1,3,2-Diselenaphospholanes with an Anellated Dicarba-*closo*-dodecaborane(12) Unit

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Dedicated to Professor Wolfgang Beck on the Occasion of his 75th Birthday

Abstract. The reaction of the 1,2-diselenido-1,2-dicarba-closo-dodecaborane dianion (1) with dichloro(phenyl)phosphane affords the 1,3,2-diselenaphospholane (2) containing an anellated dicarbacloso-docecaborane(12) unit. The phospholane 2 was oxidised by reactions with the elements to the sulfide 3 and the selenide 4, and partial hydrolysis gave a selenophosphonic acid derivative 5 along with the bis(diselane) 6 and decomposition. The reaction of 2 with (ethene)bis(triphenylphosphane)platinum(0) displaces ethene and is accompanied by oxidative addition and rearrangement into the bis(triphenylphosphane)platinum(II) complex **9**, in which the chelating unit is linked to platinum via Pt-Se and Pt-P(Se) bonds, a rare example of a metallophosphane selenide. The molecular structures of **2** and **3** were determined by X-ray analysis. The solution-state structures of the new compounds follow from consistent multinuclear magnetic resonance data (¹H, ¹¹B, ¹³C, ³¹P, ⁷⁷Se, ¹⁹⁵Pt NMR).

Keywords: Carborane; Selenium; Phosphorus; Platinum; Palladium; Oxidative addition; NMR spectroscopy; Crystal structures

Introduction

More than four decades of multifaceted chemistry focusing on 1,2-dicarba-*closo*-dodecaborane(12) ("*ortho*-carborane") and its isomers have led the way to an amazing variety of novel compounds both by cluster rearrangements and cluster substitutions [1-5]. In the case of *ortho*-carborane, various substituents at the carbon atoms in the 1,2-positions can be most conveniently varied by metalation at the carbon atom(s), e.g. to give the dilithiated carborane 1,2-Li₂- $1,2-C_2B_{10}H_{10}$, inviting for further transformations [1-3]. The current interest in the 1,2-dichalcogenido-1,2-dicarba*closo*-dodecaborane anions $[1,2-(1,2-C_2B_{10}H_{10})E_2]^{2-}$ (E = S, Se, Te) as chelating ligands in transition metal chemistry is well documented [6-12]. In contrast, the main group chemistry of these anions has received much less attention. The synthesis of the dianion with E = Te appears to be difficult [13], whereas those with E = S, Se are readily accessible, and [1,2-(1,2-C₂B₁₀H₁₀)Se₂]²⁻ is particularly attractive owing to the favourable NMR spectroscopic properties of ⁷⁷Se (spin I = $1/_2$; natural abundance 7.58 %; about three times more sensitive to NMR experiments than ¹³C) [14]. Recently, we have achieved the oxidative coupling of $[1,2-(1,2-C_2B_{10}H_{10})Se_2]^{2-}$ (1) to a bis(diselane) [15] and

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investigated the reactions of 1 with Group-14 element dihalides [16]. In the present work, we report on the reaction of 1 with dichloro(phenyl)phosphane, PhPCl₂, and on some aspects of the chemistry of the product 2 thus obtained.

Results and Discussion

The formation of the dianion $[1,2-(1,2-C_2B_{10}H_{10})Se_2]^{2-}$ (1), its conversion into the phenylphospholane 2, and the reactions of 2 with sulfur, selenium and methyl iodide, as well as partial hydrolysis and decomposition are shown in Scheme 1.

The phosphane 2 and its sulfide 3 could both be isolated as yellow crystals from CH₂Cl₂ solutions, and their molecular structures were determined by X-ray analysis (vide infra). In the case of the selenide 4, its formation required much longer reaction time, when compared with the sulfide 3, and was accompanied by extensive decomposition. The known bis(diselane) $[1,2-(1,2-C_2B_{10}H_{10})Se_2]_2$ 6 [15] was identified as a major decomposition product along with Ph₃PSe and several unidentified phosphorus compounds. Treatment of 2 with an excess of methyl iodide did not afford the expected phosphonium salt. Instead, the bis(diselane) 6 and other unknown decomposition products were formed. Traces of water present in the commercial MeI caused partial hydrolysis of 2, leading to the selenophosphonic acid derivative 5. It should be noted that the compounds 2 to 4 can in principle be formed as mixtures of isomers, depending on the orientation of the phenyl group. Apparently, only a single isomer 2 is formed, and its configuration is retained, as usual, upon addition of sulfur or



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Scheme 1 Synthesis of the 1,3,2-diselenaphospholanes 2 to 4 and partial hydrolysis of 2 to give 5.

Table 1 $\,$ $^{13}C,\,^{31}P$ and ^{77}Se NMR data $^{[a]}$ of the carborane derivatives 2 to 5

	$\delta^{31}P$ [¹ J(⁷⁷ Se, ³¹ P)]	δ^{77} Se [¹ J(⁷⁷ Se, ³¹ P)]	δ^{13} C(carborane) (¹ <i>J</i> (⁷⁷ Se, ¹³ C)) / { ² <i>J</i> (³¹ P, ¹³ C)}	$\delta^{13}C(Ph) \\ {}^{n}J({}^{31}P,{}^{13}C) \}$
E = lone pair 2	97.7 (s) [268]	643 (d) [268]	79.4 (d) (169) / {15}	133.5(d) {59} (<i>i</i>), 129.5(d) {20} (<i>o</i>), 128.3(d) {4} (<i>m</i>), 129.4(d) {2} (<i>p</i>)
$\mathbf{E} = \mathbf{S}$	77.0 (s) [350]	812 (d) [350]	74.3 (d) (159) / {6}	$134.7(d)$ {69} (<i>i</i>), 132.9(d) {13} (<i>o</i>), 129.4(d) {15} (<i>m</i>), 134.3(d) {4} (<i>p</i>)
E = Se 4	50.7 (s) [350] (Se ₂ P) [815] (Se=P)	810 (d) (Se ₂ P) [350] -354(d)(Se=P) [815]	75.5 (d) (159) / {6}	135.2(d) {57} (<i>i</i>), 132.8(d) {13} (<i>o</i>), 129.8(d) {14}(<i>m</i>), 134.9(d) {3} (<i>p</i>)
5	58.5 (s) [411] (Se-P) [820] (Se=P)	250 (d) (Se-P) [411] -200 (d)(Se=P) [820]	71.1 (d) (CSe-P) {13} 66.1 (s) (C-H)	$\begin{array}{c} 129.3(d) \ \{71\} \ (i), \\ 133.6(d) \ \{11\} \ (o), \\ 129.0(d) \ \{14\} \ (m), \\ 134.8(d) \ \{3\} \ (p), \end{array}$

[a] Measured in CD₂Cl₂ at 23 °C in concentrations < 5 %; coupling constants in Hz (\pm > 1).

selenium. The solution-state structures of 2 to 5 are supported by the NMR data given in Table 1 and in the experimental section.



Figure 1 Molecular structures of the phospholane **2** and its sulfide **3** (ORTEP plots, 50 % probability; hydrogen atoms are omitted for clarity). Selected structural parameters are given in Table 2.

X-Ray structure analysis of the phospholane 2 ant its sulfide 3

The molecular structures of 2 and 3 are shown in Figure 1, and selected structural parameters are given in Table 2. Intermolecular interactions can be safely neglected for the discussion of the molecular structures. Both phospholane rings are folded (see Table 2 for the angles between the SeCCSe and SePSe planes), the folding being more pronounced in the case of 2. There are hardly any data avail-

Table 2 Selected bond lengths /Å and angles $/^{\circ}$ for the compounds 2 and 3.

	2	3
	$[(B_{10}H_{10})C_2]Se_2PPh$	$[(B_{10}H_{10})C_2]Se_2P(S)Ph$
C1-C2	1.647(6)	1.623(12)
C1-Se1	1.930(4)	1.944(9)
C2-Se2	1.931(4)	1.933(9)
Se1-P	2.3106(15)	2.281(2)
Se2-P	2.3061(16)	2.286(2)
P-C3	1.842(6)	1.806(9)
P=S	_	2.003(3)
Se1-C1-C2	117.3(3)	119.1(6)
Se2-C2-C1	117.0(3)	118.3(6)
C1-Se1-P	94.32(14)	95.9(3)
C2-Se2-P	94.52(15)	96.8(3)
Se1-P-Se2	95.15(5)	99.45
S-P-Se1	_	114.49(12)
S-P-Se2	_	116.35(12)
Se1-C1-C2-Se2	1.21	1.70
SeCCSe/Se ₂ P	133.5	147.3
Se ₂ P/SPC3	-	92.9

able to compare the P-Se bond lengths [17] which however, appear to be confirmed by the expected slight shortening upon oxidisng the phosphorus in **3**. The crystal structure of a 1,3,2-dithiaphospholane sulfide has been reported [18] with structural parameters comparable to those of **3**. In comparison to other know P=S distances, the P=S bond length in **3** is longer than in many other phosphorus sulfides [19]. The C-C distances in the carborane are in the usual range [1, 2].

Reactions of the phospholane 2 with Pt^0 and Pd^0 complexes

The phospholane **2** can react with Pt⁰ or Pd⁰ complexes as a donor via the lone pair of electrons at phosphorus. Alternatively, the P-Se bonds may undergo oxidative addition [20]. So far only one example of an oxidative addition of a P-Se bond to Pt(0) or Pd(0) centres has been reported, using the complexes $[M(PEt_3)_3]$ and the phenylselenophosphate P(O)(OPh)₂SePh [20c]. So far, selenophosphanes comparable with 2 have not been used for such reactions. A pathway for the reaction of $[Pt(PPh_3)_2(CH_2=CH_2)]$ with 2 is shown (Scheme 2), and the intermediates 7 and 8 (principal product of the oxidative addition) are proposed. Monitoring of this reaction by ³¹P NMR spectroscopy starting at -40 °C showed that neither 7 nor 8 can be detected. Instead all new growing ³¹P NMR signals belong to the platinum(II) compound 9, a 1,3,2-selenaphosphaplatinacyclopentane derivative, a rare metallophosphane selenide (see Figure 2 for the ³¹P NMR spectrum). The complex 9 decomposes at temperatures above -20 °C into numerous species, among which Ph₃PSe and [1,2-(1,2- $C_2B_{10}H_{10}Se_2Pt(PPh_3)_2$ [15] could be identified by their characteristic ³¹P NMR data. Attempts to crystallise 9 at low temperature have failed so far. However, the proposed structure of 9 can be deduced from a consistent set of ¹³C, ³¹P (Figure 2), ⁷⁷Se (Figure 3) and ¹⁹⁵Pt NMR data (Figure 4), compiled in Table 3.

The ¹³C(carborane) resonances (a broad doublet with ${}^{1}J({}^{31}P,{}^{13}C) = 90$ Hz and a broad singlet) with identical chemical shifts $\delta^{13}C$ for **9** prove the proposed rearrangement [21] (Scheme 2), by which the phosphorus becomes linked to one carborane carbon atom, and is oxidised to the selenide. This is consistent with the ⁷⁷Se satellites for this particular ³¹P NMR signal (Figure 2) and the splitting due to ${}^{1}J({}^{77}Se,{}^{31}P) = 674$ Hz in the ⁷⁷Se NMR spectrum (Figure 3). The ³¹P NMR (Figure 1) and ¹⁹⁵Pt NMR (Figure 4) spectra show clearly that all three phosphorus atoms are directly linked to platinum. There are hardly any NMR data in the literature for comparison. A platinophosphane oxide bearing three different ³¹P nuclei at the platinum



Scheme 2 Reaction of 2 with $[Pt(PPh_3)_2(CH_2=CH_2)]$ involving displacement of ethene (7), oxidative addition (formally P^V in 7 is reduced to P^{III} and Pt^ü is oxidised to Pt^{II} in 8) and rearrangement into 9 (formally an Arbusov-type rearrangement [21]).

$\delta^{13}C$ [¹ J(³¹ P, ¹³ C)]	$ \delta^{31}P \\ {}^{2}J({}^{31}P,{}^{31}P) \} \\ [{}^{1}J({}^{77}Se,{}^{31}P)] \\ ({}^{1}J({}^{195}Pt,{}^{31}P)) $	P (³¹ P, ³¹ P)} (⁷⁷ Se, ³¹ P)] (¹⁹⁵ Pt, ³¹ P))		δ^{77} Se [¹ J(⁷⁷ Se, ³¹ P)]	δ^{195} Pt (${}^{1}J({}^{195}$ Pt, 31 P))
	P(A)	P(B)	P(C)		
92.0 (d) [90] (C-P) 92.0 (s, broad) (C-Se)	10.3 (dd) {26/392} - (2162)	14.8 (dd) {16.4/26} - (3208)	73.1 (dd) {16.4/392} [674] (2582)	-67.8 (d) [674] (Se=P) 531.8 (m broad) (Se-Pt)	-209 (ddd) (2162, P(A) (3208, P(B) (2582, P(C))

Table 3 ¹³C, ³¹P, ⁷⁷Se and ¹⁹⁵Pt NMR data ^[a] of the platinum complex 9

[a] Measured at -40 °C in CD₂Cl₂ (see also Figures 2-4); coupling constants in Hz (± 1).



Figure 2 ³¹P{¹H} NMR spectrum (121.4 MHz) of the complex 9 (in CD₂Cl₂ at -40 °C). The ³¹P^(A.B.C) NMR signals, split into doublets of doublets owing to ²*J*(³¹P,³¹P), are accompanied by ¹⁹⁵Pt (asterisks, Pt) and ⁷⁷Se satellites (arrows, Se) due to ¹*J*(¹⁹⁵Pt,³¹P) (see also Figure 4) and ¹*J*(⁷⁷Se,³¹P) (see Figure 3). Starting material (marked with a cycle) is still present, and first indications of decomposition can be noted (Ph₃PSe).



Figure 3 77 Se{¹H} NMR spectrum (57.2 MHz; spectral window 90 kHz; FT with LB = 4 Hz) of the reaction solution containing the platinum complex 9 along with decomposition products (in CD₂Cl₂ at -45 °C). Weak signals (marked by asterisks), close to those for 9, could represent an isomer of 9. However, supporting evidence from ³¹P NMR spectra is ambiguous.

atom has been described [22] with all ³¹P NMR data, and the trend of these data agrees reasonably well with that observed here for **9**. Typical are the small magnitudes of ${}^{2}J({}^{31}P,{}^{31}P)_{cis}$ and the large magnitude of ${}^{2}J({}^{31}P,{}^{31}P)_{trans}$.

The reaction of **2** with $[Pd(PPh_3)_4]$ was studied. It appears from the ³¹P NMR spectra (numerous broad ³¹P NMR signals in the range for coordinated PPh₃ and **2**) that there is exchange between **2** and PPh₃ at palladium. How-

ever, the situation is not simple, since 2 is probably more bulky than PPh₃ and therefore, may stabilise three-coordinate palladium, depending also on the number of PPh₃ groups being replaced by 2. There are no strong ³¹P NMR signals to indicate products arising from oxidative addition reactions. Considering the large number of ³¹P NMR signals observed for the reaction solution, further preparative work was discouraged.



Figure 4 53.5 MHz 195 Pt{ 1 H} NMR spectrum of the reaction solution containing the platinum complex 9. The splitting into doublets of doublets of doublets, as indicated, corresponds exactly to the 195 Pt- 31 P spin-spin coupling observed in the 31 P NMR spectrum (see Figure 2).

Experimental Section

General

All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The complex $[Pt(PPh_3)_2(C_2H_4)]$ [23] and solutions of the 1,2-diselenido-1,2-dicarba-closo-dodecaborane dianion 1 [15, 24] were prepared according to established procedures; the orthocarborane 1,2-C₂B₁₀H₁₂ (Katchem), BuLi (1.6 M in hexane), iodomethane, dichlorophenylphosphane, sulfur and selenium (Aldrich) were commercially available. - NMR measurements: Bruker ARX 250, Varian Inova 300 and Varian Inova 400 NMR spectrometers; chemical shifts are given relative to SiMe₄ (CD₂Cl₂: δ^{1} H = 5.33; $\delta^{13}C = 53.8$), external Et₂O-BF₃ [$\delta^{>11}B = 0$ for $\Xi^{(11}B) =$ 32.083971 MHz], external 85 % aqueous H_3PO_4 [$\delta^{31}P = 0$ for Ξ (³¹P) = 40.480747 MHz], external Me₂Se [δ ⁷⁷Se = 0 for Ξ (⁷⁷Se) = 19.071523 MHz], and Ξ (¹⁹⁵Pt) = 21.4 MHz for δ ¹⁹⁵Pt = 0. All NMR spectra >were recorded by single pulse methods. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

2-Phenyl-4,5-[1,2(1,2-dicarba-closo-dodecaborano)]-1,3-diselena-2-phospha-cyclopentane (**2**)

To a yellow solution of the 1,2-diselenido-1,2-dicarba-*closo*-dodecaborane dianion (1) (1.94 mmol in 100 mL of diethyl ether) at -78 °C was added dichloro(phenyl)phosphane (0.34 g; 1.94 mmol). The mixture was stirred overnight at room temperature, insoluble materials were filtered off, and the yellow solution was concentrated. Compound **2** was obtained as a yellow solid in almost quantitative yield, and it crystallised as yellow prisms from CH₂Cl₂ at room temperature (m. p. = 182 °C for isolated crystals). ¹H NMR (400 MHz; CD₂Cl₂): δ > = 7.41-7.72 (m, 5H, Ph), 1.49-3.15 (m (broad), 10H, B₁₀H₁₀). ¹¹B{¹H} NMR (96.2 MHz; CD₂Cl₂): δ = 0 (1B), -4 (1B), -6 (3B), -7 (1B), -9 (2B), -11 (2B).

2-Phenyl-2-thio-4,5-[1,2(1,2-dicarba-closo-dodecaborano)]-1,3-diselena- $2-\lambda^5$ -phospha-cyclopentane (3)

To a yellow solution of 2 (0.1 g, 0.24 mmol) in CD₂Cl₂ (1 mL) at room temperature was added sulfur (0.008 g; 0.24 mmol). The mix-

ture was stirred overnight at room temperature and analysed by NMR spectroscopy. The NMR analysis showed the presence of compound **3** (see Table 1), and **3** was isolated in quantitative yield. **3** crystallised as yellow plates from CH₂Cl₂ at room temperature (m. p. = 152 °C for isolated crystals, with beginning decomposition; total decomposition at 167 °C). ¹H NMR (300 MHz; CD₂Cl₂): δ = 7.56-8.21 (m, 5H, Ph), 1.50-3.50 (m (broad), 10H, B₁₀H₁₀). ¹¹B{¹H} NMR (96.2 MHz; CD₂Cl₂): δ = -3 (1B), -4 (2B), -7 (4B), -8 (2B), -10 (1B).

2-Phenyl-2-seleno-4,5-[1,2(1,2-dicarba-closo-dodecaborano)]-1,3-diselena-2- λ^5 -phospha-cyclopentane (4)

Compound 4 was prepared in the same way as 3. The mixture was stirred during three days at room temperature. The reaction of 2 with selenium was slow and accompanied by decomposition. Heating caused faster formation of the selenide and more extensive decomposition. ¹H NMR (400 MHz; CD₂Cl₂): δ = 7.55-7.82 (m, 5H, Ph), 1.55-3.25 (m (broad), 10H, B₁₀H₁₀). ¹¹B{¹H} NMR (96.2 MHz; CD₂Cl₂): δ = -3 (2B), -7 (5B), -8 (3B).

Reaction of 2-phenyl-4,5-[1,2(1,2-dicarba-closododecaborano)]-1,3-diselena-2-phospha-cyclopentane (2) *with methyl iodide*

To a solution of **2** (0.13 g, 0.32 mmol) in CD₂Cl₂ (1 mL) at room temperature was added methyl iodide (0.07 g, 0.48 mmol) (without previous purification). The mixture was stirred overnight at room temperature and analysed by NMR spectroscopy. The ³¹P, ⁷⁷Se, ¹³C and ¹H NMR spectra showed the presence of the selenophosphonic acid derivative **5** as the main product (see Scheme 1, Table 1), the bis(diselane) [-1,2-(1,2-C₂B₁₀H₁₀)-Se-Se-]₂ **6** and other unidentified compounds in low yield [$\delta^{31}P = 28.8 \ ^{1}J(^{77}Se,^{31}P) = 816 \ Hz; 76.1; 73.7 and 72.2 \ ppm]. 5: \ ^{1}H \ NMR \ (400 \ MHz; \ CD_2Cl_2): \delta [^{4}J(^{31}P,^{1}H)] = 7.45-8.05 \ (m, 5H, Ph), 2.29 \ [4] \ (d, 1H, CH), 1.30-3.30 \ (m \ (broad), 10H, B_{10}H_{10}). \ ^{11}B\{^{1}H\} \ NMR \ (96.2 \ MHz; CD_2Cl_2): \delta = -3 \ (2B), -7 \ (1B), -8 \ (1B), -10 \ (1B), -12 \ (2B), -13 \ (3B).$

Table 4Crystal data [25] for the compounds 2 and 3.

	2	3
Empirical formula	$C_8H_{15}B_{10}PSe_2$	$C_8H_{15}B_{10}PSSe_2$
Formula mass	408.19	440.25
Crystal size /mm	0.20x0.14x0.05	0.39x0.30x0.14
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	P21/c
a /Å	9.0450(7)	7.3055(9)
b /Å	10.8030(10)	22.160(3)
c /Å	16.3520(13)	10.6480(12)
βΙ°	101.188(6)	93.726(10)
Volume /Å	1567.4(2)	1720.2(4)
Z	4	4
D_{calcd} /g cm ⁻³	1.730	1.700
$M(Mo-K_{\alpha})/mm^{-1}$	4.797	4.495
F(000)	784	848
Data collection range Θ /°	2.27-25.74	1.84-25.77
Reflections collected	2960	3252
Independent reflections	1635	2245
Data/restraints/parameters	1635/0/250	3252/0/199
Goodness-of-fit on F ²	0.734	1.050
$R_1 [I \ge 2\sigma(I)]$	0.0860	0.1119
wR_2 (all data)	0.0638	0.1962
Max./min. ΔF /e Å ⁻³	0.694/-0.375	1.578/-1.191

3-Phenyl-2,2-bis(triphenylphosphane)-3-seleno-4,5-[1,2(1,2-dicarba-closo-dodecaborano)]-1-selena- $3-\lambda^5$ phospha-2-platina-cyclopentane (**9**)

To a solution of (ethene)bis(triphenylphosphane)platinum (0.2 g, 0.27 mmol) in CD₂Cl₂ (0.5 mL) was added a solution of **2** (0.11 g, 0.27 mmol) in CD₂Cl₂ (0.5 mL) at -78 °C. An orange-red solution was obtained and immediately analysed by ³¹P NMR spectroscopy at -40 °C. The NMR analysis indicated the presence of complex **9** as the main product (see Table 3 and Figures 2 to 4), Ph₃P=Se and the starting material [(Ph₃P)₂Pt(CH₂=CH₂)]. At room temperature, the ³¹P NMR spectrum showed the presence of Ph₃P= Se, (1,2-C₂B₁₀H₁₀-1,2-Se₂)Pt(PPh₃)₂ [15] [$\delta^{31}P = 15.7$ (s), ²*J*(⁷⁷Se, ³¹P)_{*cis/trans*} = 51 Hz, ¹*J*(¹⁹⁵Pt, ³¹P) = 2972.5 Hz] and other unidentified compounds in low concentration [$\delta^{31}P = 15.0$ (s), ¹*J*(¹⁹⁵Pt, ³¹P) = 3679 Hz; 22.6 (s), ¹*J*(¹⁹⁵Pt, ³¹P) = 2963 Hz; 19.7 (s), ¹*J*(¹⁹⁵Pt, ³¹P) = 3248 Hz]. **9**: ¹H NMR (400 MHz; CD₂Cl₂; -40 °C): $\delta > = 7.00-7.67$ (m, 35H, 7Ph), 1.40-2.60 (m (broad), 10H, B₁₀H₁₀).

Crystal structure determinations of the phosphane 2 and its sulphide 3

Details pertinent to the crystal structure determinations are listed in Table 4. The X-ray crystal structure analyses were carried out for single crystals using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit. Crystals of appropriate size were selected in perfluorinated oil at room temperature, and the data collections were carried out at 193(2) K [25]. Structure solution and refinement were accomplished using SIR97 [26], SHELXL-97 [27], and WinGX [28].

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