Syntheses and Structures of 9-Bromo-10-diphenylphosphanylanthracene and its Oxidation Products

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Treatment of 9,10-dibromoanthracene with one mole equivalent of *n*-butyllithium and chlorodiphenylphosphane yields 9-bromo-10-diphenylphosphanylanthracene (**1**). Oxidation of **1** with chalcogens leads to $\{Br(C_{14}H_8)(Ph_2P{=}E)\}$ with E = O (**2**), S (**3**) and Se (**4**). The syntheses and structure determinations of the parent compound **1** and the oxidized species **2** – **4** are reported.

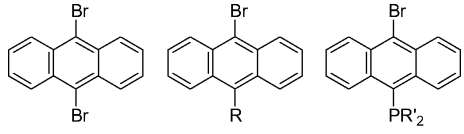
Key words: Anthracene, Asymmetrical Synthesis, Phosphane, Phosphorylation, Selenium

Introduction

9,10-Dibromoanthracene (**A** in Scheme 1) is a common reactant to obtain anthracene derivatives, both symmetrically and asymmetrically substituted in the 9- and 10-positions. However, reports on 10-heterosubstituted 9-bromoanthracenes of type **B** are rare. In almost all cases published so far, the compounds are bearing nitrogen, oxygen, boron or silicon in position 10; phosphorus derivatives of type **C** are completely unknown, although such compounds would be of great synthetic interest as the remaining halogen atom should be easily replaceable by various substituents.

Yamaguchi *et al*. synthesized a 9-bromo-10-borylanthracene as an intermediate for trianthrylboranes [1], and more recently they reported on a *B*,*B*′,*B*″-tris(10-bromoanthryl)borazine derivative which can be used as a key precursor for a variety of 10-substituted 9-anthrylborazins [2]. The palladium-catalyzed reaction of **A** with secondary amines can be performed without the use of strong bases to obtain the corresponding 9-bromo-10-aminoanthracene selectively [3, 4]. Another example of a group 15 substituted bromoanthracene is a bromoanthrylcarbazole whose structure was determined in the early 1990s [5].

Treating 9,10-dibromoanthracene with two equivalents of ^{n}BuLi leads to 9,10-dilithioanthracene which can react with a variety of electrophiles to give symmetrically substituted compounds. Although the reaction was also used to form P–C-bonds, and the disubstituted compounds feature interesting properties



A **B** **C**

Scheme 1. Heterosubstituted anthracenes. R = BR'_2, NR'_2, OR', SiR'_3; R′ = alkyl, aryl.

like self-assembly and molecular recognition [6, 7], the method is restricted to the formation of symmetrically substituted anthracene derivatives and so far no attempts were made to replace only one bromo-substituent of **A** by a PR_2 group to give **C**.

The first 9-phosphanyl substituted anthracene was synthesized by Akasaka *et al*. in the reaction of lithium diphenylphosphanide and 9-bromoanthracene [8]. Its ligand properties in transition metal chemistry were investigated and the [4+4] dimerization upon irradiation was observed [9]. 1,8-Bis(diphenylphosphanyl)anthracene serves as a chelating neutral donor ligand in transition metal chemistry [10], and recently the synthesis of the symmetrically substituted 9,10-bis(diphenylphosphanyl)anthracene was communicated. Upon gold complexation a flexible cyclic $[Au\{C_{14}H_8(Ph_2P)_2\}]_3$ trication is formed [6].

Results and Discussion

We reported the synthesis and oxidation of the parent 9,10-bis(diphenylphosphanyl)anthracene, to give the products $\{C_{14}H_8(Ph_2P)_2\}$, $\{C_{14}H_8(Ph_2P{=}O)_2\}$, $\{C_{14}H_8(Ph_2P{=}S)_2\}$, and $\{C_{14}H_8(Ph_2P{=}Se)_2\}$ [11].

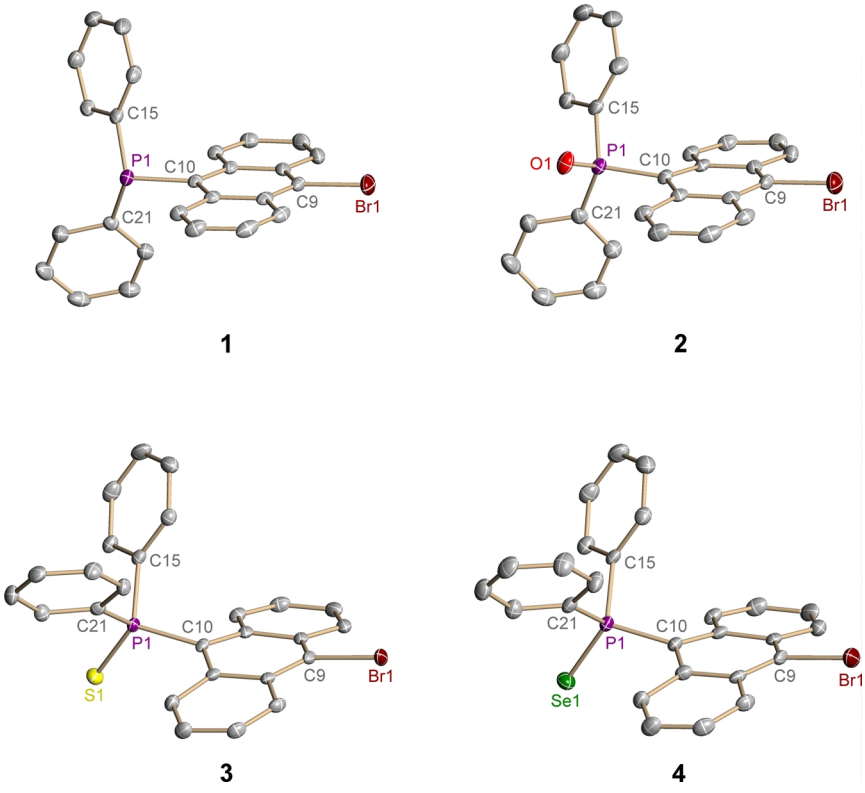
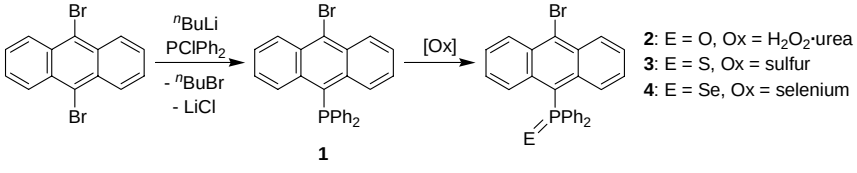


Fig. 1. Molecular structures of **1**–**4**. For **3** and **4** only one of the two crystallographically independent molecules is shown. Anisotropic displacement parameters are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.



Scheme 2. Syntheses of compounds **1**–**4**.

Surprisingly, the sulfur oxidized species is a solid-state fluorescent chemosensor for toluene. The host/guest complex of $\{C_{14}H_8(Ph_2P{=}S)_2\}$ and toluene (mole ratio 1 : 2) shows a very intense green fluorescence in the solid state at 508 nm (λ_{ex} = 380 nm). In the course of designing novel chemosensors [12] we have now isolated and characterized $\{Br(C_{14}H_8)(Ph_2P)\}$ (**1**) as the first 9-bromo-10-phosphanylanthracene. In addition, we describe here the preparation and structure determination of the oxidized derivatives $\{Br(C_{14}H_8)(Ph_2P{=}O)\}$ (**2**), $\{Br(C_{14}H_8)(Ph_2P{=}S)\}$ (**3**), and $\{Br(C_{14}H_8)(Ph_2P{=}Se)\}$ (**4**).

Lithiation of 9,10-dibromoanthracene with one equivalent of ^{n}BuLi leads to a mono-lithiated bromoanthracene [13] which was reacted *in situ* with a stoichiometric amount of chlorodiphenylphosphane (Scheme 2). In contrast to the 9,10-diphosphanyl-substituted compound, the solubility of **1** in diethyl ether is very good and insoluble by-products can easily be removed by filtration.

The oxidation reactions of **1** were performed according to literature methods [14]. For the synthesis of **2** (E = O) the mild oxidizing agent $H_2O_2{\cdot}(H_2N)_2C{=}O$ was used at r. t. in dichloromethane. The reaction of **1** with elemental sulfur and gray selenium in toluene at reflux gave **3** (E = S) and **4** (E = Se), respectively. All oxidation products were obtained in high yields. The $\delta(^{31}P)$ chemical shifts of the phosphorus atoms in **1**–**4** are similar to the values published for the 9,10-diphosphanyl-substituted analogues [11]. All compounds were isolated as crystalline yellow solids and their identities were established by elemental analyses, mass spectrometry, NMR spectroscopy (^{31}P, ^1H, ^{77}Se) and single crystal X-ray diffraction.

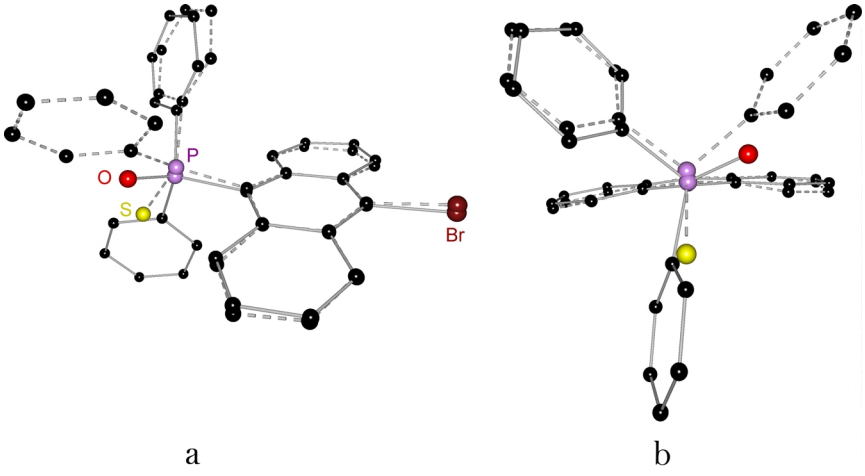


Fig. 2. Superposition plots of **2** (solid lines) and **3** (dashed lines) fitted by employing the C4a, C8a, C9a and C10a positions viewed from the side (a) and along the P1–C10 bond (b).

Table 1. Selected bond lengths (pm) and angles (deg) of **1** – **4**.

	1	**2** (E = O)	**3** (E = S)	**4** (E = Se)
Br1–C9	190.40(17)	189.9(2)	190.2(3)	190.2(4)
P1–C10	184.50(17)	183.8(2)	182.6(3)	183.3(3)
P1–E1		148.93(18)	195.48(10)	211.23(11)
P1–C15	183.20(18)	181.1(3)	182.7(3)	183.3(4)
P1–C21	182.73(18)	181.0(3)	183.2(3)	182.4(4)
out-of-plane[a] Br/P	1.16/4.98	2.23/6.41	7.00/10.45	6.93/10.23
folding angle An[b]	177.4	170.8	162.7	163.0

[a] Angle of the Br–C and P–C10 bond to the C9···C10 vector of the anthracene moiety; [b] angle included by the two outer C_6-perimeters.

The results of the structure determinations of **1** – **4** are shown in Fig. 1, selected bond lengths and angles are given in Table 1. The crystal data and the experimental parameters used for the crystal structure analyses are listed in Table 2.

All compounds crystallize in the monoclinic space group $P2_1/n$. The asymmetric units of **1** and **2** contain one molecule, while those of the derivatives **3** and **4** show two molecules. Different to the oxidized 9,10-disubstituted analogues, **1** – **4** crystallize without any interstitial solvent molecules in the crystal. The bond lengths and angles and the conformations of the Ph_2P and Ph_2P=E substituents of **1** – **4** are very similar to those in the disubstituted derivatives.

The molecules of **1** and **2** have the same orientation of the Ph_2P and Ph_2P=O substituents relative to the anthracene plane, each with one phenyl group on either side. The anthracene plane bisects the Ph–P–Ph bond angle in **1** (106.3°), and the oxygen atom in **2** is almost in plane (O–P–C10–C4a torsion angle 18.1°). This alignment of the phenyl substituents corresponds to the structures of analogous 1-phosphanylnaphthalenes. While the dihedral angle between the naphthalene C1–C2 and one P–$C_{ipso-Ph}$ bond is close to zero for the unsubstituted vicinal position 2 [15], a larger substituent causes the same bisectional orientation [16] like in **1** and **2**.

Differently, the two phenyl substituents of **3** and **4** are oriented towards the same side of the anthracene chromophore. The P=E bonds are arranged almost orthogonally relative to the anthracene plane with torsion angles of 86.7° in **3** and 87.5° in **4**. A superposition of **2** and **3** depicted in different projections is shown in Fig. 2. The different orientations of the Ph_2P=O and the Ph_2P=S substituents are obvious.

The anthracene moiety in **1** is slightly folded (angle along C9···C10 = 177.4°), while the *boat*-like conformation is more distinct in **2** – **4** due to the different orientations of the Ph_2P=E substitutents (folding angle 163.0° in **4**). The *cisoid* orientations of the phenyl substituents in **3** and **4** cause the two lateral anthracene rings to bend towards the sulfur and selenium atom, respectively. The bromine and phosphorus atoms are not located in the best plane of the central anthracene C_6 perimeter and the deviation from the plane increases drastically when proceeding from **2** (*transoid*) to **3** and **4** (*cisoid*).

Conclusions

In conclusion, the 9-bromo-10-phosphanylanthracenes {Br($C_{14}H_8$)(Ph_2P)} (**1**), {Br($C_{14}H_8$)(Ph_2P=O)} (**2**), {Br($C_{14}H_8$)(Ph_2P=S)} (**3**), and {Br($C_{14}H_8$)(Ph_2P=Se)} (**4**) can easily be synthesized in high yields using common reagents. Their spectral and structural properties are widely in accord with the 9,10-diphosphanyl compounds, but they do not crystallize as host

molecules for toluene like their diphosphanyl analogues do. The monofunctional derivatives open the door for the syntheses of asymmetrically substituted anthracenes with mixed P/B, P/C, P/Si or P/N centered substituents. Our future work is aimed to evaluate how these changes will influence the sensoric and photonic properties of the related host/guest complexes. Metal complexes of *d* and *f* block elements will also be investigated.

Experimental Section

The syntheses were performed under an inert gas atmosphere of dry nitrogen with Schlenk techniques. All solvents were dried and purified according to standard procedures and stored under nitrogen. 1D and 2D NMR spectra were obtained on a Bruker Avance 500 instrument operating at 500.13, 202.46, and 95.38 MHz, respectively, for ^{1}H, ^{31}P, and ^{77}Se. Melting points were measured in sealed capillaries using a Büchi melting point instrument. Mass spectra were recorded on a MAT 95 spectrometer. Elemental analyses were performed by Analytisches Labor, Anorganische Chemie, Göttingen.

*9-Bromo-10-(diphenylphosphanyl)anthracene (**1**)*

^{n}BuLi in *n*-hexane (1.37 mL, 2.22 M, 3.04 mmol) is added to a suspension of 9,10-dibromoanthracene (1.00 g, 2.98 mmol) in 25 mL of diethyl ether at −15 °C. The reaction mixture is stirred for 30 min before addition of chlorodiphenylphosphane (660 mg, 2.99 mmol). The suspension is stirred for 30 min and insoluble products are removed by filtration. After removal of the solvent, the product is obtained as a yellow powder. Crystals are obtained from a saturated solution in diethyl ether upon a few days' storage at r. t. Yield: 1.17 g (89 %). – M. p. 156 °C. – ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 8.84 (dd, $^{3}J_{HH}$ = 9.00 Hz, $^{4}J_{HP}$ = 5.33 Hz, 2H, $H_{4,5}$, An), 8.66 (d, $^{3}J_{HH}$ = 8.85 Hz, 2H, $H_{1,8}$, An), 7.54 (ddd, $^{3}J_{HH}$ = 8.88 Hz, $^{3}J_{HH}$ = 6.50 Hz, $^{4}J_{HH}$ = 1.09 Hz, 2H, $H_{2,7}$, An), 7.41 – 7.37 (m, 4H, H_{ortho}, Ph), 7.33 (ddd, $^{3}J_{HH}$ = 9.00 Hz, $^{3}J_{HH}$ = 6.50 Hz, $^{4}J_{HH}$ = 1.20 Hz, 2H, $H_{3,6}$, An), 7.27 – 7.22 (m, 6H, $H_{meta/para}$, Ph). – ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ = −22.7 (s). – MS (EI, 70 eV): *m/z* (%) = 442 (100) $[M]^+$, 361 (35) $[M–Br]^+$, 207 (10) $[C_{14}H_8P]^+$, 176 (24) $[C_{14}H_8]^+$. – $C_{26}H_{18}BrP$ (441.30): calcd. C 70.76, H 4.11; found C 70.71, H 4.73.

*9-Bromo-10-(diphenylphosphoryl)anthracene (**2**)*

An excess of $H_2O_2{\cdot}(H_2N)_2C{=}O$ (300 mg, 3.19 mmol) is added to a solution of **1** (330 mg, 0.75 mmol) in 40 mL of dichloromethane. The reaction mixture is stirred for 1 h and then filtered. The filtrate is washed with water (2 × 10 mL) and dried with magnesium sulfate over night. After filtration and removal of the solvent, the product is obtained as yellow crystals by recrystallization from toluene. Yield: 310 mg (91 %). – M. p. 164 °C. – ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 8.64 (d, $^{3}J_{HH}$ = 8.93 Hz, 2H, $H_{1,8}$, An), 8.59 (d, $^{3}J_{HH}$ = 8.92 Hz, 2H, $H_{4,5}$, An), 7.68 – 7.63 (m, 4H, H_{ortho}, Ph), 7.52 – 7.46 (m, 4H, $H_{2,7}$, An / H_{para}, Ph), 7.40 – 7.36 (m, 4H, H_{meta}, Ph), 7.23 (ddd, $^{3}J_{HH}$ = 8.92 Hz, $^{3}J_{HH}$ = 6.66 Hz, $^{4}J_{HH}$ = 1.20 Hz, 2H, $H_{3,6}$, An). – ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ = 31.6 (s). – MS (EI, 70 eV): *m/z* (%) = 457 (100) $[M]^+$, 377 (26) $[M–Br]^+$, 201 (8) $[P(O)Ph_2]^+$, 185 (21) $[PPh_2]^+$, 176 (17) $[C_{14}H_8]^+$. – $C_{26}H_{18}BrOP$ (457.30): calcd. C 68.29, H 3.97; found C 68.04, H 4.05.

*9-Bromo-10-(diphenylthiophosphoryl)anthracene (**3**)*

Elemental sulfur (80 mg, 2.50 mmol) is added to a solution of **1** (1.10 g, 2.49 mmol) in 30 mL of toluene. The reaction mixture is then heated to reflux for 4 h. After removal of the solvent the product is obtained by crystallization of the residue from diethyl ether. Yield: 1.10 g (93 %). – M. p. 181 °C. – ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 8.55 (d, $^{3}J_{HH}$ = 8.90 Hz, 2H, $H_{1,8}$, An), 8.04 (d, $^{3}J_{HH}$ = 8.84 Hz, 2H, $H_{4,5}$, An), 7.72 – 7.67 (m, 4H, H_{ortho}, Ph), 7.40 (ddd, $^{3}J_{HH}$ = 8.90 Hz, $^{3}J_{HH}$ = 6.54 Hz, $^{4}J_{HH}$ = 0.70 Hz, 2H, $H_{2,7}$, An), 7.29 – 7.26 (m, 2H, H_{para}, Ph), 7.23 – 7.20 (m, 4H, H_{meta}, Ph), 7.01 (ddd, $^{3}J_{HH}$ = 8.84 Hz, $^{3}J_{HH}$ = 6.54 Hz, $^{4}J_{HH}$ = 1.03 Hz, 2H, $H_{3,6}$, An). – ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ = 34.7 (s). – MS (EI, 70 eV): *m/z* (%) = 474 (100) $[M]^+$, 363 (25) $[M–SPh]^+$, 286 (17) $[Br(C_{14}H_8)P]^+$, 185 (86) $[PPh_2]^+$, 176 (12) $[C_{14}H_8]^+$. – $C_{26}H_{18}BrPS$ (473.36): calcd. C 65.97, H 3.83; found C 64.54, H 4.08.

*9-Bromo-10-(diphenylselenophosphoryl)anthracene (**4**)*

This compound was prepared in analogy to **3** from **1** (240 mg, 0.54 mmol) and an excess of gray selenium (120 mg, 1.52 mmol) in 30 mL of toluene and subsequent crystallization of the product from toluene. Yield: 230 mg (81 %). – M. p. 235 °C. – ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 8.59 (d, $^{3}J_{HH}$ = 8.92 Hz, 2H, $H_{1,8}$, An), 8.08 (d, $^{3}J_{HH}$ = 8.92 Hz, 2H, $H_{4,5}$, An), 7.79 – 7.74 (m, 4H, H_{ortho}, Ph), 7.44 (ddd, $^{3}J_{HH}$ = 8.92 Hz, $^{3}J_{HH}$ = 6.70 Hz, $^{4}J_{HH}$ = 0.72 Hz, 2H, $H_{2,7}$, An), 7.33 – 7.29 (m, 2H, H_{para}, Ph), 7.26 – 7.22 (m, 4H, H_{meta}, Ph), 7.07 (ddd, $^{3}J_{HH}$ = 8.92 Hz, $^{3}J_{HH}$ = 6.70 Hz, $^{4}J_{HH}$ = 1.06 Hz, 2H, $H_{3,6}$, An). – ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ = 25.9 (s). – ^{77}Se{^{1}H} NMR (95.38 MHz, $CDCl_3$): δ = −281.1 (d, $^{1}J_{SeP}$ = 734.9 Hz). – MS (EI, 70 eV): *m/z* (%) = 520 (59) $[M]^+$, 442 (100) $[M–Se]^+$, 363 (62) $[M–SePh]^+$, 185 (57) $[PPh_2]^+$, 176 (32) $[C_{14}H_8]^+$. – $C_{26}H_{18}BrPSe$ (520.26): calcd. C 60.02, H 3.49; found C 60.19, H 3.64.

Table 2. Crystal Data and Structure Refinement for **1**–**4**.

Compound	**1**	**2**	**3**	**4**
CCDC number	610420	610421	610422	610423
Empirical formula	$C_{26}H_{18}BrP$	$C_{26}H_{18}BrOP$	$C_{26}H_{18}BrPS$	$C_{26}H_{18}BrPSe$
Formula mass	441.30	457.30	473.36	520.26
T [K]	100(2)	100(2)	100(2)	133(2)
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [pm]	928.19(6)	944.01(5)	1723.27(11)	1717.1(3)
b [pm]	1687.62(11)	1682.77(9)	1392.49(9)	1414.5(3)
c [pm]	1258.22(8)	1265.86(7)	1733.47(11)	1737.8(4)
β [deg]	91.2870(10)	92.7740(10)	90.4330(10)	90.90(3)
V [nm^3]	1.9704(2)	2.00853(19)	4.1596(5)	4.2203(15)
Z	4	4	8	8
ρ_{calc} [g cm^{-3}]	1.488	1.512	1.512	1.638
$F(000)$ [e]	896	928	1920	2064
θ range [deg]	2.02 – 25.03	2.01 – 26.39	1.67 – 26.37	1.65 – 24.77
No. of collected reflexions	38038	16414	51924	63532
No. of independent reflexions	3468	4108	8512	7213
R_{int}	0.0225	0.0246	0.0397	0.0938
Data / parameters	3468 / 253	4108 / 262	8512 / 533	7213 / 533
Goof	1.068	1.097	1.118	0.964
$R1$, $wR2$ [$I > 2\sigma(I)$][a,b]	0.0248, 0.0667	0.0381, 0.1027	0.0391, 0.0839	0.0379, 0.0653
$R1$, $wR2$ (all data)	0.0264, 0.0676	0.0419, 0.1050	0.0468, 0.0870	0.0662, 0.0712
g_1, g_2[c]	0.0388, 1.2738	0.0575, 1.8977	0.0365, 4.4777	0.0339, 0.0000
Largest diff peak / hole [e·Å^{-3}]	0.580 / −0.181	0.519 / −0.349	0.565 / −0.269	0.348 / −0.516

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; [c] $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$.

Structure Determination of ***1*** *–* ***4***

Crystal data are presented in Table 2. The data were collected from oil-coated shock-cooled crystals. Compounds **1**–**3** were measured on a Bruker SMART-APEX diffractometer with a D8 goniometer, and **4** on a Stoe IPDS-2. Both diffractometers were equipped with low-temperature devices and used graphite-monochromated MoK_α radiation, λ = 71.073 pm [17]. The data of **1**–**3** were integrated with SAINT [18], and an empirical absorption correction (SADABS) was applied [19]. The data collection and reduction of **4** were performed with X-ARES and X-RED32 [20]. The structures were solved by Direct Methods (SHELXS-97) [21] and refined by full-matrix least-squares methods against F^2 (SHELXL-97) [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp^2 carbon atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 times the U_{eq} value of the parent atom.

Crystallographic data (excluding structure factors) for the structures **1**–**4** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 2. Copies of the 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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