Crystal and molecular structures of three germylated steroids

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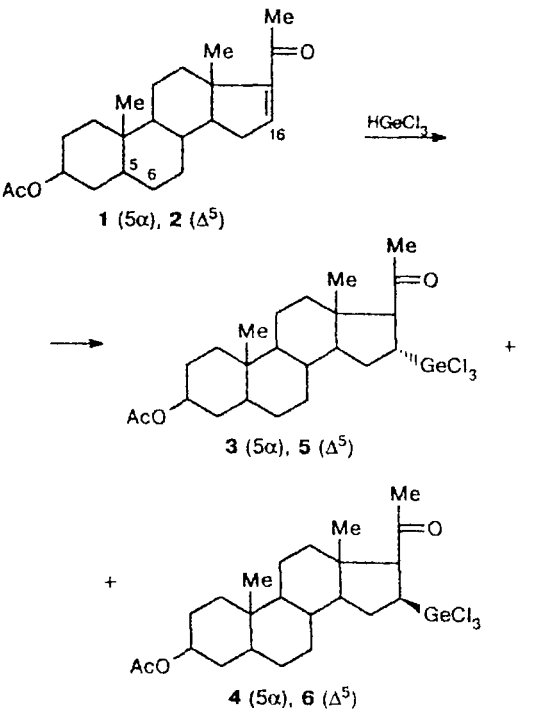
Germylated steroids were studied by X-ray diffraction analysis for the first time. The conformational parameters of the molecules in the crystals are discussed. The three-center hypervalent O—Ge—Cl bonds are observed in two β-isomers. The geometric parameters of the hypervalent units are compared.

Key words: X-ray diffraction analysis; steroids, germanium derivatives, hypervalent bond.

Steroids belong to one of the most important classes of natural biologically active compounds. Previously, we for the first time synthesized steroids modified with germanium by hydrogermylation of the double bond.[1] Fused steroid enones, namely, 3β-acetoxy-5α-pregn-16-en-20-one (**1**) and 3β-acetoxypregna-5,16-dien-20-one (**2**), were objects of studies. Addition of $HGeCl_3$ at the Δ^{16} double bond of the above enones afforded two stereoisomers (of four theoretically possible isomers), namely, 3β-acetoxy-16α-trichlorogermyl-5α-pregnan-20-one (**3**) and 3β-acetoxy-16β-trichlorogermyl-5α-pregnan-20-one (**4**) in the case of enone **1** and 3β-acetoxy-16α-trichlorogermylpregn-5-en-20-one (**5**) and 3β-acetoxy-16β-trichlorogermylpregn-5-en-20-one (**6**) in the case of enone **2**.

The crystal and molecular structures of three synthesized compounds **4**—**6** were established by X-ray diffraction analysis. Therefore, addition of trichlorogermane at the conjugated Δ^{16} double bond of steroids afforded not only α-isomers, which is typical of the chemistry of steroids, but also β-isomers. The formation of the latter is attributable to the benefit from the coordination bond between the Ge atom and the O atom of the carbonyl group.



Results and Discussion

The structures of molecules **4**—**6** are shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2, respectively. The endocyclic torsion angles are listed in Table 3. In crystals **4** and **5**, there are two symmetrically independent molecules (**A** and **B**) per asymmetric unit. The differences in the corresponding geometric parameters of molecules **A** and **B** are no more than 3σ, except for the fragments containing the Ge atom. Note that the very poor accuracy of determination of the structure of **5** does not allow one to discuss the deviations of its geometric parameters from the normal values. For example, these deviations for the bond lengths are as large as 0.1 Å (see Table 1). The bond lengths and bond angles in the steroid frameworks are close to those

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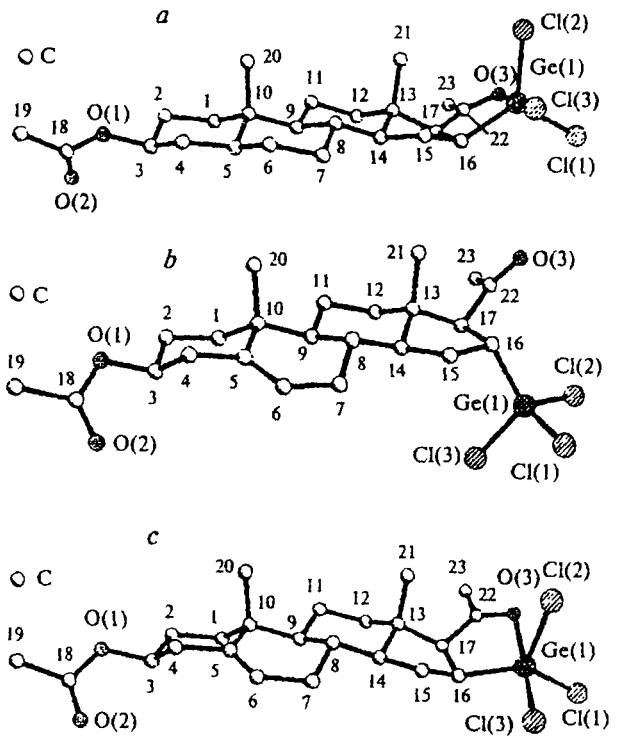

Fig. 1. Structures of molecules **4** (*a*), **5** (*b*), and **6** (*c*) (the hydrogen atoms are omitted; for compounds **4** and **5**, one of two crystallographically independent molecules is shown).

in the analogous derivatives of steroids to within the experimental errors.[2] The conformations of rings *A*—*D* (Table 4) are also typical of the compounds of this series. In all the molecules under study, rings *A* and *C* adopt the 3α,10β-chair and 9α,13β-chair conformations, respectively. In compounds **5** and **6**, ring *B* adopts the 9α,8β-half-chair conformation due to the presence of the double C(5)=C(6) bond, unlike the 5α,8β-chair conformation in molecule **4**, in which the above bond is saturated. The conformations of ring *D* are typical of the majority of steroids (13α,14β-twist (**4** and **5**) or 14α-envelope (**6**)). In the case of the actually observed configuration of the C(3) atom, the planar (to within ±0.04 Å) 3β-acetoxy group can add to the saturated ring *A* in two energetically equivalent orientations (either the first or the second fragment, C(2)C(3)O(1)C(18) or C(4)C(3)O(1)C(18), has a transoid configuration). In molecules **5A,B** and **6**, the first orientation is realized (the C(2)—C(3)—O(1)—C(18) torsion angles are 156°, 148°, and 158°, respectively). In molecules **4A,B**, the second orientation is observed (the C(4)—C(3)—O(1)—C(18) torsion angles are 152° and 132°, respectively). The crystallographically independent molecules in the structures of **4** and **5** have fundamentally different molecular environments. Therefore, it can be suggested that the variations in the values of the above-mentioned angles in two groups of the molecules

Table 1. Bond lengths (*d*) in molecules **4**, **5**, and **6**

Bond	*d*/Å				
	4A	**4B**	**5A**	**5B**	**6**
Ge(1)—Cl(1)	2.149(3)	2.138(3)	2.08(1)	2.10(1)	2.138(1)
Ge(1)—Cl(2)	2.102(4)	2.132(4)	2.04(1)	2.06(1)	2.137(1)
Ge(1)—Cl(3)	2.202(3)	2.172(4)	2.12(1)	2.15(1)	2.197(1)
Ge(1)—O(3)	2.292(7)	2.393(7)	—	—	2.381(3)
Ge(1)—C(16)	1.96(1)	1.95(1)	1.89(2)	1.93(2)	1.946(5)
O(1)—C(3)	1.46(2)	1.45(2)	1.46(2)	1.45(2)	1.459(5)
O(1)—C(18)	1.32(2)	1.32(2)	1.32(2)	1.32(3)	1.352(6)
O(2)—C(18)	1.20(2)	1.17(2)	1.22(2)	1.26(3)	1.199(6)
O(3)—C(22)	1.22(1)	1.20(1)	1.22(2)	1.24(3)	1.217(6)
C(1)—C(2)	1.53(1)	1.51(1)	1.49(2)	1.58(3)	1.530(7)
C(1)—C(10)	1.54(1)	1.52(1)	1.60(3)	1.57(3)	1.547(7)
C(2)—C(3)	1.46(2)	1.48(2)	1.47(3)	1.48(3)	1.515(7)
C(3)—C(4)	1.53(2)	1.50(2)	1.55(3)	1.53(3)	1.507(8)
C(4)—C(5)	1.56(2)	1.52(1)	1.49(3)	1.46(3)	1.520(6)
C(5)—C(6)	1.52(2)	1.50(1)	1.38(3)	1.39(3)	1.323(7)
C(5)—C(10)	1.53(2)	1.55(2)	1.56(3)	1.56(3)	1.529(7)
C(6)—C(7)	1.56(2)	1.52(1)	1.47(2)	1.45(3)	1.502(7)
C(7)—C(8)	1.53(1)	1.52(2)	1.54(3)	1.50(3)	1.554(6)
C(8)—C(9)	1.56(1)	1.53(2)	1.49(3)	1.47(3)	1.533(7)
C(8)—C(14)	1.51(2)	1.54(1)	1.54(3)	1.49(3)	1.519(6)
C(9)—C(10)	1.55(1)	1.57(1)	1.59(2)	1.61(3)	1.562(6)
C(9)—C(11)	1.53(1)	1.51(1)	1.55(3)	1.58(3)	1.535(6)
C(10)—C(20)	1.54(1)	1.52(1)	1.53(2)	1.54(3)	1.534(7)
C(11)—C(12)	1.55(1)	1.54(1)	1.59(2)	1.59(3)	1.545(6)
C(12)—C(13)	1.52(1)	1.53(1)	1.54(3)	1.49(3)	1.521(7)
C(13)—C(14)	1.52(1)	1.54(1)	1.47(3)	1.59(3)	1.543(6)
C(13)—C(21)	1.54(1)	1.53(1)	1.57(2)	1.59(3)	1.544(7)
C(13)—C(17)	1.56(1)	1.54(1)	1.54(2)	1.51(3)	1.564(6)
C(14)—C(15)	1.56(1)	1.53(1)	1.61(3)	1.63(3)	1.529(7)
C(15)—C(16)	1.56(1)	1.53(1)	1.67(3)	1.64(3)	1.545(7)
C(16)—C(17)	1.55(1)	1.54(1)	1.56(3)	1.49(4)	1.542(7)
C(17)—C(22)	1.49(1)	1.54(1)	1.59(3)	1.52(3)	1.523(6)
C(18)—C(19)	1.47(2)	1.49(2)	1.54(3)	1.54(3)	1.504(7)
C(22)—C(23)	1.46(1)	1.49(1)	1.44(3)	1.53(4)	1.504(7)

are due to intermolecular interactions. Their average values (140—150°) are consistet with the conformations of the molecules in the "free" state.

In 16β-trichlorogermylated steroids **4** and **6**, the three-center hypervalent O(3)→Ge(1)—Cl(3) bond is observed. The configuration about the five-coordinate Ge atom in compounds **4** and **6** is a strongly distorted trigonal bipyramid with the O(3) and Cl(3) atoms in axial positions and the C(16), Cl(1), and Cl(2) atoms in equatorial positions. In this case, the central Ge(1) atom deviates from the plane of the equatorial substituents toward the chlorine atom, which is typical of the compounds of this type.[3] In the hypervalent fragments, the Ge(1)—O(3) distances (2.29(1)—2.39(1) Å, see Table 1) are close to the average values for the coordination bonds. The Ge(1)—Cl(3) distances (2.172(4)—2.202(3) Å) are only 0.03 Å larger than the standard values for the four-coordinate germanium atom.[4] The distortion of the geometry from the ideal trigonal-

Table 2. Bond angles (ω) in molecules **4**, **5**, and **6**

Angle	ω/deg				
	4A	**4B**	**5A**	**5B**	**6**
C(16)—Ge(1)—Cl(2)	128.5(4)	121.9(4)	112.7(8)	113.9(8)	123.0(2)
C(16)—Ge(1)—Cl(1)	113.8(4)	120.3(4)	115.1(8)	114.6(8)	119.2(2)
Cl(2)—Ge(1)—Cl(1)	110.5(2)	110.7(2)	104.8(8)	108.5(4)	110.6(6)
C(16)—Ge(1)—Cl(3)	101.3(3)	99.2(3)	112.3(8)	112.2(7)	100.3(1)
Cl(2)—Ge(1)—Cl(3)	97.2(2)	98.9(2)	106.6(9)	100.7(4)	97.7(6)
Cl(1)—Ge(1)—Cl(3)	98.0(1)	98.6(1)	104.6(4)	105.8(4)	98.8(6)
C(16)—Ge(1)—O(3)	79.5(4)	78.2(4)	—	—	79.1(6)
Cl(2)—Ge(1)—O(3)	80.2(2)	83.4(2)	—	—	80.8(5)
Cl(1)—Ge(1)—O(3)	84.2(2)	82.1(2)	—	—	83.5(5)
Cl(3)—Ge(1)—O(3)	177.1(2)	177.2(2)	—	—	177.7(5)
C(18)—O(1)—C(3)	121(1)	119(1)	114(1)	118(2)	117.7(4)
C(22)—O(3)—Ge(1)	112.2(6)	111.9(5)	—	—	111.1(4)
C(2)—C(1)—C(10)	114.0(8)	113.6(8)	113(2)	110(2)	114.7(5)
C(3)—C(2)—C(1)	112.1(9)	112(1)	113(2)	112(2)	110.6(4)
O(1)—C(3)—C(2)	111(1)	112(1)	105(2)	106(2)	106.0(4)
O(1)—C(3)—C(4)	105(1)	107(1)	106(1)	110(2)	109.6(5)
C(2)—C(3)—C(4)	115(1)	112(1)	111(1)	114(2)	111.8(4)
C(3)—C(4)—C(5)	109.8(9)	113(1)	109(2)	112(2)	112.5(5)
C(6)—C(5)—C(10)	113.3(9)	115.4(9)	123(2)	121(2)	123.8(4)
C(6)—C(5)—C(4)	109.6(9)	112.6(9)	122(2)	124(2)	120.9(4)
C(10)—C(5)—C(4)	115(1)	111.6(9)	116(2)	114(2)	115.3(4)
C(5)—C(6)—C(7)	110.1(9)	110.8(9)	122(2)	127(2)	125.3(5)
C(8)—C(7)—C(6)	113(1)	111.0(9)	116(2)	113(2)	112.0(4)
C(14)—C(8)—C(7)	112(1)	111.6(9)	114(2)	111(2)	110.4(4)
C(14)—C(8)—C(9)	109(1)	108.3(9)	108(2)	110(2)	108.6(4)
C(7)—C(8)—C(9)	110.0(9)	113.7(9)	110(2)	112(2)	110.3(4)
C(11)—C(9)—C(10)	114.0(8)	114.3(8)	110(2)	108(2)	112.2(4)
C(11)—C(9)—C(8)	111.5(8)	113.2(9)	115(2)	116(2)	111.3(4)
C(10)—C(9)—C(8)	112.2(8)	111.0(8)	113(2)	115(2)	113.7(4)
C(5)—C(10)—C(1)	107.6(9)	106.9(9)	106(1)	110(2)	108.1(4)
C(5)—C(10)—C(20)	111.2(9)	111.6(9)	111(2)	112(2)	108.4(4)
C(1)—C(10)—C(20)	108.2(9)	111.0(9)	110(2)	111(2)	110.3(4)
C(5)—C(10)—C(9)	107.3(9)	106.6(8)	110(2)	107(2)	110.4(4)
C(1)—C(10)—C(9)	111.3(8)	110.2(8)	109(1)	107(2)	108.2(4)
C(20)—C(10)—C(9)	111.2(9)	110.3(8)	111(1)	109(2)	111.4(4)
C(9)—C(11)—C(12)	113.2(8)	114.7(8)	113(2)	111(2)	114.0(4)
C(13)—C(12)—C(11)	111.4(7)	110.9(8)	108(2)	112(2)	110.8(4)
C(12)—C(13)—C(14)	107.8(8)	106.8(8)	108(1)	108(2)	107.3(4)
C(12)—C(13)—C(21)	109.6(8)	111.8(9)	112(2)	111(2)	111.7(4)
C(14)—C(13)—C(21)	113.6(8)	110.9(9)	115(2)	112(2)	112.0(4)
C(12)—C(13)—C(17)	116.6(7)	117.0(8)	113(2)	118(2)	115.3(4)
C(14)—C(13)—C(17)	99.7(8)	100.3(8)	100(2)	99(2)	100.3(3)
C(21)—C(13)—C(17)	109.3(7)	109.4(8)	108(1)	109(2)	109.7(4)
C(8)—C(14)—C(13)	116(1)	115.3(9)	115(2)	116(2)	113.5(4)
C(8)—C(14)—C(15)	117(1)	120(1)	113(2)	119(2)	120.6(4)
C(13)—C(14)—C(15)	103.7(9)	104.4(9)	108(2)	105(2)	104.5(4)
C(16)—C(15)—C(14)	101.4(8)	103.1(9)	98(2)	97(2)	101.1(4)
C(17)—C(16)—C(15)	106.9(8)	107.2(8)	106(2)	110(2)	106.7(4)
C(17)—C(16)—Ge(1)	113.1(7)	116.9(7)	112(2)	111(2)	116.1(3)
C(15)—C(16)—Ge(1)	114.6(8)	112.6(8)	108(1)	105(1)	112.8(4)
C(22)—C(17)—C(16)	113.2(8)	113.3(9)	110(2)	111(2)	114.1(4)
C(22)—C(17)—C(13)	118.3(8)	115.5(9)	114(2)	114(2)	114.9(4)
C(16)—C(17)—C(13)	104.6(7)	105.8(8)	107(2)	109(2)	106.4(4)
O(2)—C(18)—O(1)	123(2)	125(2)	125(2)	122(2)	123.7(5)
O(2)—C(18)—C(19)	126(1)	127(2)	124(2)	126(3)	125.8(5)
O(1)—C(18)—C(19)	112(2)	108(2)	111(2)	113(2)	110.5(4)
O(3)—C(22)—C(23)	119.5(9)	122(1)	121(2)	119(2)	120.9(4)
O(3)—C(22)—C(17)	119.5(9)	119(1)	122(2)	121(2)	119.6(4)
C(23)—C(22)—C(17)	121.0(9)	120(1)	116(2)	118(2)	119.5(4)

Table 3. Endocyclic torsion angles (φ) in molecules **4**, **5**, and **6**

Angle	φ/deg				
	4A	**4B**	**5A**	**5B**	**6**
			Ring *A*		
C(1)—C(2)—C(3)—C(4)	52(1)	52(1)	59(2)	54(2)	54.3(7)
C(2)—C(3)—C(4)—C(5)	−50(1)	−53(1)	−58(2)	−54(3)	−53.1(7)
C(3)—C(4)—C(5)—C(10)	53(1)	56(1)	57(2)	53(2)	52.4(7)
C(4)—C(5)—C(10)—C(1)	−54(1)	−56(1)	−53(2)	−53(2)	−49.6(6)
C(5)—C(10)—C(1)—C(2)	54(1)	56(1)	50(2)	51(2)	51.5(6)
C(10)—C(1)—C(2)—C(3)	−54(1)	−56(1)	−56(2)	−53(2)	−55.3(7)
			Ring *B*		
C(5)—C(6)—C(7)—C(8)	53(1)	52(1)	14(3)	13(3)	13.9(9)
C(6)—C(7)—C(8)—C(9)	−53(1)	−54(1)	−44(2)	−41(2)	−42.8(7)
C(7)—C(8)—C(9)—C(10)	56(1)	56(1)	60(2)	59(2)	58.2(6)
C(8)—C(9)—C(10)—C(5)	−58(1)	−54(1)	−45(2)	−43(2)	−41.0(6)
C(9)—C(10)—C(5)—C(6)	59(1)	56(1)	14(2)	14(3)	10.4(8)
C(10)—C(5)—C(6)—C(7)	−57(1)	−57(1)	1(3)	0(3)	2.8(1)
			Ring *C*		
C(8)—C(9)—C(11)—C(12)	52(1)	50(1)	47(2)	49(2)	51.5(6)
C(9)—C(11)—C(12)—C(13)	−55(1)	−54(1)	−52(2)	−52(2)	−53.6(6)
C(11)—C(12)—C(13)—C(14)	56(1)	55(1)	60(2)	54(2)	55.8(6)
C(12)—C(13)—C(14)—C(8)	−60(1)	−60(1)	−66(2)	−58(2)	−62.1(6)
C(13)—C(14)—C(8)—C(9)	57(1)	57(1)	58(2)	53(2)	60.5(6)
C(14)—C(8)—C(9)—C(11)	−51(1)	−49(1)	−46(2)	−49(2)	−52.9(6)
			Ring *D*		
C(13)—C(14)—C(15)—C(16)	−40(1)	−38(1)	−35(2)	−36(2)	−44.3(5)
C(14)—C(15)—C(16)—C(17)	15(1)	16(1)	8(2)	14(2)	26.8(5)
C(15)—C(16)—C(17)—C(13)	14(1)	11(1)	19(2)	14(2)	−0.3(5)
C(16)—C(17)—C(13)—C(14)	−39(1)	−33(1)	−40(2)	−36(2)	−26.0(5)
C(17)—C(13)—C(14)—C(15)	49(1)	44(1)	48(2)	46(2)	43.8(5)
			Ring *E*		
C(16)—C(17)—C(22)—O(3)	−10(1)	−12(1)	—	—	−0.6(7)
C(17)—C(22)—O(3)—Ge(1)	−1(1)	8(1)	—	—	0.2(6)
C(22)—O(3)—Ge(1)—C(16)	9(1)	−1(1)	—	—	0.2(6)
O(3)—Ge(1)—C(16)—C(17)	−14(1)	−5(2)	—	—	−0.5(6)
Ge(1)—C(16)—C(17)—C(22)	18(1)	11(1)	—	—	0.8(6)
			AcO group		
C(2)—C(3)—O(1)—C(18)	84(1)	105(1)	156(2)	148(2)	158.3(5)
C(4)—C(3)—O(1)—C(18)	−152(1)	−132(1)	−86(2)	−88(2)	−80.9(6)
C(3)—O(1)—C(18)—C(19)	−177(1)	−180(1)	−177(2)	−178(2)	175.4(5)
C(3)—O(1)—C(18)—O(2)	1(2)	0(2)	5(3)	6(4)	−6.0(5)

Table 4. Conformations of the rings in compounds **4**—**6**

Molecule	Ring *A*	Ring *B*	Ring *C*	Ring *D*	Ring *E*
4A	3α,10β-Chair	5α,8β-Chair	9α,13β-Chair	13α,14β-Twist	Strongly flattened 16α-envelope
4B	3α,10β-Chair	5α,8β-Chair	9α,13β-Chair	13α,14β-Twist	Strongly flattened 16α-envelope
5A	3α,10β-Chair	9α,8β-Half-chair	9α,13β-Chair	13α,14β-Twist	—
5B	3α,10β-Chair	9α,8β-Half-chair	9α,13β-Chair	13α,14β-Twist	—
6	3α,10β-Chair	9α,8β-Half-chair	9α,13β-Chair	14α-Envelope	Planar to within 0.004 Å

bipyramidal configuration, in which the Ge atom lies in the plane of the equatorial substituents, is characterized by the value ΔΩ (ΔΩ = 2π − Ω, where Ω is the solid angle formed by the directions of three equatorial bonds of the Ge atom[5]). For all three units, the value ΔΩ = 91±1 degrees of the solid angle, *i.e.*, it is intermediate between the values for the ideal trigonal bipyramid (0°) and for the ideal tetrahedral coordination (180°). In spite of the equality of the values of ΔΩ, the O(3)—Ge(1) bond length in molecule **4A** differs substantially from the corresponding bond lengths in molecules **4B** and **6**. This fact is not surprising because it is known[3] that the parameters of the hypervalent bond can change noticeably under the action of even weak van der Waals

Table 5. Principal characteristics of X-ray diffraction studies and the crystal-structural data for compounds **4**—**6**

Parameter	Compound **4**	Compound **5**	Compound **6**
Molecular formula	$C_{23}H_{35}Cl_3GeO_3$	$C_{23}H_{33}Cl_3GeO_3$	$C_{23}H_{33}Cl_3GeO_3$
Diffractometer	Siemens P3/PC	Siemens P3/PC	Siemens P3/PC
Radiation (T/K)	Mo-Kα (150)	Mo-Kα (160)	Mo-Kα (150)
Scan mode ($2\theta_{max}$/deg)	θ/2θ (48)	θ/2θ (46)	θ/2θ (60)
a/Å	8.695(1)	18.598(7)	5.967(1)
b/Å	12.469(2)	7.321(3)	13.490(1)
c/Å	13.788(2)	19.25(2)	30.328(4)
α/deg	106.42(1)	90	90
β/deg	107.33(1)	110.78(3)	90
γ /deg	105.77(1)	90	90
V/Å^3	1261.2(4)	2450(2)	2441.4(5)
d_{calc}/g cm^{-3}	1.418	1.454	1.459
Space group	$P\bar{1}$	$P2_1$	$P2_12_12_1$
Z	2	4	4
Number of measured reflections	4164	3862	4064
Number of reflections used in the least-squares refinement	4143	2540	4033
Number of parameters in the least-squres refinement	549	312	276
Flack parameter	0.00(2)	0.0(1)	0.05(2)
R_1 ($I > 2\sigma$)	0.053	0.104	0.049

Table 6. Coordinates (×10^4) of nonhydrogen atoms in the structure of **4**

Atom	x	y	z	Atom	x	y	z
	Molecule **4A**				Molecule **4B**		
Ge(1)	15000	5000	10000	Ge(1)	−339(1)	9(1)	2565(1)
Cl(1)	17738(4)	6006(3)	11033(3)	Cl(1)	−2641(4)	−951(3)	1058(3)
Cl(2)	13829(6)	3889(4)	10691(3)	Cl(2)	−580(6)	1493(4)	3652(4)
Cl(3)	15238(5)	3575(3)	8751(3)	Cl(3)	1352(5)	1009(4)	1963(3)
O(1)	2183(12)	4097(8)	2926(7)	O(1)	12309(13)	854(10)	9659(8)
O(2)	1731(14)	5726(11)	2811(9)	O(2)	13238(15)	−633(11)	9252(11)
O(3)	14637(9)	6409(6)	11299(5)	O(3)	−2127(9)	−1159(7)	3224(6)
C(1)	5331(13)	5684(9)	5933(8)	C(1)	7443(13)	−838(9)	8027(8)
C(2)	3601(13)	5137(9)	4911(9)	C(2)	9201(15)	−294(9)	8998(9)
C(3)	3851(17)	4801(13)	3879(11)	C(3)	10666(19)	196(14)	8699(11)
C(4)	4904(15)	4000(10)	3791(9)	C(4)	10373(14)	1050(10)	8149(9)
C(5)	6638(16)	4577(11)	4851(10)	C(5)	8610(14)	495(10)	7169(8)
C(6)	7700(16)	3792(12)	4747(9)	C(6)	8412(14)	1285(11)	6532(9)
C(7)	9528(14)	4431(10)	5742(8)	C(7)	6727(13)	638(10)	5494(8)
C(8)	9396(17)	4800(12)	6860(10)	C(8)	5168(15)	165(11)	5764(9)
C(9)	8245(12)	5565(9)	6892(8)	C(9)	5372(12)	−640(8)	6410(7)
C(10)	6396(14)	4880(9)	5935(9)	C(10)	7082(15)	42(10)	7507(9)
C(11)	8236(12)	6063(8)	8042(7)	C(11)	3748(13)	−1211(10)	6566(9)
C(12)	10094(12)	6746(8)	8983(7)	C(12)	2057(13)	−1862(9)	5500(8)
C(13)	11155(11)	5955(8)	8961(7)	C(13)	1799(11)	−1017(8)	4909(7)
C(14)	11171(16)	5531(12)	7817(10)	C(14)	3463(16)	−548(12)	4714(9)
C(15)	12520(13)	4915(10)	7938(8)	C(15)	2963(12)	20(9)	3882(8)
C(16)	13965(14)	5798(11)	9109(9)	C(16)	1074(15)	−834(11)	3116(9)
C(17)	13157(11)	6608(8)	9681(8)	C(17)	404(12)	−1605(9)	3709(8)
C(18)	1254(20)	4643(16)	2480(13)	C(18)	13448(18)	340(16)	9824(13)
C(19)	−417(20)	3761(16)	1569(13)	C(19)	15008(20)	1198(15)	10857(13)
C(20)	5366(15)	3722(10)	6031(9)	C(20)	6926(14)	1087(10)	8306(9)
C(21)	10387(12)	4912(9)	9279(8)	C(21)	1476(14)	37(10)	5586(8)
C(22)	13784(13)	6920(9)	10891(8)	C(22)	−1475(13)	−1777(10)	3586(8)
C(23)	13352(13)	7806(10)	11595(8)	C(23)	−2448(14)	−2683(10)	3924(9)

Table 7. Coordinates ($\times 10^4$) of nonhydrogen atoms in the structure of **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
	Molecule **5A**				Molecule **5B**		
Ge(1)	3826(2)	0	8648(2)	Ge(1)	1112(2)	640(4)	6175(2)
Cl(1)	3833(6)	−2798(12)	8943(5)	Cl(1)	1620(5)	−1941(12)	6222(5)
Cl(2)	2694(6)	627(39)	8133(11)	Cl(2)	1910(5)	2599(15)	6195(5)
Cl(3)	4194(7)	1386(12)	9660(5)	Cl(3)	316(4)	927(12)	5055(3)
O(1)	10118(7)	4480(20)	10778(6)	O(1)	−5129(8)	4154(21)	4204(7)
O(2)	10281(8)	2696(19)	11776(7)	O(2)	−5218(9)	2612(24)	3162(8)
O(3)	3678(9)	2217(22)	6640(7)	O(3)	1368(9)	2600(22)	8307(8)
C(1)	8094(10)	5773(30)	9772(9)	C(1)	−3102(11)	5651(36)	5292(11)
C(2)	8952(10)	5847(31)	10100(10)	C(2)	−4005(13)	5667(40)	4923(12)
C(3)	9288(10)	4282(26)	10585(9)	C(3)	−4298(11)	4041(28)	4452(10)
C(4)	9065(11)	2464(33)	10153(11)	C(4)	−4020(15)	2230(41)	4858(14)
C(5)	8212(10)	2321(28)	9842(10)	C(5)	−3184(11)	2152(31)	5203(11)
C(6)	7832(10)	803(30)	9964(9)	C(6)	−2732(11)	715(31)	5122(10)
C(7)	6995(10)	569(30)	9604(9)	C(7)	−1908(10)	524(30)	5477(10)
C(8)	6595(11)	1858(26)	8948(10)	C(8)	−1567(12)	1858(31)	6102(11)
C(9)	6888(10)	3762(29)	9143(10)	C(9)	−1906(10)	3695(27)	5920(9)
C(10)	7785(10)	3922(28)	9322(9)	C(10)	−2822(12)	3807(33)	5718(12)
C(11)	6454(10)	5247(29)	8581(9)	C(11)	−1516(12)	5222(37)	6511(12)
C(12)	5544(10)	5073(30)	8335(10)	C(12)	−605(11)	5193(30)	6737(10)
C(13)	5322(10)	3104(26)	8076(9)	C(13)	−282(10)	3347(28)	6972(10)
C(14)	5714(11)	1893(28)	8706(10)	C(14)	−717(11)	1948(31)	6324(11)
C(15)	5327(10)	−103(32)	8526(10)	C(15)	−224(11)	63(33)	6542(11)
C(16)	4425(12)	571(34)	8062(11)	C(16)	625(13)	1014(36)	6900(12)
C(17)	4475(10)	2671(29)	7957(10)	C(17)	536(12)	2996(34)	7026(12)
C(18)	10538(11)	3664(31)	11403(11)	C(18)	−5533(15)	3480(43)	3543(15)
C(19)	11403(12)	4015(32)	11583(11)	C(19)	−6403(15)	3769(45)	3339(14)
C(20)	7963(10)	3929(28)	8605(10)	C(20)	−3001(10)	3737(31)	6443(11)
C(21)	5463(11)	2641(30)	7336(10)	C(21)	−371(11)	2781(33)	7734(11)
C(22)	3888(11)	3266(28)	7167(11)	C(22)	1137(13)	3626(34)	7757(13)
C(23)	3670(11)	5167(32)	7082(10)	C(23)	1312(13)	5668(42)	7867(13)

Table 8. Coordinates ($\times 10^4$) of nonhydrogen atoms in the structure of **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ge(1)	−304(1)	−7153(1)	−1709(1)	C(9)	−1980(9)	−2481(3)	−1173(2)
Cl(1)	−2274(2)	−8432(1)	−1860(1)	C(10)	−1061(8)	−1451(3)	−1022(2)
Cl(2)	2597(2)	−7089(1)	−2122(1)	C(11)	−2989(10)	−2443(3)	−1638(2)
Cl(3)	1350(3)	−7702(1)	−1109(1)	C(12)	−3928(9)	−3445(4)	−1801(2)
O(1)	−402(7)	1012(2)	−129(1)	C(13)	−2167(8)	−4256(3)	−1764(2)
O(2)	−30(9)	460(3)	567(1)	C(14)	−1374(9)	−4282(3)	−1280(2)
O(3)	−1981(7)	−6506(3)	−2361(1)	C(15)	−145(10)	−5272(3)	−1236(2)
C(1)	−3080(10)	−774(4)	−915(2)	C(16)	−1777(9)	−5975(3)	−1478(2)
C(2)	−2468(10)	211(4)	−696(2)	C(17)	−3065(9)	−5339(3)	−1816(1)
C(3)	−1105(10)	34(3)	−282(2)	C(18)	173(11)	1109(4)	300(2)
C(4)	929(10)	−597(4)	−371(2)	C(19)	1028(11)	2137(4)	390(2)
C(5)	345(10)	−1562(3)	−604(2)	C(20)	406(11)	−977(4)	−1380(2)
C(6)	985(10)	−2426(4)	−440(2)	C(21)	−206(10)	−4084(4)	−2087(2)
C(7)	532(11)	−3419(4)	−645(2)	C(22)	−3007(9)	−5746(4)	−2284(2)
C(8)	−274(9)	−3325(3)	−1130(2)	C(23)	−4328(10)	−5234(4)	−2640(2)

interactions. Chelate ring *E* of molecules **4A,B** adopts a substantially flattened 16α-envelope conformation, while in the structure of **6**, this ring is planar to within 0.004 Å. The slight difference in the corresponding torsion angles in rings *E* of molecules **4A** and **4B** (10°) is apparently due to the difference in the Ge(1)—O(3) bond lengths.

From a comparison of the endocyclic angles and bond lengths in the chelate rings of molecules **4** and **6** with the corresponding geometric parameters of com-

pound **5** (the corresponding values are identical to within 3σ), it can be concluded that the hypervalent bond has no effect on the distances and bond angles between the atoms involved in the rings of compounds **4** and **6**.

Experimental

The crystals of compounds **4**—**6** (with the minimum dimensions of 0.1—0.5 mm) were grown from ether under isothermal conditions. All crystals are air-stable.

The principal characteristics of X-ray diffraction studies and the crystal-structural parameters of compounds **4**—**6** are given in Table 5. For the X-ray intensity data set collected from the crystal of **5**, we carried out the profile analysis using the PROFIT program.[6] The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. All H atoms in the structures of **4** and **6** were placed in calculated positions and refined using the riding model with fixed values of U_{iso}, which were equal to nU_{eq} of the C atoms to which the hydrogen atoms are attached (n = 1.5 for the H atoms of the methyl groups and 1.2 for the remaining H atoms). In the structure of **5**, the positions of the hydrogen atoms were not revealed. In all the structures, the absolute configurations were determined from the refined Flack parameters.[7] All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program package (version 5.0).[8] The coordinates of nonhydrogen atoms in the structures of **4**—**6** are given in Tables 6—8, respectively.

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