

Synthesis and Characterisation of Molecular Bismuth Phosphorus Compounds Containing Bi₂ Units with Bi–Bi Single and Double Bonds

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The compound [BiP(SiPh₂tBu)₂]₂ (**1**), featuring a Bi–Bi double bond and two Bi–P single bonds, has been obtained from the reaction of BiCl₃ with the lithium phosphanide LiP(Si^{*t*}BuPh₂)₂. As a byproduct of this transmetallation/redox reaction the diphosphane P₂(Si^{*t*}BuPh₂)₄ (**2**) has been isolated. This compound shows a remarkably short P–P bond due to π interactions of the phosphorus atoms. The reaction of the dilithium

phosphandiide Li₂PSi^{*t*}BuPh₂ with BiCl₃ yielded the bicyclic compound [Bi₂(PSiPh₂tBu)₄] (**3**), exhibiting a Bi–Bi single bond. NMR studies of **3** show the availability of four different P atoms, as observed in the crystal structure.

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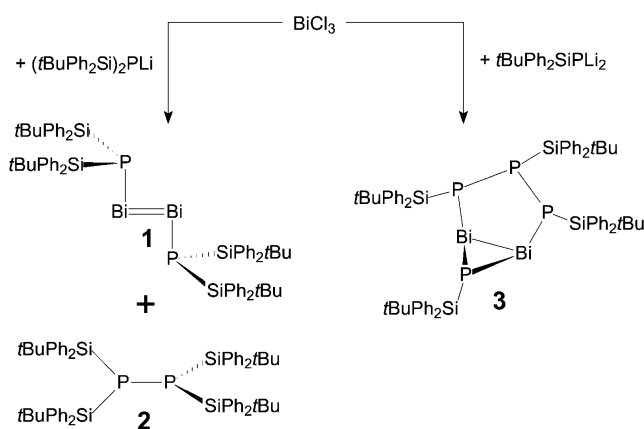
Introduction

Organobismuth compounds containing Bi–Bi bonds are of considerable interest because of their chemical and physical properties.^[1] In contrast to the extensive investigation of dibismuthanes,^[2] very few dibismuthenes are known as yet. The first evidence for a Bi–Bi double bond was observed in the compound (Tbt)Bi=Bi(Tbt),^[3] where Tbt = 2,4,6-[(Me₃Si)₂CH]₃C₆H₂. The compounds [BiC₆H₃-2,6-Mes₂]₂ and [BiC₆H₃-2,6-Trip₂]₂ (Mes = 2,4,6-Me₃C₆H₂, Trip = 2,4,6-*i*Pr₃C₆H₂), also featuring Bi–Bi double bonds, were obtained by Power et al.'s group.^[4] On the other hand, the use of less bulky substituents expands the knowledge in the field of the homonuclear cyclic and polycyclic compounds of bismuth. A remarkable development in the last years is

the synthesis of the first cyclo-R₄Bi₄ [R = (Me₃Si)₂CH]^[5] compound in equilibrium with the cyclo-R₃Bi₃ species. Parallel work described the isolation of [(Me₃Si)₃Si]₄Bi₄ and the bicycle [(Me₃Si)₃Sn]₆Bi₈.^[6] Molecular compounds containing Bi–P bonds are still rare, and for that reason we investigate whether sterically demanding phosphanyl groups can be used for the synthesis of new polynuclear bismuth compounds. We report here on the synthesis and crystal structures of the new binuclear bismuth compounds [BiP(SiPh₂tBu)₂]₂ (**1**) and [Bi₂(PSiPh₂tBu)₄] (**3**) as well as the diphosphane P₂(Si^{*t*}BuPh₂)₄ (**2**) (Scheme 1).

Results and Discussion

By reaction of (tBuPh₂Si)₂PLi with BiCl₃ in molar ratio 3:1 the dibismuthene [BiP(SiPh₂tBu)₂]₂ (**1**) and the diphosphane P₂(SiPh₂tBu)₄ (**2**) were obtained. Compound **1** forms red crystals and crystallises in the triclinic space group *P* $\bar{1}$ with the centre of inversion located in the middle of the molecule (Figure 1). The X-ray investigation revealed that **1** exists as a binuclear complex. There are no significant intermolecular Bi...Bi contacts between the Bi atoms of adjacent molecules because of the large steric requirement of the (tBuPh₂Si)₂P substituents. The molecule shows a *trans* conformation, a structural feature represented by the majority of the previously known organobismuth compounds with a Bi–Bi double bond.^[3,4,7] In particular, *cis* forms of dibismuthenes have been described in tungsten pentacarbonyl complexes.^[8] The bismuth atoms and the phosphorus atoms show a planar alignment. The Bi–Bi bond length is 282.1 pm, which is in the usual range for double bonds between bismuth atoms. Similar Bi–Bi bond lengths of 282.1 and 283.3 pm, for example, can be observed in (TbtBi)₂^[3] and (2,6-Mes₂C₆H₃Bi)₂,^[4] whereas in [RBi=BiR{W-



Scheme 1. Synthesis of compounds 1–3.

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(CO)₅]₂]^[8] (R = Me₃CCH₂, Me₃SiCH₂) these bonds are slightly longer (287.7–300.2 pm). The Bi–P bonds are 264.8 pm long. In the Bi^{III} phosphide complex [Bi(P₃tBu₃)₂][–], described by Wright and co-workers, the Bi–P bonds are between 263.0 and 291.1 pm long.^[9] The Bi–Bi–P angle of 89.38° provides evidence for the very low tendency of bismuth to take part in hybridisation; the double bond is mostly composed from the orthogonally placed p orbitals.^[10] Relatively wider Bi–Bi–C angles of 92.5° and 100.5° are observed in the structurally analogous dibismuthenes, mentioned above. One reason for the very low value of the Bi–Bi–P angle in **1** could be attractive interactions between Bi(1) and P(1') [and Bi(1') and P(1)]. The distances between these atoms are, at 386.5 pm, considerably shorter than the sum of the van der Waals radii (430 pm).

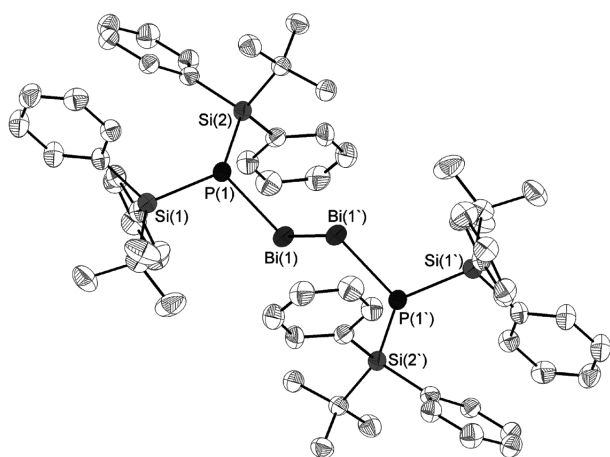


Figure 1. Molecular structure of **1** (ORTEP, thermal ellipsoids set at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Bi(1)–Bi(1') 282.06(9), Bi(1)–P(1) 264.82(17), P(1)–Si(1) 227.3(3), P(1)–Si(2) 228.9(2); Bi(1')–Bi(1)–P(1) 89.38(4), Bi(1)–P(1)–Si(1) 103.91(8), Bi(1)–P(1)–Si(2) 95.12(7), Si(1)–P(1)–Si(2) 110.78(9).

The ³¹P{¹H} NMR spectrum of **1** in [D₈]THF displays one singlet at δ = –202.0 ppm. Compound **1** is stable in the solid but decomposes in THF solution within a few days, with formation of **2**, (tBuPh₂Si)₂PH, elemental bismuth as well as different oligophosphanes.

The second product of the transmetallation/redox reaction of BiCl₃ and (tBuPh₂Si)₂PLi is the diphosphane **2**. It crystallises in the space group *P* $\bar{1}$ and is composed of two diorganophosphorus moieties, linked through a P–P single bond (Figure 2). Because of the steric effects of the bulky silyl groups, the geometry at each phosphorus atom is essentially planar (sum of bond angles: 353.8°) and the P(Si-tBuPh₂)₂ fragments show a twisted arrangement. An interesting aspect of the structure is the relatively short P–P bond length of 217.3 pm in comparison with the corresponding values in organophosphanes such as P₂Ph₄ (221.7 pm) and tBu₄P₆ (219.2–220.8 pm).^[11,12] It seems that the twist structure and the almost planar environment of the phosphorus atoms is favourable for bond shortening

due to some π bonding.^[13] A similar explanation has recently been given for the short P–P bond in Hittorf's phosphorus.^[14]

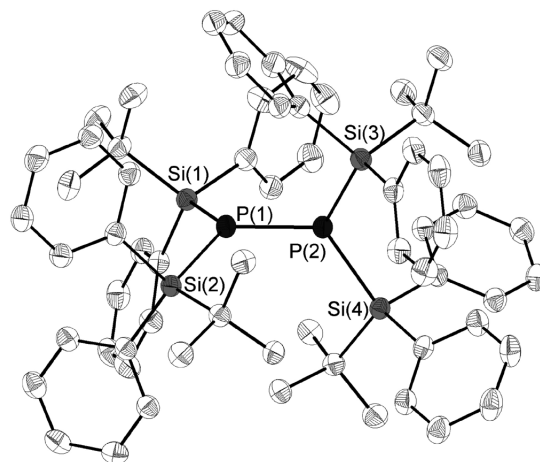


Figure 2. Molecular structure of **2** (ORTEP, thermal ellipsoids set at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: P(1)–P(2) 217.31(13), P(1)–Si(1) 230.33(13), P(1)–Si(2) 231.16(15), P(2)–Si(3) 230.30(13), P(2)–Si(4) 231.12(14); P(1)–P(2)–Si(3) 108.62(5), P(1)–P(2)–Si(4) 125.36(5), P(2)–P(1)–Si(1) 108.55(6), P(2)–P(1)–Si(2) 124.81(6), Si(1)–P(1)–Si(2) 119.93(5), Si(3)–P(2)–Si(4) 119.36(5).

The reaction of tBuPh₂SiPLi₂ with BiCl₃ in molar ratio 3:2 affords the bicycle [Bi₂(PSiPh₂tBu)₄] (**3**), which can be isolated in the form of red crystals. The compound crystallises in the triclinic space group *P* $\bar{1}$. It is constructed of five-membered P₃Bi₂ and three-membered PBi₂ rings sharing a common bridgehead (Figure 3). Of particular interest is the appearance of P–P and Bi–Bi single bonds in the molecule, obviously due to a reduction of the Bi atoms and corresponding oxidation of the P atoms. The central Bi₂P₄ unit features a nonplanar array; the plane through Bi(1), Bi(2), P(4) is virtually perpendicular to the Bi₂P₃ ring. Examination of the bond lengths and angles found in the bicyclic core of **3** indicates that there is a considerable amount of strain in this arrangement. The fold angles P(1)–Bi(1)–P(4) and P(3)–Bi(2)–P(4) are 82.65° and 103.36°, respectively. The comparatively large difference between these angles results from the manner of orientation of the sterically demanding silyl groups coordinated to P(1) and P(3). The tBuPh₂Si substituent of P(1) is in *trans* position to the Bi(1)–P(4) bond, whereas the silyl group bonded to P(3) is in *cis* position to the Bi(2)–P(4) bond. The torsion angles Si(3)–P(3)–Bi(2)–P(4) and Si(1)–P(1)–Bi(1)–P(4) are 49.1° and 134.0° respectively. A similar structural pattern has been observed for the analogous antimony species [Sb₂(PSiPh₂tBu)₄] in the course of our investigations.^[15] The homonuclear bicyclic compound tBu₄P₆ reported by Baudler and co-workers however shows an all-*trans* arrangement of the tBu groups.^[12] The Bi–Bi bond is 294.1 pm and therefore shorter than the corresponding bond lengths in the structures of already known dibismuthanes, such as Ph₄Bi₂ (299.0 pm)^[2a] and (Me₃Si)₄Bi₂ (303.5 pm).^[2b] The bond shortening is possibly a conse-

quence of the fact that the Bi₂ moiety is bridged by the P(4) atom. The P–P and Bi–P bonds in **3** are 221.5 pm and 268.6 pm on average.

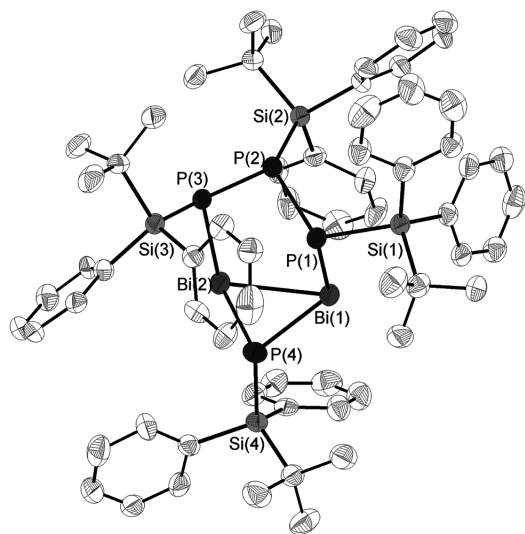


Figure 3. Molecular structure of **3** (ORTEP, thermal ellipsoids set at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Bi(1)–Bi(2) 294.2(2), Bi(1)–P(1) 266.3(6), Bi(1)–P(4) 269.2(6), Bi(2)–P(3) 269.3(6), Bi(2)–P(4) 269.5(6), P(1)–P(2) 221.9(8), P(2)–P(3) 221.2(7), P(1)–Si(1) 229.8(7), P(2)–Si(2) 232.0(8), P(3)–Si(3) 227.2(8), P(4)–Si(4) 227.7(9); Bi(1)–Bi(2)–P(4) 56.86(2), Bi(2)–Bi(1)–P(1) 90.26(2), Bi(2)–Bi(1)–P(4) 56.95(2), Bi(1)–P(4)–Bi(2) 66.19(4), Bi(1)–P(1)–P(2) 111.2(3), Bi(1)–P(3)–P(2) 113.1(2), P(1)–P(2)–P(3) 101.2(3), P(1)–Bi(1)–P(4) 82.65(8), P(3)–Bi(2)–P(4) 103.36(8).

The structure of **3** can be deduced from the ³¹P{¹H} NMR spectrum, which shows, at room temperature, two triplet signals at $\delta = -77$ ppm and $\delta = -265.5$ ppm for the P(2) and P(4) atoms, respectively. An additional broad signal appears at $\delta = -115$ ppm. At +70 °C two triplet signals and one doublet of doublets can be observed, which is con-

sistent with chemically identical P(1) and P(3) atoms (AM₂X spin system, ¹J_{P,P} = 400, ²J_{P,P} = 87 Hz). At –50 °C the ³¹P{¹H} NMR spectrum of **3** shows four multiplets, corresponding to four different P atoms, as observed in the crystal structure (Table 1).

As can be shown by the synthesis of compound **1**, sterically demanding disilylphosphanid ligands can be used for the kinetic stabilisation of unusual bonding situations. Hence they are an alternative to the frequently used bulky silyl or aryl groups such as Si(SiMe₃)₃ or 2,6-Mes₂C₆H₃. R₃SiP fragments, however, can be used to build up binary polycycles, as can be seen from the synthesis of compound **3**.

Experimental Section

All manipulations were carried out under rigorous exclusion of oxygen and moisture, using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. The starting material *t*BuPh₂SiPH₂ was prepared by LiCl-elimination reaction of *t*BuPh₂SiCl with [(dme)LiPH₂] in THF, in the manner described by us previously.^[15] BiCl₃ was obtained from Aldrich and used as received. The ³¹P NMR spectra were recorded with Bruker AC 250 and a Bruker Avance 300 spectrometers.

(*t*BuPh₂Si)₂PH: This compound was isolated as a byproduct from the synthesis of *t*BuPh₂SiPH₂ and could be obtained as colourless crystals by recrystallisation of the distillation residue from *n*-pentane.^[15] C₃₂H₃₉PSi₂ (510.81): calcd. C 75.24, H 7.70; found C 75.23, H 7.83. ¹H NMR (C₆D₆): δ = 1.21 [s, C(CH₃)₃, 18 H], 1.82 (d, *PH*, ¹J_{P,H} = 200.1 Hz, 1 H), 7.04 (m, *o*-Ph, 8 H), 7.10 (m, *p*-Ph, 4 H), 7.60 (m, *m*-Ph, 8 H) ppm. ¹³C{¹H} NMR (C₆D₆): δ = 20.8 [d, C(CH₃)₃, ²J_{P,C} = 12.4 Hz], 28.3 [d, C(CH₃)₃, ³J_{P,C} = 2.6 Hz], 127.7 (s, Ph), 129.3 (s, Ph), 134.7 (d, *J*_{P,C} = 5.7 Hz, Ph), 136.8 (d, *J*_{P,C} = 3.3 Hz, Ph) ppm. ²⁹Si{¹H} NMR (C₆D₆): δ = 4.9 (d, ¹J_{P,Si} = 36.6 Hz) ppm. ³¹P NMR (C₆D₆): δ = –267 (d, ¹J_{P,H} = 200.1 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3071 (m), 3043 (m), 2964 (s), 2930 (s), 2892 (m), 2856 (s), 2295 (m), 1959 (w), 1896 (w), 1820 (w), 1776 (w),

Table 1. Crystallographic data of **1–3**.^[16]

	1	2	3
Empirical formula	C ₆₄ H ₇₆ Bi ₂ P ₂ Si ₄	C ₆₄ H ₇₆ P ₂ Si ₄ ·2Et ₂ O	C ₆₄ H ₇₆ Bi ₂ P ₄ Si ₄
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Formula units	1	2	2
Temperature [K]	200	200	200
<i>a</i> [pm]	961.72(2)	1403.6(3)	1400.3(3)
<i>b</i> [pm]	1114.6(2)	1644.3(3)	1424.9(3)
<i>c</i> [pm]	1651.9(3)	1748.4(4)	2157.2(4)
α [°]	71.52(3)	66.97(3)	106.36(3)
β [°]	87.71(3)	69.99(3)	92.13(3)
γ [°]	68.79(3)	71.44(3)	118.87(3)
Volume [Å ³]	1560.0(5)	3409.1(12)	3539.0(12)
Density [g cm ^{–3}]	1.530	1.138	1.407
2 θ range [°]	3–49	3–48	2–45
Reflections measured	9429	14639	17447
Independent reflections	5044 (<i>R</i> _{int} = 0.0371)	9570 (<i>R</i> _{int} = 0.0254)	8825 (<i>R</i> _{int} = 0.0797)
Independent reflections with <i>F</i> _o > 4 σ (<i>F</i> _o)	4593	7717	5634
Parameters	325	671	667
μ (Mo- <i>K</i> α) [mm ^{–1}]	5.798	0.177	5.158
<i>R</i> ₁	0.0474	0.0609	0.0739
<i>wR</i> ₂ (all data)	0.1263	0.1738	0.1531
Residual electron density [e Å ^{–3}]	–1.957/1.063	–0.862/1.29	–2.91/1.92

1588 (w), 1567 (w), 1486 (w), 1470 (m), 1426 (s), 1389 (m), 1359 (m), 1309 (w), 1262 (w), 1188 (m), 1157 (w), 1102 (vs), 1028 (w), 1007 (m), 934 (m), 846 (w), 816 (s), 740 (s), 698 (vs), 620 (w), 597 (s), 561 (w), 518 (vs), 483 (s), 454 (s), 402 (m) cm⁻¹.

1 and 2: Butyllithium solution (0.37 mL, 1.6 M) was added to a solution of (*t*BuPh₂Si)₂PH (0.3 g, 0.59 mmol) in Et₂O (10 mL) at 0 °C. After warming to room temperature, the solution of (*t*BuPh₂Si)₂PLi was added to a suspension of 0.06 g (0.2 mmol) BiCl₃ in 10 mL Et₂O at -60 °C. Subsequently the red mixture was slowly warmed to room temperature while stirring and then agitated overnight. The solution was reduced to 5 mL in vacuo. After filtration and cooling to 0 °C red crystals of **1** were obtained within a few hours. Subsequent reduction of the volume to 3 mL in vacuo and cooling of the solution for two days yielded a second crystal fraction consisting of **1** and colourless crystals of **2**.

1: Yield: 0.12 g (41.7%). C₆₄H₇₆Bi₂P₂Si₄ (1437.56): calcd. C 53.47, H 5.33; found C 53.84, H 5.32. ¹H NMR ([D₈]THF): δ = 1.21 (s, CCH₃, 36 H), 7.28 (m), 7.50 (m), 7.54 (m); SiPh (40 H) ppm. ²⁹Si{¹H} NMR ([D₈]THF): δ = 13.9 (m) ppm. ³¹P{¹H} NMR ([D₈]THF): δ = -202.0 (s) ppm. IR (KBr): ν̄ = 3132 (w), 3049 (m), 2961 (s), 2928 (s), 2889 (m), 2855 (s), 1958 (w), 1895 (w), 1822 (w), 1587 (w), 1567 (w), 1468 (m), 1426 (s), 1388 (w), 1360 (w) 1309 (w), 1262 (m), 1188 (w), 1155 (vw), 1099 (vs), 1006 (m), 935 (w), 884 (w) 814 (s), 737 (s), 701 (vs), 593 (s), 523 (vs), 485 (m), 408 (w) cm⁻¹. UV/Vis: λ (ε in L mol⁻¹ cm⁻¹) = 820 (shoulder, 100), 564 (2944), 466 nm (shoulder, 1180).

2: Yield: about 0.02 g after sorting by hand. No satisfying elemental analysis can be obtained because of co-crystallisation of compound **1**. ¹H NMR ([D₈]toluene): δ = 1.20 (s, CCH₃, 36 H), 7.06 (m), 7.19 (m), 7.57 (m); SiPh (40 H) ppm. ²⁹Si{¹H} NMR ([D₈]toluene): δ = 8.1 (pseudo-t, J_{PSi} = 18.2 Hz) ppm. ³¹P{¹H} NMR ([D₈]toluene): δ = -199.8 (s) ppm. MS (EI = 70 eV, 180 °C): m/z (%) = 1019 (22) [M⁺], 961 (3.4) [M⁺ - *t*Bu], 904 (4.4) [M⁺ - 2 *t*Bu], 779 (21) [M⁺ - Si*t*BuPh₂], 722 (36) [M⁺ - Si*t*BuPh₂ - *t*Bu], 665 (37) [M⁺ - Si*t*BuPh₂ - 2 *t*Bu], 453 (100) [M⁺/2 - C₄H₈], 397 (100) [M⁺/2 - 2 C₄H₈].

3: Butyllithium solution (1.1 mL, 1.6 M) was added to a solution of *t*BuPh₂SiPH₂ (0.24 g, 0.88 mmol) in Et₂O 5 mL) at 0 °C. After stirring for 10 min, this solution was added to a suspension of BiCl₃ (0.19 g, 0.59 mmol) in Heptan (20 mL) at -70 °C. The reaction mixture was warmed up to room temperature and then stirred for an additional 16 h. Some of the solvent (20 mL) was removed in vacuo. The resulting black-green solution was filtered to remove the precipitated LiCl and elemental bismuth and cooled to -35 °C. Red crystals of **3** were obtained over a period of some days. Yield: 0.1 g (22.6%). C₆₄H₇₆Bi₂P₄Si₄ (1499.5): calcd. C 51.26, H 5.11; found C 51.63, H 5.30. ¹H NMR (C₆D₆): δ = 1.36 (s, Si*t*Bu, 9 H), 1.39 (s, Si*t*Bu, 9 H), 1.52 (s, Si*t*Bu, 18 H), 6.86 (m), 7.15 (m), 7.36 (m), 7.58 (m), 7.80 (m), 8.06 (m); SiPh (40 H) ppm. ³¹P{¹H} NMR ([D₈]toluol, 70 °C): δ = -256.6 (t, ²J_{PP} = 87 Hz), -113 (dd, ¹J_{PP} = 400 Hz, ²J_{PP} = 87 Hz), -73.7 (t, ¹J_{PP} = 400 Hz)

ppm. ³¹P{¹H} NMR ([D₈]toluol, -50 °C): -82.3 (m), -102.0 (m), -145.1 (m), -279.5 (m) ppm. IR (KBr): ν̄ = 3132 (w), 3068 (m), 3046 (m), 3013 (w), 2959 (s), 2925 (s), 2889 (m), 2854 (s), 1955 (w), 1890 (w), 1822 (w), 1719 (w), 1586 (w), 1565 (w), 1484 (w), 1468 (m), 1426 (s), 1389 (m), 1361 (m) 1303 (w), 1262 (m), 1192 (w), 1156 (vw), 1100 (vs), 1008 (m), 936 (w), 853 (w) 814 (s), 737 (s), 699 (vs), 620 (w), 595 (m), 516 (vs), 484 (s), 405 (m) cm⁻¹.

CCDC-606897 to -606899 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [16] STOE-IPDS2 (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques against F² (Bi, P, Si, C refined anisotropically, H atoms were calculated at ideal positions). Numerical absorption correction was applied for compound **1**.

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