0.12 g (25%), yellow powder, m.p. 70°C (dec.). – $^1$H NMR ($C_6D_6$): δ = 2.34 (s, 3H, Me), 3.62 [br. d, $^2J$(PH) = 14.2 Hz, 2H, HC–P], 6.90–7.07 (m, 12H, *m/p*-H), 7.75–7.78 (m, 8H, *o*-H). – $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ = 30.51 ["t", $^3J$(PC) = 21.9 Hz, Me], 55.70 [ddd, $^1J$(PC) = 90.6, $^2J$(PC) = 43.5, $^3J$(PC) = 8.6 Hz, HC–P], 128.6–140.5 (m, Ph), 159.5 [t, $^2J$(PC) = 9.5 Hz, *C*–Me]. – $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ = 16.10 [d,

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound **4b** · 0.5 $CH_3CN$. [$U_{eq} = (U_1U_2U_3)^{1/3}$, where $U_i$ are the eigenvalues of the $U_{ij}$ matrix; E.s.d.'s in parentheses]

| ATOM | X/A | Y/B | Z/C | U(eq.) |
|---|---|---|---|---|
| SN | 0.25000 | 0.70774(3) | 0.50000 | 0.044 |
| CL1 | 0.17873(6) | 0.59109(7) | 0.45008(5) | 0.066 |
| CL2 | 0.15378(8) | 0.70884(9) | 0.57552(6) | 0.099 |
| CL3 | 0.18115(8) | 0.82188(8) | 0.44669(6) | 0.094 |
| AS | 0.20262(2) | 0.27390(3) | 0.17761(2) | 0.060 |
| P1 | 0.08604(6) | 0.27886(7) | 0.13495(4) | 0.047 |
| P2 | 0.22280(6) | 0.13308(7) | 0.14946(5) | 0.050 |
| C1 | 0.0796(2) | 0.2210(3) | 0.0638(2) | 0.053 |
| C2 | 0.1046(2) | 0.1266(3) | 0.0654(2) | 0.050 |
| C3 | 0.1888(2) | 0.1093(3) | 0.0754(2) | 0.052 |
| C4 | 0.0558(3) | 0.0594(3) | 0.0559(2) | 0.065 |
| C11 | 0.0680(3) | 0.3949(3) | 0.1184(2) | 0.053 |
| C111 | 0.1256(3) | 0.4578(3) | 0.1241(2) | 0.077 |
| C112 | 0.1116(4) | 0.5459(4) | 0.1069(3) | 0.091 |
| C113 | 0.0436(4) | 0.5678(3) | 0.0829(2) | 0.089 |
| C114 | -0.0132(3) | 0.5070(4) | 0.0763(2) | 0.096 |
| C115 | -0.0006(3) | 0.4198(3) | 0.0941(2) | 0.079 |
| C12 | 0.0092(2) | 0.2369(2) | 0.1793(2) | 0.045 |
| C121 | -0.0579(2) | 0.2049(3) | 0.1542(2) | 0.053 |
| C122 | -0.1156(2) | 0.1733(3) | 0.1909(2) | 0.064 |
| C123 | -0.1079(3) | 0.1742(3) | 0.2505(2) | 0.064 |
| C124 | -0.0424(3) | 0.2059(3) | 0.2744(2) | 0.068 |
| C125 | 0.0176(2) | 0.2376(3) | 0.2403(2) | 0.057 |
| C21 | 0.3252(2) | 0.1208(3) | 0.1489(2) | 0.053 |
| C211 | 0.3634(3) | 0.0658(3) | 0.1872(2) | 0.069 |
| C212 | 0.4425(3) | 0.0569(3) | 0.1839(3) | 0.085 |
| C213 | 0.4822(3) | 0.1037(4) | 0.1441(3) | 0.088 |
| C214 | 0.4464(3) | 0.1587(4) | 0.1061(2) | 0.088 |
| C215 | 0.3656(3) | 0.1693(3) | 0.1082(2) | 0.076 |
| C22 | 0.1882(2) | 0.0478(3) | 0.1978(2) | 0.049 |
| C221 | 0.1945(2) | -0.0413(3) | 0.1825(2) | 0.059 |
| C222 | 0.1762(3) | -0.1075(3) | 0.2215(2) | 0.076 |
| C223 | 0.1509(3) | -0.0844(4) | 0.2769(3) | 0.098 |
| C224 | 0.1427(3) | 0.0038(4) | 0.2922(2) | 0.099 |
| C225 | 0.1621(3) | 0.0704(3) | 0.2528(2) | 0.071 |
| N | 0.2656(6) | 0.3116(5) | 0.0088(5) | 0.064 |
| C1 | 0.25000 | 0.3820(5) | 0.00000 | 0.095 |
| C2 | 0.2702(7) | 0.4743(7) | 0.0180(5) | 0.109 |

$^1J$(PP) = 374.5 Hz, $P_2$P], −232.94 [t, $^1J$(PP) = 374.5 Hz, P$P_2$]. − MS (CI), *m/z* (%): 425 (100) [$M^+$ − P].

$C_{28}H_{25}P_3$ (455.4) Calcd. C 74.00 H 5.54 P 20.45
Found C 74.86 H 5.78 P 21.25

*Crystal Structure Determination of Compound* **4b** · 0.5 $CH_3CN$: Enraf Nonius CAD4 diffractometer, Mo-$K_\alpha$ radiation, $\lambda$ = 0.71069 Å, graphite monochromator, $T$ = +20°C. Crystal data: $C_{56}H_{52}As_2Cl_6P_4Sn$ · 0.5 $CH_3CN$, $M_r$ = 1330.18, monoclinic space group *I2/a* (No. 15) with $a$ = 17.499(4), $b$ = 15.055(2), $c$ = 22.768(2) Å, $\beta$ = 90.71(1)°, $V$ = 5997.7 Å$^3$, $Z$ = 4, $d_{(calcd.)}$ = 1.47 gcm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 18.28 cm$^{-1}$, 10351 reflections, 5331 unique, and 5330 observed with $F_o \geqslant 4\sigma(F_o)$ [*hkl* range: +/−25, +22, +23, $(\sin\Theta/\lambda)_{max}$ = 0.746]; data correction for absorption effects (empirical). The structure was solved by means of the Patterson map[10] and refined with anisotropic displacement parameters for all non-hydrogen atoms, with the tin atom at (0.25, *y*, 0.5) and the central carbon atom of the solvent molecule at (0.25, *y*, 0.0). 5 hydrogen atoms were calculated with idealized geometry, 21 hydrogen atoms could be located and were included in the refinement with fixed isotropic displacement parameters ($U_{iso}$ = 0.05 Å$^2$); $R$ ($R_w$) = 0.057 (0.038) for 325 refined parameters; [$R = \Sigma \parallel F_o \mid - \mid F_c \parallel / \Sigma \mid F_o \mid$; $R_w = [\Sigma w(\mid F_o \mid - \mid F_c \mid)^2 / wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$]; residual electron density +2.07/−1.29 eÅ$^{-3}$, located near the disordered solvent molecule and the chlorine atoms of the anion.

Further information on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56545, the names of the authors, and the journal citation.

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[10] Calculations were done by using a Micro-VAX station 3100 M76 (Micro VMS V5.3) computer with the programs SHELXS-86 (structure solution), SHELX-76 (structure refinement), DELOS, LEPAGE (cell reduction), and the commercial package SDP/V V3.0.

[309/92]