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Synthesis of germylcopper compounds by hydride method. Crystal structure of $(C_6F_5)_3GeCu(PPh_3)_2$

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Abstract

Germylcopper compounds $Ph_3GeCu(PPh_3)_3$ (**1**) and $(C_6F_5)_3GeCu(PPh_3)_2$ (**2**) were synthesized by reaction of organogermanium hydrides R_3GeH (R = Ph, C_6F_5) with *t*-BuOCu in the presence of PPh_3. The crystal structure of **2** and its analogous $\{(C_6F_5)_3GeCu(PPh_3)_2\}(THF)_2$ (**3**) with two additional solvate THF molecules have been determined by X-ray diffraction method. In both **2** and **3** crystals the Cu atom is bonded to the Ge atom of $(C_6F_5)_3Ge$ group and the two P atoms of PPh_3 ligands and have a slightly distorted planar-trigonal environments. The Cu–Ge distances are 2.370(2), 2.382(2) Å in **2** (for two independent molecules) and 2.348(1) Å in **3**.

Keywords: Germanium; Copper; Hydride method; X-ray diffraction

1. Introduction

Organocopper compounds and organocuprates are well known and widely used in organic synthesis [1]. Organometallic analogs with copper–silicon [2] and copper–germanium bonds [3,4] are rare and not much known about their chemical behavior. Nevertheless such type of organocopper derivatives might be expected as promising reagents in organometallic synthesis. Reported synthetic route to organogermanium derivatives of copper consists of metal–halogen exchange reaction [3]. This method allowed to obtain the germylcopper compounds only in very low yield and they are rather difficult to purify from lithium chloride as a side product. Here we report that the titled compounds can be synthesized in high yields and without additional purification by hydride method which is known to be a convenient synthetic pathway to bi- and polyelement organometallic compounds [5].

2. Results and discussion

Organogermanium hydrides R_3GeH (R = Ph, C_6F_5) were found to react with *t*-BuOCu in DME at 50°C and form organogermanium derivatives of copper **1** and **2** in 83.8–92.0% yield.

$$R_3GeH + t\text{-BuOCu} + n PPh_3 \xrightarrow[50°C]{DME} \mathbf{1(2)} + nt\text{-BuOH}$$

R = Ph, $n = 3$; R = C_6F_5, $n = 2$

Complex **1** was isolated as colorless unstable in air crystalline solid which according elemental analysis, m. pt. and IR data is identical to germylcopper compound originally obtained by the reaction of Ph_3GeLi with CuCl [3]. The novel compound **2** was isolated as stable in air colorless crystals soluble in THF, DME, sparingly soluble in benzene, insoluble in hexane. It melts with decomposition at 212–214°C. IR spectrum shows the absorption bands of $(C_6F_5)_3Ge$ fragment and of coordinated PPh_3 ligands. The THF solvate compound **3** was isolated after recrystallization of **2** from THF.

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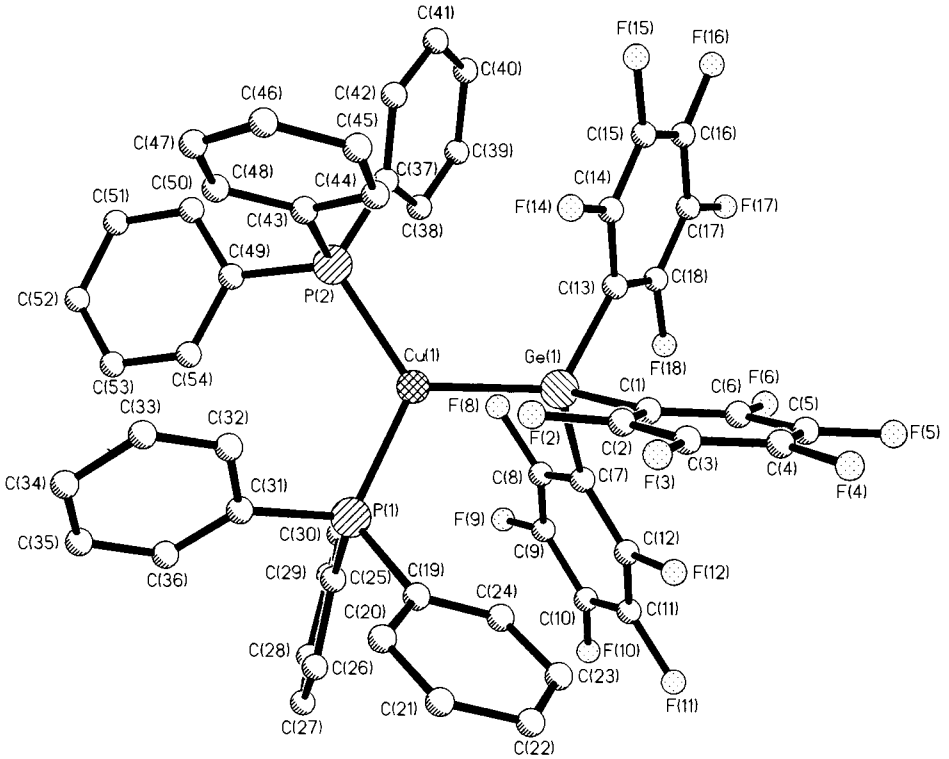

Fig. 1. The general view of the $(C_6F_5)_3GeCu(PPh_3)_2$ in **3** and atom labeling.

The crystal structure of **2** and its analogous **3** with two additional solvate THF molecules have been determined by X-ray diffraction method. In both crystals the $(C_6F_5)_3GeCu(PPh_3)_2$ molecule have a similar structure. The Cu atom is bonded to the Ge atom of $(C_6F_5)_3Ge$ group and the two P atoms of PPh_3 ligands and have a slightly distorted planar-trigonal environments (Fig. 1). Sums of the bond angles at the Cu atoms are 360.0° (359.8°) in **2** (here and below the values for second symmetrically independent molecule in **2** are given in parenthesis) and 359.9° in **3** and the values of these angles are in the ranges 117.2(1)–123.1(1)° (115.0(1)–123.1(1)°) in **2** and 116.7(1)–122.0(1)° in **3** (Table 1).

The Cu–Ge distances 2.382(2), 2.370(2) and 2.348(1) Å found in neutral **2** and **3** are slightly longer then those in anion $[(Ph_3Ge)_2Cu]^-$ 2.339 and 2.336 Å [4]. The Cu(1)–P(1), Cu(1)–P(2) distances are 2.269(3), 2.256(3) Å (2.272(3), 2.274(3) Å) in **2** and 2.255(3), 2.248(3) Å in **3**. Some differences between the similar bond lengths found in **2** and **3** seem to be related with differences of crystal packing in these compounds.

The Ge and P atoms of the $(C_6F_5)_3Ge$ groups and PPh_3 ligands in **2** and **3** have a distorted tetrahedral coordination (Table 1). The Ge–C and P–C distances are in the ranges: 1.994(9)–2.028(7) Å (average 2.013(21) Å) and 1.811(7)–1.845(9) Å (average 1.825(12) Å) in **2** (for two independent molecules); 1.998(9)–2.025(9) Å (average 2.008(13) Å) and 1.806(9)–1.840(10) Å (average 1.827(12) Å) in **3**, respectively. The average C–F, C–C distances of $(C_6F_5)_3Ge$ groups and the C–C distances of PPh_3 ligands are 1.35(1), 1.38(2) and 1.38(2) Å in **2** (the average values for two independent molecules); 1.35(1), 1.37(2) and 1.38(2) Å in **3**.

3. Experimental section

3.1. Preparation of *1* and *2*

The synthesis and isolation of **1** and **2** were performed under vacuum in sealed ampoules using thoroughly dried solvents. The IR spectra were recorded on a Perkin–Elmer-577 spectrometer.

3.1.1. Preparation of *1*

A mixture of Ph_3GeH (3.80 g, 12.5 mmol), *t*-BuOCu (1.68 g, 12.3 mmol) and PPh_3 (9.75 g, 37.2 mmol) in 40 ml of DME was heated to 50°C for ca. 2 h. The solvent and volatile products were removed from the reaction solution and the residue was washed with hexane (3 × 15 ml), dried in vacuum to yield 13.06 g, (92.0%) of **1**, m. pt: (dec.) 132–134°C. Anal. Calcd. for $C_{72}Cu_1H_{60}Ge_1P_3$: C, 74.93; Cu, 5.50; H, 5.20. Found: C, 74.40; Cu, 5.71; H,5.95. IR (Nujol, cm^{-1}): (Ph–Ge) 3040, 1480, 1425, 1085, 1065, 1020, 995, 730, 690, 460; (coordinated PPh_3) 3040, 1420, 1090, 1020, 740, 685, 500. In volatile products 0.77 g (84.6%) of *t*-BuOH was found.

Table 1
Selected bond lengths (Å) and bond angles (°) in **2** and **3**

	2, molecule A	**2**, molecule B	**3**
Bond lengths			
Cu(1)–Ge(1)	2.370(2)	2.382(2)	2.348(1)
Cu(1)–P(1)	2.269(3)	2.272(3)	2.255(3)
Cu(1)–P(2)	2.256(3)	2.274(3)	2.248(3)
Ge(1)–C(1)	2.000(7)	1.994(9)	1.988(9)
Ge(1)–C(7)	2.028(7)	2.014(8)	2.025(9)
Ge(1)–C(13)	2.016(8)	2.017(8)	2.003(9)
P(1)–C(19)	1.818(9)	1.826(10)	1.820(10)
P(1)–C(25)	1.841(7)	1.816(9)	1.823(9)
P(1)–C(31)	1.822(8)	1.835(8)	1.839(10)
P(2)–C(37)	1.825(8)	1.825(9)	1.840(10)
P(2)–C(43)	1.829(8)	1.845(9)	1.823(9)
P(2)–C(49)	1.811(7)	1.827(10)	1.806(9)
Bond angles			
Ge(1)–Cu(1)–P(1)	117.2(1)	115.0(1)	116.7(1)
Ge(1)–Cu(1)–P(2)	119.7(1)	121.7(1)	122.0(1)
P(1)–Cu(1)–P(2)	123.1(1)	123.1(1)	121.2(1)
Cu(1)–Ge(1)–C(1)	121.5(2)	122.8(3)	115.4(2)
Cu(1)–Ge(1)–C(7)	109.8(2)	120.6(2)	112.6(2)
Cu(1)–Ge(1)–C(13)	118.0(2)	95.1(3)	121.1(3)
C(1)–Ge(1)–C(7)	104.8(3)	108.4(3)	104.6(4)
C(1)–Ge(1)–C(13)	95.7(3)	103.9(3)	96.8(4)
C(7)–Ge(1)–C(13)	105.1(3)	103.3(4)	104.1(4)
Cu(1)–P(1)–C(19)	117.1(3)	116.1(3)	117.5(3)
Cu(1)–P(1)–C(25)	110.7(3)	111.5(3)	110.0(3)
C(19)–P(1)–C(25)	104.6(4)	105.9(4)	102.6(4)
Cu(1)–P(1)–C(31)	115.1(3)	116.7(3)	114.8(3)
C(19}–P(1)–C(31)	103.3(4)	101.7(4)	103.9(4)
C(25)–P(1)–C(31)	104.8(4)	103.5(4)	106.9(4)
Cu(1)–P(2)–C(37)	115.0(3)	113.2(3)	114.5(3)
Cu(1)–P(2)–C(43)	121.7(3)	121.7(2)	111.7(3)
C(37)–P(2)–C(43)	102.4(4)	102.4(4)	104.8(4)
Cu(1)–P(2)–C(49)	105.3(3)	110.0(3)	117.1(3)
C(37)–P(2)–C(49)	107.1(4)	104.0(4)	117.1(3)
C(43)–P(2)–C(49)	104.2(4)	103.8(4)	104.6(4)

3.1.2. Preparation of ***2***

A mixture of $(C_6F_5)_3GeH$ (1.94 g, 3.38 mmol), *t*-BuOCu (0.46 g, 3.37 mmol) and PPh_3 (1.77 g, 6.76 mmol) in 20 ml of DME was heated to 50°C for ca. 4 h. The solvent and volatile products were removed from the reaction solution and the residue was washed with hexane (3x15 ml), dried in vacuum to yield 3.28 g, (83.8%) of **2**, m. pt: (dec.) 212–214°C. Anal. Calcd for $C_{54}Cu_1H_{30}Ge_1F_{15}P_2$: C, 55.82; Cu, 5.65; H, 2.60. Found: C, 55.53; Cu, 5.15; H, 2.81. IR (Nujol, cm^{-1}): (C_6F_5-Ge) 1640, 1500, 1490, 1370, 1260, 1070, 960, 770, 605 (coordinated PPh_3) 3040, 1420, 1090, 1020, 740, 685, 500. In volatile products 0.20 g (80.0%) of *t*-BuOH was found.

The crystalline samples of unsolvated **2** suitable for X-ray analysis were obtained by crystallization of the compound from benzene–hexane mixture. The crystals of THF-solvate **3** for X-ray study were isolated after recrystallization of **2** from THF.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **2**

	x	*y*	*z*	U_{eq}
Cu(1A)	4385(1)	5591(1)	7545(1)	34(1)
Ge(1A)	5974(1)	5105(1)	7632(1)	35(1)
P(1A)	3232(2)	5116(1)	8071(1)	38(1)
P(2A)	4076(2)	6483(1)	6948(1)	36(1)
F(2A)	6175(5)	6101(3)	9061(3)	80(3)
F(3A)	7828(6)	6586(4)	10 149(3)	126(4)
F(4A)	9723(5)	6131(4)	10 178(3)	125(4)
F(5A)	9922(4)	5177(4)	9113(3)	98(3)
F(6A)	8296(4)	4696(3)	8009(3)	63(2)
F(8A)	4413(4)	4129(3)	6483(3)	62(2)
F(9A)	3710(4)	2776(3)	6283(3)	84(3)
F(1OA)	4649(5)	1949(3)	7191(3)	93(3)
F(11A)	6231(5)	2521(3)	8320(3)	87(3)
F(12A)	6907(4)	3869(3)	8549(3)	64(2)
F(14A)	7244(4)	6430(2)	7519(3)	59(2)
F(15A)	8284(4)	6799(3)	6609(3)	77(3)
F(16A)	8358(4)	5851(4)	5478(3)	89(3)
F(17A)	7485(4)	4531(3)	5328(3)	83(3)
F(18A)	6502(4)	4134(3)	6262(3)	64(2)
C(1A)	7169(6)	5375(4)	8490(4)	39(3)
C(2A)	7106(7)	5861(5)	9064(5)	53(4)
C(3A)	7934(9)	6112(5)	9622(5)	68(4)
C(4A)	8884(9)	5877(6)	9642(5)	78(5)
C(5A)	8999(7)	5396(5)	9093(5)	62(4)
C(6A)	8142(6)	5159(4)	8540(4)	45(3)
C(7A)	5701(6)	4054(4)	7510(4)	37(3)
C(8A)	4881(7)	3737(4)	6951(4)	45(3)
C(9A)	4521(7)	3048(5)	6836(5)	60(4)
C(10A)	4962(8)	2638(5)	7294(5)	59(4)
C(11A)	5783(8)	2920(5)	7857(5)	59(4)
C(12A)	6125(7)	3625(4)	7965(4)	47(3)
C(13A)	6799(6)	5289(4)	6937(4)	38(3)
C(14A)	7291(6)	5928(4)	6978(4)	38(3)
C(15A)	7833(7)	6141(5)	6521(5)	52(4)
C(16A)	7881(6)	5681(5)	5963(5)	55(4)
C(17A)	7417(6)	4997(5)	5868(4)	55(4)
C(18A)	6911(6)	4808(5)	6363(4)	44(3)
C(19A)	3557(6)	4349(4)	8459(4)	44(3)
C(20A)	4469(7)	4428(5)	8996(5)	65(4)
C(21A)	4794(9)	3882(6)	9332(5)	73(5)
C(22A)	4224(11)	3246(6)	9111(7)	85(6)
C(23A)	3327(10)	3148(5)	8579(6)	81(5)
C(24A)	3005(8)	3698(5)	8244(5)	66(4)
C(25A)	1957(6)	4841(4)	7434(4)	43(3)
C(26A)	1959(8)	4459(6)	6790(5)	80(5)
C(27A)	1063(9)	4271(7)	6285(6)	98(6)
C(28A)	131(8)	4456(6)	6376(6)	75(5)
C(29A)	124(7)	4848(5)	7005(5)	66(4)
C(30A)	1024(6)	5026(4)	7530(4)	48(3)
C(31A)	2957(6)	5698(4)	8789(4)	41(3)
C(32A)	3294(7)	6393(5)	8892(4)	52(4)
C(33A)	3083(8)	6856(5)	9416(5)	71(5)
C(34A)	2563(8)	6597(6)	9877(5)	67(4)
C(35A)	2244(7)	5911(6)	9794(4)	61(4)
C(36A)	2441(7)	5445(5)	9255(4)	56(4)
C(37A)	4857(5)	6578(4)	6322(4)	33(3)
C(38A)	4845(6)	6003(4)	5830(4)	45(3)
C(39A)	5334(7)	6052(5)	5298(4)	55(4)
C(40A)	5872(7)	6667(5)	5258(5)	59(4)
C(41A)	5920(7)	7246(5)	5759(5)	65(4)
C(42A)	5401(6)	7208(4)	6287(4)	48(3)
C(43A)	2769(6)	6575(4)	6434(4)	42(3)

Table 2 (continued)

	x	y	z	U_{eq}
C(44A)	1915(8)	6342(6)	6632(6)	82(5)
C(45A)	931(8)	6387(6)	6260(7)	97(6)
C(46A)	771(8)	6659(5)	5660(6)	73(5)
C(47A)	1596(9)	6906(6)	5445(6)	83(5)
C(48A)	2597(7)	6863(5)	5823(5)	67(4)
C(49A)	4422(6)	7259(4)	7614(4)	41(3)
C(50A)	3715(6)	7717(4)	7745(5)	49)3)
C(51A)	3970(8)	8249(5)	8328(5)	64(4)
C(52A)	4945(9)	8339(6)	8768(5)	80(5)
C(53A)	5669(8)	7902(6)	8646(5)	76(5)
C(54A)	5417(7)	7360(5)	8069(5)	58(4)
Cu(1B)	11 302(1)	9730(1)	12 651(1)	38(1)
Ge(1B)	10 133(1)	10 582(1)	12 707(1)	41(1)
P(1B)	10 836(2)	8906(1)	11 664(1)	43(1)
P(2B)	12 706(2)	9707(1)	13 564(1)	41(1)
F(2B)	8729(4)	11 835(3)	12 588(3)	72(2)
F(3B)	8882(5)	12 977(3)	12 005(4)	105(3)
F(4B)	10 358(7)	13 172(4)	11 299(4)	126(4)
F(5B)	11 686(6)	12 222(4)	11 185(4)	119(4)
F(6B)	11 553(4)	11 073(3)	11 765(3)	82(3)
F(8B)	8471(4)	10 692(3)	13 738(3)	76(3)
F(9B)	8746(5)	11 450(3)	15 008(3)	99(3)
F(1OB)	10 509(6)	12 352(3)	15 602(3)	98(3)
F(11B)	11 994(5)	12 485(3)	14 898(3)	82(3)
F(12B)	11 781(4)	11 671(3)	13 641(3)	62(2)
F(14B)	9193(4)	9369(3)	13 198(3)	63(2)
F(15B)	7479(5)	8449(3)	12 662(3)	91(3)
F(16B)	5982(5)	8680(4)	11 547(4)	112(3)
F(17B)	6240(4)	3838(4)	10 960(3)	103(3)
F(18B)	7984(4)	10 718(3)	11 430(3)	72(2)
C(1B)	10 133(6)	11 395(4)	12 205(4)	43(3)
C(2B)	9482(7)	11 901(4)	12 232(5)	52(4)
C(3B)	9539(8)	12 506(5)	11 947(5)	64(4)
C(4B)	10 289(10)	12 602(5)	11 589(6)	77(5)
C(5B)	10 945(8)	12 115(6)	11 527(5)	72(5)
C(6B)	10 863(7)	11 517(5)	11 824(5)	55(4)
C(7B)	10 120(6)	11 142(4)	13 638(4)	44(3)
C(8B)	9376(7)	11 111(4)	14 011(5)	56(4)
C(9B)	9490(8)	11 505(5)	14 655(5)	66(4)
C(1OB)	10 378(9)	11 964(5)	14 964(5)	63(4)
C(11B)	11 142(8)	12 033(5)	14 604(5)	58(4)
C(12B)	10 990(7)	11 618(4)	13 967(5)	50(4)
C(13B)	8663(6)	10 101(4)	12 339(5)	51(4)
C(14B)	8469(7)	9510(5)	12 631(4)	51(4)
C(15B)	7593(8)	9029(5)	12 367(5)	63(4)
C(16B)	6830(8)	9142(7)	11 817(6)	78(5)
C(17B)	6991(7)	9730(6)	11 520(6)	68(5)
C(18B)	7882(7)	10 161(5)	11 777(5)	52(4)
C(19B)	11 744(7)	8863(4)	11 107(4)	47(3)
C(20B)	12 757(8)	9160(6)	11 395(6)	76(5)
C(21B)	13 467(10)	9158(7)	10 992(8)	102(7)
C(22B)	13 152(12)	8852(7)	10 298(8)	97(7)
C(23B)	12 177(12)	8552(6)	10 000(6)	84(6)
C(24B)	11 469(9)	8558(5)	10 407(5)	65(4)
C(25B)	10 652(7)	8040(4)	11 877(4)	50(3)
C(26B)	10 992(8)	7457(5)	11 565(5)	68(4)
C(27B)	10 820(11)	6827(5)	11 769(6)	93(6)
C(28B)	10 349(11)	6767(6)	12 292(7)	99(7)
C(29B)	10 002(10)	7315(7)	12 603(7)	98(7)
C(30B)	10149(8)	7966(6)	12 405(5)	75(5)
C(31B)	9608(6)	8966(4)	11 023(4)	45(3)
C(32B)	8778(8)	8448(5)	10 823(5)	66(4)

Table 2 (continued)

	x	y	z	U_{eq}
C(33B)	7875(9)	8535(6)	10 347(6)	83(5)
C(34B)	7811(9)	9128(7)	10 045(5)	81(5)
C(35B)	8624(8)	9651(6)	10 244(5)	70(4)
C(36B)	9518(8)	9567(5)	10 730(5)	60(4)
C(37B)	12 668(7)	10 261(4)	14 378(4)	47(3)
C(38B)	11 794(8)	10 137(5)	14 634(5)	58(4)
C(39B)	11 761(10)	10 532(6)	15 275(5)	79(5)
C(40B)	12 540(12)	11 061(7)	15 618(5)	88(6)
C(41B)	13 385(10)	11 181(6)	15 362(6)	83(5)
C(42B)	13 449(8)	10 777(5)	14 737(5)	60(4)
C(43B)	13 045(6)	8888(4)	13 869(4)	41(3)
C(44B)	12 845(7)	8278(4)	13 384(5)	59(4)
C(45B)	13 106(8)	7659(5)	13 602(6)	72(5)
C(46B)	13 543(8)	7657(5)	14 311(5)	65(4)
C(47B)	13 731(8)	8253(5)	14 790(6)	69(5)
C(48B)	13 476(7)	8870(5)	14 573(5)	56(4)
C(49B)	13 891(7)	10 065(5)	13 369(4)	52(4)
C(50B)	14 842(7)	9818(6)	13 560(5)	71(5)
C(51B)	15 705(9)	10 110(7)	13 392(7)	94(6)
C(52B)	15 645(9)	10 631(7)	13 022(7)	90(6)
C(53B)	14 709(9)	10 885(5)	12 814(6)	78(5)
C(54B)	13 844(8)	10 588(5)	12 989(5)	65(4)

3.2. X-ray diffraction studied

X-ray data for **2** and **3** were collected on a Siemens P3/PC diffractometer at 296 and 153 K, respectively (Mo K_α radiation, graphite monochromator, θ–2θ scan mode, $2 \le \theta \le 48$ and $2 \le \theta \le 52°$, 14911 and 5109 independent reflections measured, 11073 ($F > 6\sigma(F)$) and 3811 ($F > 4\sigma(F)$) reflections observed for **2** and **3**, respectively). Crystal data at 296 K for **2**: $C_{54}H_{30}CuF_{15}GeP_2$, fw 1161.8, space group $P\bar{1}$, $a =$ 13.339(7) Å, $b = 19.575(9)$ Å, $c = 19.829(12)$ Å, $\alpha =$ 98.22(4)°, $\beta = 104.10(4)°$, $\gamma = 94.62(4)°$, $V = 4934(4)$ Å^3, $Z = 4$ (two independent molecules), $D_{calc} = 1.564$ g cm^{-3}, $\mu = 1.199$ mm^{-1}. Crystal data at 153 K for **3**: $C_{62}H_{46}CuF_{15}GeP_2$, fw 1306.10, space group $P2_12_12_1$, $a = 15.821(2)$ Å, $b = 18.904(3)$ Å, $c = 18.926(3)$ Å, $V =$ 5660.3(14) Å^3, $Z = 4$, $D_{calc} = 1.533$ g cm^{-3}, $\mu = 1.060$ mm^{-1}. The structures of **2** and **3** were solved by the direct methods. Besides main molecules the crystal structure of **3** contains two solvate THF molecules. In both structures all non-H atoms were refined anisotropically. The positions of the H atoms were calculated using a geometrical conditions and do not refined. The crystal structure of **3** has the polar $P2_12_12_1$ space group symmetry. Therefor it has been also refined with invert atomic coordinates to obtain the absolute configuration of molecules **3**. Given herein the atomic coordinates corresponding the absolute configuration of **3** because of it give the less value of R-factor. The final refinements converged at $R = 0.081$, $R_w = 0.089$, $S = 3.16$ (**2**)

Table 3
Atomic coordinates ($\times 10^3$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **3**

	x	y	z	U_{eq}
Cu(1)	3962(1)	5274(1)	28(1)	29(1)
Ge(1)	4125(1)	4056(1)	230(1)	28(1)
P(1)	5063(1)	5841(1)	−474(1)	31(1)
P(2)	2791(1)	5862(1)	358(1)	30(1)
F(2)	3929(3)	4461(2)	−1366(2)	51(2)
F(3)	4024(4)	3693(3)	−2548(3)	72(2)
F(4)	4247(4)	2282(3)	−2479(3)	72(2)
F(5)	4360(3)	1630(3)	−1220(3)	62(2)
F(6)	4334(3)	2393(2)	−15(3)	47(2)
F(8)	4656(3)	4441(3)	1703(3)	53(2)
F(9)	6111(4)	4366(3)	2416(3)	74(2)
F(10)	7463(4)	3679(4)	1847(3)	85(3)
F(11)	7338(3)	3109(3)	534(3)	69(2)
F(12)	5914(3)	3205(2)	−189(3)	45(2)
F(14)	2288(3)	3958(2)	−97(2)	43(2)
F(15)	964(3)	3308(3)	493(3)	55(2)
F(16)	1186(3)	2476(3)	1648(3)	64(2)
F(17)	2749(3)	2282(3)	2182(3)	63(2)
F(18)	4078(3)	2950(3)	1624(3)	50(2)
C(1)	4157(5)	3457(4)	−631(4)	30(3)
C(2)	4067(6)	3763(4)	−1301(4)	32(3)
C(3)	4089(7)	3370(5)	−1920(5)	51(4)
C(4)	4191(6)	2664(5)	−1884(5)	45(3)
C(5)	4264(5)	2336(4)	−1259(5)	42(3)
C(6)	4245(5)	2735(4)	−630(4)	32(3)
C(7)	5210(5)	3824(4)	746(4)	27(3)
C(8)	5319(5)	4110(5)	1395(5)	39(3)
C(9)	6052(7)	4060(5)	1777(5)	54(4)
C(10)	6740(6)	3735(5)	1469(6)	52(4)
C(11)	6662(6)	3440(5)	832(6)	42(4)
C(12)	5908(5)	3502(4)	463(4)	32(3)
C(13)	3239(5)	3502(4)	744(4)	29(3)
C(14)	2431(5)	3556(4)	488(4)	29(3)
C(15)	1750(5)	3220(4)	779(5)	36(3)
C(16)	1848(6)	2793(4)	1340(5)	39(3)
C(17)	2645(6)	2710(4)	1639(5)	42(3)
C(18)	3316(5)	3063(4)	1317(4)	32(3)
C(19)	5629(5)	5385(4)	−1177(4)	36(3)
C(20)	5754(6)	5691(5)	−1851(5)	51(3)
C(21)	6159(7)	5308(7)	−2373(6)	77(5)
C(22)	6473(8)	4633(7)	−2219(7)	89(6)
C(23)	6323(9)	4348(6)	−1594(8)	97(6)
C(24)	5932(6)	4727(5)	−1052(5)	58(4)
C(25)	5888(5)	5992(4)	181(4)	35(3)
C(26)	6708(5)	6183(4)	11(5)	50(3)
C(27)	7290(6)	6301(6)	545(7)	66(4)
C(28)	7070(7)	6224(6)	1234(6)	67(5)
C(29)	6271(8)	6010(6)	1417(5)	66(4)
C(30)	5667(6)	5906(5)	887(5)	50(3)
C(31)	4803(5)	6705(4)	−862(4)	35(3)
C(32)	4093(6)	6755(5)	−1261(5)	52(3)
C(33)	3843(7)	7381(8)	−1546(7)	86(5)
C(34)	4297(7)	7993(6)	−1398(7)	83(5)
C(35)	4972(7)	7953(5)	−975(6)	70(5)
C(36)	5242(6)	7314(5)	−689(5)	52(4)
C(37)	2101(5)	5372(4)	963(4)	35(3)
C(38)	2471(6)	5067(5)	1546(4)	40(3)
C(39)	1095(7)	4689(5)	2027(5)	53(4)
C(40)	1152(6)	4592(5)	191O(5)	51(4)
C(41)	787(6)	4882(5)	1323(5)	54(4)
C(42)	1247(5)	5278(5)	843(5)	44(3)
C(43)	2126(5)	6080(4)	−394(4)	31(3)

Table 3 (continued)

	x	y	z	U_{eq}
C(44)	1937(6)	5545(4)	−877(4)	43(3)
C(45)	1431(7)	5683(5)	−1442(5)	62(4)
C(46)	1156(7)	6358(5)	−1594(5)	57(4)
C(47)	1368(7)	6883(5)	−1139(6)	59(4)
C(48)	1857(6)	6752(5)	−540(5)	47(3)
C(49)	2941(5)	6694(4)	811(4)	31(3)
C(50)	2332(5)	7002(4)	1237(4)	40(3)
C(51)	2467(7)	7661(5)	1547(5)	53(4)
C(52)	3207(7)	8023(5)	1413(5)	48(4)
C(53)	3804(7)	7739(5)	1010(6)	60(4)
C(54)	3677(6)	7083(5)	698(5)	55(4)
O(1)	5410(11)	1376(13)	2199(11)	293(13)
O(2)	9056(10)	5259(8)	137(13)	238(11)
C(1T)	6651(12)	1848(10)	1686(10)	136(9)
C(2T)	5785(14)	1848(14)	1575(15)	288(18)
C(3T)	6812(14)	1199(9)	2061(10)	145(10)
C(4T)	6093(12)	945(8)	2329(8)	102(6)
C(5T)	9344(22)	5217(22)	−599(18)	281(22)
C(6T)	8434(19)	4605(15)	106(23)	255(21)
C(7T)	8504(33)	4367(20)	−524(18)	286(27)
C(8T)	8635(22)	5021(24)	−949(16)	287(23)

and $R = 0.047$, $R_w = 0.047$, $S = 1.42$ (**3**) for observed reflections. The weight scheme was $w = 1/[\sigma^2(F_o^2) + aF_o^2]$ with a equal 0.0003 (**2**), 0.0003 (**3**). All calculations were performed using the SHELXTL-PLUS [6]. The final atomic coordinates for **2** and **3** were given in Tables 2 and 3, respectively.

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