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Oxidation of germanium(II) azides with HN_3: a convenient route to six-co-ordinate triazidogermanium(IV) compounds

Alexander C. Filippou,* Peter Portius, Gabriele Kociok-Köhn and Volker Albrecht

Fachinstitut für Anorganische und Allgemeine Chemie, Humboldt-Universität zu Berlin, Hessische Str. 1-2, D-10115 Berlin, Germany. E-mail: filippou@chemie.hu-berlin.de

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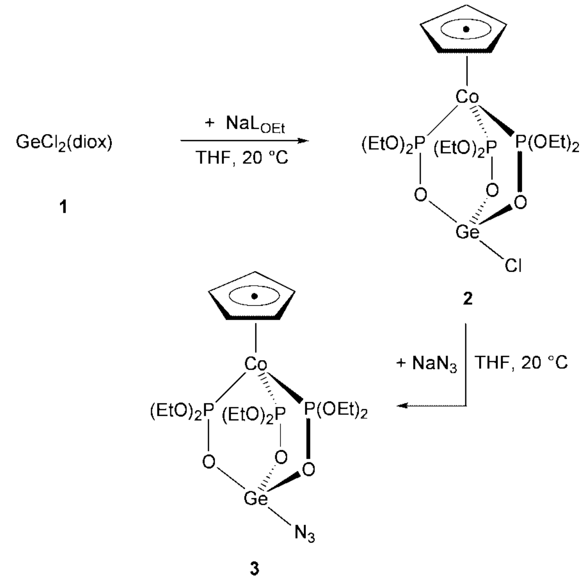
Reaction of $GeCl_2(C_4H_8O_2)$ **1** with NaL_{OEt} [$L_{OEt} = (C_5H_5)Co\{P(O)(OEt)_2\}_3$] gave $L_{OEt}GeCl$ **2**, which reacts with NaN_3 to afford the germanium(II) azide $L_{OEt}GeN_3$ **3**. A dissociation equilibrium between **3** and the ions $[L_{OEt}Ge]^+$ and N_3^- exists in solution, which is strongly dependent on the solvent polarity. Dissociation into ions is observed in solution for a variety of other four-co-ordinate germanium(II) azides bearing an anionic tridentate ligand. The crystal structures of **2** and **3** revealed a pseudo trigonal-bipyramidal co-ordination geometry around the germanium atom and an unsymmetric bonding of the L_{OEt} ligand with one long Ge–O_{ax} and two considerably shorter Ge–O_{eq} bonds. The structural data are compared with those of other four-co-ordinate germanium(II) chlorides and azides indicating the presence of a polar Ge–X bond (X = Cl or N_3) in **2** and **3**. Oxidation of **3** with two equivalents of HN_3 gave selectively the six-co-ordinate triazidogermanium(IV) compound $L_{OEt}Ge(N_3)_3$ **4**. Similarly, oxidation of the germanium(II) azide $Tp'GeN_3$ **5** [$Tp' = HB(3,5\text{-}Me_2pz)_3$, 3,5-$Me_2pz$ = 3,5-dimethylpyrazol-1-yl] with HN_3 affords selectively $Tp'Ge(N_3)_3$ **6**. The crystal structures of **4** and **6** have been determined and are compared with those of other six-co-ordinate germanium(IV) polyazides.

Introduction

Germanium(II) azides (azidogermylenes) are metastable compounds, which are promising precursors to germanium nitrides. Kinetic stabilization of these germylenes can be achieved using sterically demanding chelate ligands as demonstrated recently by the synthesis of $(Mamx)GeN_3$ [Mamx = 2,4-di-*tert*-butyl-6-(2-*N*,*N*-dimethylaminoethyl)phenyl][1] and $Tp'GeN_3$ [$Tp' = HB(3,5\text{-}Me_2pz)_3$].[2] In view of the remarkable thermal stability of $Tp'GeN_3$ (decomp. 216 °C),[2] we envisaged that also other tridentate ligands could enhance the thermal stability of germanium(II) azides. A class of tripod ligands, which proved to be particularly useful in transition metal chemistry forming stable complexes with various metals in low and high oxidation states, are cyclopentadienyltris(diorganylphosphonato-*P*)cobaltates-(1−) ($[(C_5H_5)Co\{P(O)(R)_2\}_3]^-$; R = alkyl or alkoxy).[3] UV-VIS spectroscopic studies[4] have shown these ligands to be very weak and hard, their position being close to that of fluoride in the spectrochemical series[5] and near that of water in the nephelauxetic series.[6] This let us suggest that these ligands would be also suitable for the stabilization of germanium(II) species as demonstrated by the present work describing the synthesis and crystal structures of the germanium(II) compounds $L_{OEt}GeCl$ and $L_{OEt}GeN_3$ [$L_{OEt} = (C_5H_5)Co\{P(O)(OEt)_2\}_3$]. Furthermore, oxidation of the latter or the germanium(II) azide $Tp'GeN_3$ with HN_3 is shown to provide a general route to hitherto unknown six-co-ordinate triazidogermanium(IV) compounds of the general formula $L_3Ge(N_3)_3$ [$L_3 = L_{OEt}$ or Tp′].

Results and discussion

When $GeCl_2(C_4H_8O_2)$ **1** ($C_4H_8O_2$ = 1,4-dioxane) was treated with one equivalent of NaL_{OEt} in THF at −78 °C and the reaction solution was warmed to room temperature, rapid precipitation of NaCl was observed and the germanium(II) chloride **2** was selectively formed (Scheme 1). After work-up of the reaction solution compound **2** was isolated as a yellow, slightly air-sensitive, microcrystalline solid in 95% yield. It is very soluble in CH_2Cl_2, THF and Et_2O, moderately soluble in pentane and decomposes at 122 °C, when heated in a sealed capillary tube *in vacuo*. The thermal stability of **2** is lower than that of the related germanium(II) chloride Tp′GeCl which decomposes according to simultaneous thermal analysis (TG-DTA) at 295 °C.[2]



Scheme 1

Compound **2** reacts with various nucleophiles and is therefore a useful starting material for the preparation of other L_{OEt}-stabilized germanium(II) derivatives. Thus, treatment of **2** with an excess of NaN_3 in THF at ambient temperature afforded selectively $L_{OEt}GeN_3$ **3** (Scheme 1). Evidence for the selective formation of **3** was given by IR monitoring of the reaction in the region of 2200–1500 cm^{-1}. This revealed the appearance of only one absorption at 2053 cm^{-1} resulting from the $\nu_{asym}(N_3)$ vibration of **3**. After approximately 24 h the intensity of this absorption had stopped increasing and the reaction mixture

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Table 1 $\nu_{asym}(N_3)$ absorptions (cm^{-1}) of selected azides of Ge^{II} and Ge^{IV} and $[N(PPh_3)_2]N_3$ in different solvents

Compound	$\nu_{asym}(N_3)$	Solvent	Compound	$\nu_{asym}(N_3)$	Solvent
$L_{OEt}GeN_3$ **3**	2063vs	*a*	Tp′GeN_3 **5**	2051vs	*b*
	2053vs	*b*		2042vs	*d*
	2060vs, 2013vw	*c*		2040vs, 1999w	*e*
	2055vs, 2005w	*d*		2040vs, 2005m	*f*
	2049vs, 1999s	*e*	$L_{OEt}Ge(N_3)_3$ **4**	2114s, 2095vs	*d*
	2051vs, 2005vs	*f*	$L_{OEt}{*}Ge(N_3)_3$[i]	2111s, 2092vs	*b*
	2058vs	*g*		2112s, 2093vs	*d*
	2056vs	*h*	$TpGe(N_3)_3$[i]	2115vs, 2096vs, 2090s(sh)	*b*
				2117vs, 2097vs	*d*
$L_{OEt}{*}GeN_3$[i]	2056vs	*a*	Tp′$Ge(N_3)_3$ (**6**)	2115s, 2111 m, 2097vs, 2089vs	*b*
	2043vs	*b*		2117s, 2098vs, 2092vs	*d*
	2048w, 2013vs	*c*	$[N(PPh_3)_2]N_3$	1993vs	*b*
	2005vs	*d*		2013vs	*c*
$TpGeN_3$[i]	2068vs	*a*		2005vs	*d*
	2063vs	*b*		1999vs	*e*
	2060vs	*d*		2005vs	*f*

[a] Pentane. [b] THF. [c] $CHCl_3$. [d] CH_2Cl_2. [e] DMF. [f] MeCN. [g] Et_2O. [h] Toluene. [i] Ref. 9: $L_{OEt}{*} = (C_5Me_5)Co\{P(O)(OEt)_2\}_3$, Tp = $HB(pz)_3$, pz = pyrazolyl.

was worked up to give **3** as a yellow, microcrystalline solid in 80% yield. The germanium(II) azide **3** is easily hydrolysed in solution releasing HN_3, which then oxidizes **3** to give the triazidogermanium(IV) compound $L_{OEt}Ge(N_3)_3$ **4** (see below). Therefore exclusion of water is essential during the synthesis to obtain **3** in high yield. Compound **3** is very soluble in CH_2Cl_2, THF and Et_2O and moderately soluble in pentane. It is rapidly oxidized by CCl_4 to give $L_{OEt}GeCl_2(N_3)$. Evidence for this is given by the IR spectrum in CCl_4, which reveals a rapid replacement of the $\nu_{asym}(N_3)$ absorption of **3** at 2060 cm^{-1} by that of the germanium(IV) azide at 2098 cm^{-1}. Compound **3** decomposes smoothly upon heating at 98 °C and is less stable than Tp′GeN_3 **5** (decomp. 216 °C).[2]

The germanium(II) compounds **2** and **3** were fully characterized. Thus, their IR spectra in KBr show the characteristic absorptions of the L_{OEt} group (see Experimental section). In addition, **3** displays a very strong $\nu_{asym}(N_3)$ absorption at 2049 cm^{-1} and a very weak absorption at 1279 cm^{-1}, which can tentatively be assigned to the $\nu_{sym}(N_3)$ vibration. Both compounds show two strong absorptions for the δ(P=O) deformation vibrations at 600 and 571 (**2**) and 604 and 567 cm^{-1} (**3**). This rules out a C_{3v}-symmetric co-ordination of the L_{OEt} ligand to the germanium(II) center,[7] which is verified by the crystal structures of **2** and **3** showing one long and two considerably shorter Ge–O bonds (see below). Such a bonding mode implies also the existence of several ν(P=O) absorptions.[7] A comparison of the KBr spectra of **2** and **3** with those of $Co(L_{OEt})_2$[7,8] NaL_{OEt} [ν(P=O) 1171 cm^{-1}], $L_{OEt}GeCl_3$ [ν(P=O) 1073 cm^{-1}],[9] $L_{OEt}{*}GeCl_3$ [ν(P=O) 1063 cm^{-1}][9] and $L_{OEt}Ge(N_3)_3$ **6** [ν(P=O) 1064 cm^{-1}] allows a tentative assignment of one of the expected ν(P=O) absorptions of **2** and **3** at 1133 and 1139 cm^{-1}, respectively. These absorptions are close in position to those of the octahedral complexes $M(L_{OEt})_2$ (M = Ca, Sr, Ba, Mn, Fe, Co, Ni or Zn) [ν(P=O) at 1130–1140 cm^{-1}].[7] This suggests a considerable reduction of the P=O bond strength and a strong Ge–O bonding interaction in **2** and **3**. Solution IR spectra of **3** were also recorded in the region 2200–1500 cm^{-1} and the data are listed with those of other germanium(II) azides and related germanium(IV) azides in Table 1. The IR spectrum of **3** in THF, toluene, Et_2O and pentane displays only one strong absorption for the $\nu_{asym}(N_3)$ vibration (Table 1). In comparison, the IR spectra of **3** in $CHCl_3$ and CH_2Cl_2 show two $\nu_{asym}(N_3)$ absorptions, one very strong absorption at 2060 ($CHCl_3$) and 2055 cm^{-1} (CH_2Cl_2), and one weak absorption at 2013 ($CHCl_3$) and 2005 cm^{-1} (CH_2Cl_2) (Table 1). The latter absorption is more intense in CH_2Cl_2 than in $CHCl_3$ and is assigned to the $\nu_{asym}(N_3)$ vibration of the azide anion by comparison with the IR spectra of $[N(PPh_3)_2]N_3$ in $CHCl_3$ and CH_2Cl_2 (Table 1). This indicates that $L_{OEt}GeN_3$ dissociates to a small extent to the ions $[L_{OEt}Ge]^+$ and N_3^- in $CHCl_3$ or CH_2Cl_2 solutions, the degree of dissociation being higher in CH_2Cl_2 than in $CHCl_3$.

The dissociation equilibrium is established slowly on the timescale of IR spectroscopy and is therefore detectable by this method. It is furthermore fully reversible upon change of the solvent, being shifted completely to the side of undissociated $L_{OEt}GeN_3$ in less polar solvents such as pentane, Et_2O, toluene and THF, and to the side of the ions $[L_{OEt}Ge]^+$ and N_3^- in more polar solvents such as DMF (*N,N*-dimethylformamide) and MeCN.[10] In fact, the IR spectra of **3** in DMF and MeCN show an increased $\nu_{asym}(N_3)$ absorption of the azide anion at the expense of the $\nu_{asym}(N_3)$ absorption of undissociated $L_{OEt}GeN_3$ (Table 1). The dissociation equilibrium is also dependent on the tridentate ligand bonded to the germanium(II) center. Thus, no evidence is given by IR spectroscopy for a dissociation of Tp′GeN_3 **5** in CH_2Cl_2,[2] whereas dissociation occurs to a small extent in DMF and MeCN (Table 1). In comparison, $L_{OEt}{*}GeN_3$[9] is fully dissociated to the ions $[L_{OEt}{*}Ge]^+$ and N_3^- in CH_2Cl_2 or MeCN solutions (Table 1). All these data indicate an increase of the degree of dissociation in the series $L_{OEt}{*}GeN_3 > L_{OEt}GeN_3 >$ Tp′GeN_3. The $\nu_{asym}(N_3)$ absorption of **3** appears at a frequency between that observed for the azide anion in $[N(PPh_3)_2]N_3$ and those of germanium(IV) azides [Me_3GeN_3, $\nu_{asym}(N_3)$ 2103 cm^{-1};[11] $Me_2Ge(N_3)_2$, $\nu_{asym}(N_3)$ 2126 and 2105 cm^{-1};[12] $[CpFe(CO)_2]_2Ge(N_3)_2$, $\nu_{asym}(N_3)$ 2091 and 2073 cm^{-1}[13]] (see also Table 1). This suggests for **3** the presence of a covalent Ge–N bond with considerable ionic character.

Variable temperature $^{31}P\{^1H\}$ NMR spectra (121.5 MHz) of compounds **2** and **3** in toluene-d_8 show these compounds to be fluxional. Thus the slow-exchange limit ^{31}P-$\{^1H\}$ NMR spectra of **2** (T = 175 K) and **3** (T = 168 K) display one triplet resonance at δ 97.1 (**2**) and 95.8 (**3**) and one doublet resonance at δ 120.1(**2** and **3**) resulting in both cases from a AX_2 spin system with a $^2J(P_A,P_X)$ coupling constant of 135 Hz (Fig. 1). This suggests the presence of two inequivalent phosphonato groups in the ratio 1 : 2 and an idealized C_s molecular symmetry of **2** and **3**. Therefore the six ethyl groups in **2** and **3** are expected to give rise to three different groups of signals in the slow-exchange limit ^1H and ^{13}C-$\{^1H\}$ NMR spectra. One group of signals should originate from the enantiotopic ethyl groups of the axial phosphonato arm and the other two groups of signals from the diastereotopic ethyl groups of the equatorial phosphonato arms of the L_{OEt} ligand. This is verified by the slow-exchange limit ^1H NMR spectrum of **3** in toluene-d_8 at T = 168 K, which shows three broad methyl proton signals at δ 1.12, 1.18 and 1.26 with intensities in the ratio 1 : 1 : 1, or the slow-exchange limit ^{13}C-$\{^1H\}$ NMR spectrum of **2** in toluene-d_8 at T = 175 K, which shows three broad methylene carbon resonances at δ 60.3, 62.1 and 62.4 in the intensity ratio 1 : 1 : 1.

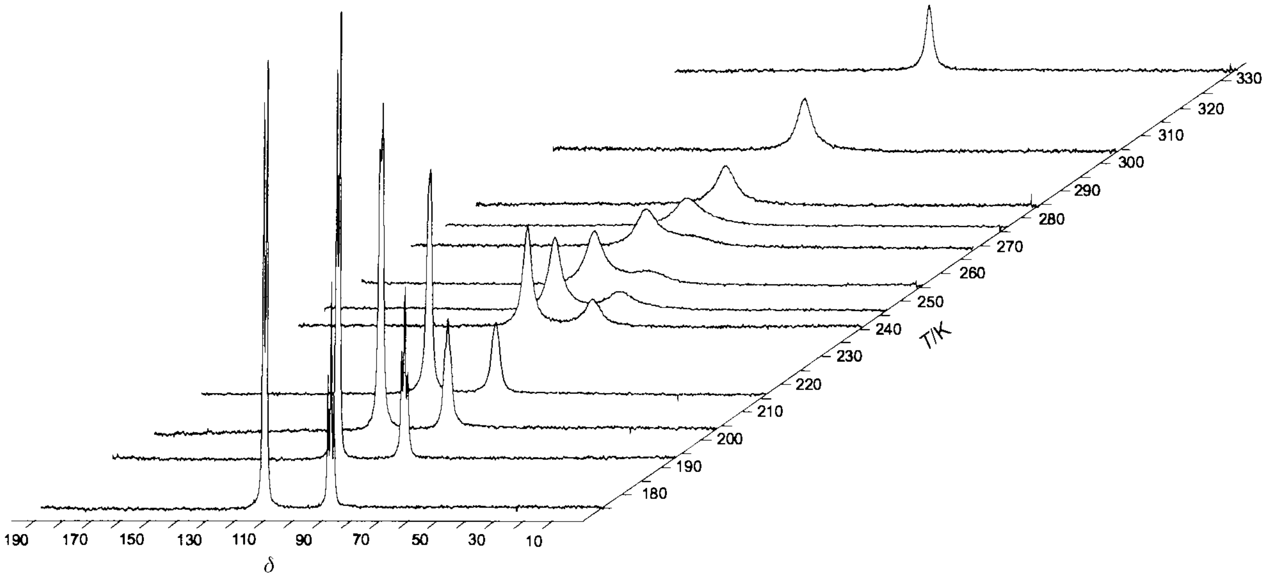


Fig. 1 Temperature-dependent $^{31}P-\{^1H\}$ NMR spectra of compound **2** in the range 175–335 K.

As the temperature of the NMR sample is raised the ^{31}P signals of compounds **2** and **3** first broaden, then coalesce at $T = 273$ (**2**) and 227 K (**3**) and finally appear in the fast exchange limit spectra at $T = 335$ K as one singlet at δ 109.3 (**2**) and 108.6 (**3**), which is slightly broad due to the presence of the ^{59}Co quadrupole nucleus (Fig. 1). Moreover the ^1H and $^{13}C-\{^1H\}$ NMR spectra of **2** and **3** in toluene-d_8 or $CDCl_3$ at 297 K display a single set of resonances for the ethyl groups giving additional evidence for a dynamic process in **2** and **3**, which results in an interchange of the positions of the phosphonato groups. The dynamic process could involve a Berry pseudorotation as has been observed for other four-co-ordinate germanium(II) compounds.[14] However, an alternative mechanism involving a dissociation of **2** and **3** into $[L_{OEt}Ge]^+$, which has approximately C_{3v} molecular symmetry, and X^- ($X = Cl$ or N_3) followed by a recombination of the ions would also result in an interchange of the phosphonato groups. Given the IR evidence that **3** is not dissociated in toluene solution (Table 1), one is tempted to suggest the Berry mechanism. However, NMR studies aimed to determine the influence of the solvent polarity on the activation parameters and the dependence of the NMR spectra on the concentration of X^- are necessary to elucidate, which process is operative.

The solid-state structures of compounds **2** and **3** were determined by single-crystal X-ray diffraction. Suitable single crystals were obtained upon slow cooling of a saturated pentane solution of **2** and **3** from ambient temperature to −30 °C. ZORTEP plots of the molecular structures with the atom-labeling schemes adopted are depicted in Figs. 2 and 3, respectively. Selected bond lengths and angles are listed in Table 2. Both molecules have a "see-saw" shape, the molecular geometry being derived from a trigonal bipyramid. The chloro atom (**2**) and the azido group (**3**) occupy one axial site and the L_{OEt} ligand spans the other axial and two equatorial sites of the bipyramid. The stereochemically active lone pair at germanium is oriented towards the remaining vacant equatorial vertex and pushes back the atoms O(3) and X [Cl or N(1)] at the axial positions towards the equatorial bonded oxygen atoms of the L_{OEt} ligand. The resulting distortion towards a tetragonal pyramid is evident in the $X–Ge–O_{ax}$ bond angles of 166.40(5)° for **2** and 160.95(14)° for **3** and the $O_{ax}–Ge–O_{eq}$ bond angles of 81.94(7) and 80.07(7)° for **2** and 80.04(16) and 79.62(15)° for **3**. Compound **2** has approximately C_s symmetry, if one neglects the ethyl groups, with the symmetry plane passing through the atoms Co, P(1), O(3), Ge and Cl and bisecting the angle O(6)–Ge–O(9). In comparison, compound **3** has C_1 symmetry

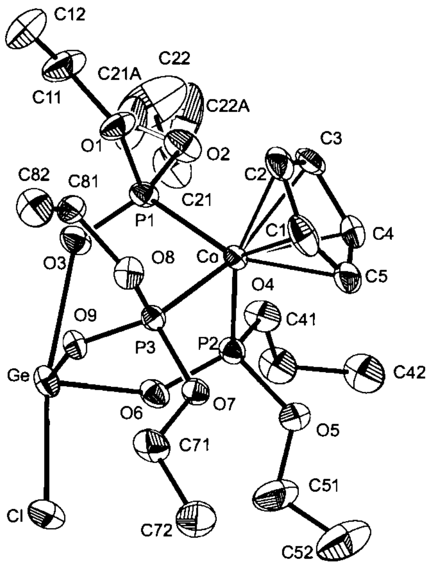


Fig. 2 ZORTEP plot of the molecular structure of compound **2** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

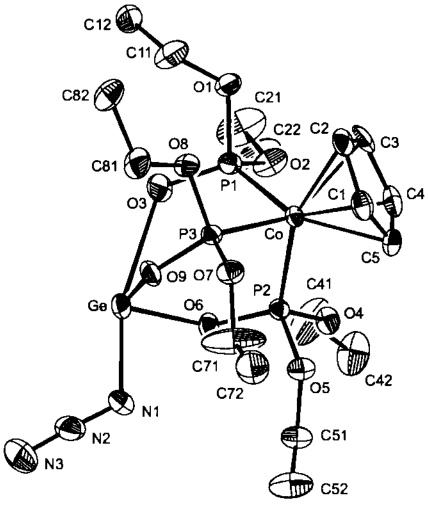


Fig. 3 ZORTEP plot of the molecular structure of compound **3** with thermal ellipsoids drawn at 15% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for $L_{OEt}GeX$ (X = Cl **2** or N_3 **3**)

	2 (X = Cl)	**3** (X = N_3)		**2** (X = Cl)	**3** (X = N_3)
Ge–X	241.93(9)	209.4(7)	X–Ge–O(3)	166.40(5)	160.95(14)
Ge–O(3)	249.49(19)	256.7(5)	X–Ge–O(6)	90.31(6)	87.25(19)
Ge–O(6)	192.94(18)	190.5(3)	X–Ge–O(9)	89.50(6)	87.56(19)
Ge–O(9)	191.86(17)	190.1(3)	O(3)–Ge–O(6)	81.94(7)	80.04(16)
P(1)–O(1)	159.3(2)	160.2(5)	O(3)–Ge–O(9)	80.07(7)	79.62(15)
P(1)–O(2)	160.7(2)	157.7(4)	O(6)–Ge–O(9)	94.63(7)	95.36(12)
P(1)–O(3)	149.1(2)	149.0(4)	P(1)–O(3)–Ge	125.25(10)	123.4(2)
P(2)–O(4)	158.16(19)	158.3(3)	P(2)–O(6)–Ge	135.62(11)	132.27(19)
P(2)–O(5)	158.70(19)	158.4(4)	P(3)–O(9)–Ge	132.61(10)	136.9(2)
P(2)–O(6)	152.97(19)	154.5(3)	Co–P(1)–O(1)	104.15(7)	111.00(12)
P(3)–O(7)	158.50(19)	159.7(4)	Co–P(1)–O(2)	110.01(8)	104.75(14)
P(3)–O(8)	159.59(18)	157.7(4)	Co–P(1)–O(3)	118.66(8)	118.06(18)
P(3)–O(9)	153.39(18)	153.9(3)	Co–P(2)–O(4)	108.00(8)	114.19(16)
Co–P(1)	218.84(10)	219.04(13)	Co–P(2)–O(5)	112.28(8)	108.64(14)
Co–P(2)	215.02(8)	214.59(16)	Co–P(2)–O(6)	118.99(7)	118.58(15)
Co–P(3)	214.14(8)	214.71(13)	Co–P(3)–O(7)	108.42(7)	114.54(13)
Co–C(1)	208.8(3)	209.7(4)	Co–P(3)–O(8)	115.60(7)	108.79(15)
Co–C(2)	207.6(3)	208.0(5)	Co–P(3)–O(9)	118.23(8)	118.59(13)
Co–C(3)	207.1(3)	207.2(6)	P(1)–Co–P(2)	89.68(3)	91.33(5)
Co–C(4)	207.5(3)	205.9(4)	P(1)–Co–P(3)	93.65(3)	91.11(5)
Co–C(5)	207.6(3)	209.4(4)	P(2)–Co–P(3)	91.59(3)	92.12(5)
N(1)–N(2)		118.0(7)	Ge–N(1)–N(2)		119.9(5)
N(2)–N(3)		115.9(8)	N(1)–N(2)–N(3)		177.4(8)

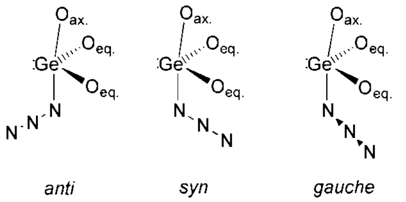


Fig. 4 Possible conformations of the azide group in compound **3**. Only the germanium-bonded O atoms of the L_{OEt} ligand and the N atoms of the azide group are depicted. Lines represent bonds and the dots the lone electron pair at the germanium atom.

due to the azide group, which adopts a *gauche* conformation as indicated by the torsion angle O(3)–Ge–N(1)–N(2) of 152.2° (Fig. 4). The same conformation is adopted by the azide group in **5** the corresponding torsion angle being 76.2°.[2]

The Ge–Cl bond of compound **2** is with 241.93(9) pm considerably longer than those reported for most germanium(II) chlorides, *e.g.* $[Ge(C_6H_3Mes_2\text{-}2,6)Cl]_2$ (Mes = $C_6H_2Me_3$-2,4,6) [Ge–Cl 212.0(2) pm],[15] $GeCl_2(g)$ [218.6(4) pm],[16] $GeCl_2$-$(C_4H_8O_2)$ [228.00(7) pm],[17] $[HPMe_3][GeCl_3]$ [average Ge–Cl 230.71(9) pm][18] and Cp*GeCl [238.41(8) pm].[19] However this bond is shorter than those found in the analogous germanium(II) compounds, *e.g.* $L_{OMe}GeCl$ [L_{OMe} = $(C_5H_5)Co\{P(O)(OMe)_2\}_3$],[9] L_{OEt}*GeCl,[9] Tp′GeCl[2] (Table 3, see below) and $TpGeCl{\cdot}CH_2Cl_2$ [Tp = $HB(pz)_3$; 297.02(14) pm].[20] These structural data as well as the fast reactions of Tp′GeCl and $L_{OEt}GeCl$ with $InCl_3$ to give the ionic compounds [Tp′Ge][$InCl_4$] and [L_{OEt}Ge][$InCl_4$][9] suggest the presence of a weak and polar Ge–Cl bond in germanium(II) chlorides bearing the tridentate ligands L_{OMe}, L_{OEt}, L_{OEt}*, Tp and Tp′. Similarly, the Ge–N_{azide} distance in **3** [209.4(7) pm] is larger than those found in other germanium(II) compounds, *e.g.* $\overline{GeN(^tBu)(CH_2)_2N}{}^tBu$ [Ge–N 183.3(2) pm],[21] $\overline{GeN(SiMe_3)C_6H_4N}(SiMe_3)$ [average Ge–N 186.4(8) pm][22] and $Ge[N(SiMe_3)_2]_2$ [average Ge–N 187.5(5) pm].[23] It is also larger than that of germanium(IV) azides (Ge–N 187–197 pm, see discussion of the crystal structures of **4** and **6**) and larger than that calculated for a Ge–N single bond (184 pm) using the modified Schomaker–Stevenson equation of Blom and Haaland.[24] In addition, the N_α–N_β bond of the azide group [118.0(7) pm] is slightly longer than the N_β–N_γ bond [115.9(8) pm], the difference ΔNN of 2.1 pm being considerably smaller than that observed for various covalent azides of main-group elements, such as HN_3 [ΔNN = 10.9(6) pm],[25] alkyl azides [average ΔNN = 8.3 pm][26,27] and germanium(IV) azides (Table 6, see below). The angle at the N_α atom of the azide group of 119.9(5)° is similar to that found in various germanium(IV) azides (Table 6, see below) and the azide group is slightly bent at the N_β atom as shown by the angle N(1)–N(2)–N(3) of 177.4(8)°. Deviation of the nitrogen atoms from collinearity is observed in several azides of the Group IV elements[2,13,26,28] and is not surprising since the energy required to bend the azide group is predicted to be very small.[29] All these structural data indicate in agreement with the IR spectroscopic results (see above) the presence of a polar Ge–N_{azide} bond in **3**. Thus, this bond can be described in the context of the valence bond model by the three canonical forms **A**–**C**, the resonance forms **B** and **C** contributing substantially to the bond (Fig. 5).

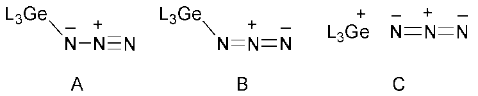


Fig. 5 Canonical forms for the description of the Ge–N_{azide} bond in compounds **3** and **5** (L_3 = L_{OEt} or Tp′).

Compound **3** has a shorter Ge–N_{azide} bond than Tp′GeN_3 **5** (Table 3), a longer N_α–N_β bond [**3**, 118.0(7) pm; **5**: 113.6(5) pm] and its $\nu_{asym}(N_3)$ absorption appears at higher frequency than that of **5** (Table 1). These data indicate a more covalent Ge–N_{azide} bond in **3** than in **5**, which might be also the reason for the lower thermal stability of **3** compared with **5**. Further evidence for the presence of a more covalent bond in **3** is given by comparing the degree of distortion of the tridentate ligand. This is best manifested in the difference of the Ge–L_{ax} and Ge–L_{eq} bond lengths and can be calculated using the expression $D = [d(\text{Ge–L}_{ax}) - d(\text{Ge–L}_{eq})]/d(\text{Ge–L}_{eq}) \times 100\%$. The D values were calculated for various germanium(II) compounds of the general formula L_3GeX and are listed with other relevant structural data in Table 3.

In all compounds the Ge–L_{ax} bonds are considerably longer than the Ge–L_{eq} bonds, which can be explained using the three-center, four-electron semilocalized orbital bonding model,[30] and agrees with the results of extended Hückel[31] and *ab initio* MO calculations[32] on related hypervalent compounds. Moreover the more ionic the Ge–X bond the shorter the Ge–L_{ax} bond and the smaller D would be expected to become. This is verified by the structural data of various germanium(II) chlorides bearing L_{OR} and Tp′ ligands, which show a continuous increase of the Ge–Cl bond length upon decreasing D (Table 3).

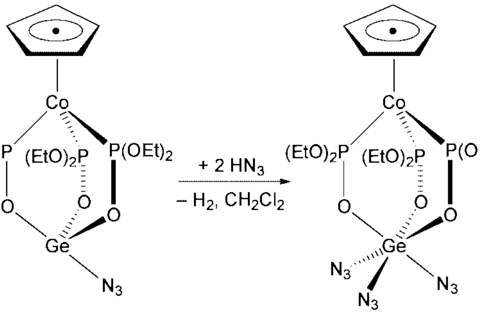
Table 3 Some structural data of germanium(II) compounds of the general formula L_3GeX[a]

Compound	Ge–X[b]	Ge–L_{ax}[b]	Ge–L_{eq}[b,c]	D	L_{ax}–Ge–X[b]	L_{eq}–Ge–X[b,c]	L_{ax}–Ge–L_{eq}[b,c]
$L_{OEt}GeCl$ **2**	241.93(9)	249.49(19)	192.40(17)	29.7	166.40(5)	89.90(6)	81.00(7)
$L_{OMe}GeCl$[d]	245.82(16)	242.9(4)	191.9(4)	26.6	166.63(9)	88.92(12)	82.28(15)
L_{OEt}*GeCl	247.48(14)	237.0(3)	191.8(3)	23.6	166.55(8)	88.68(9)	82.23(11)
Tp′GeCl	253.6(1)	237.9(3)	201.8(3)	17.9	163.15(9)	88.1(1)	79.90(13)
$L_{OEt}GeN_3$ **3**	209.4(7)	256.7(5)	190.3(3)	34.9	160.95(14)	87.40(19)	79.83(15)
Tp′GeN_3 **5**	226.2(4)	229.7(3)	202.4(3)	13.5	162.81(16)	87.09(15)	81.07(13)
Tp′GeBr	290.71(14)	223.2(3)	200.2(3)	11.5	162.87(8)	85.11(9)	82.72(12)
Tp′GeNCS	265.1(2)	209.0(2)	200.4(2)	4.3	160.76(9)	81.54(9)	84.65(9)

[a] $L_3 = L_{OMe}$, L_{OEt}, L_{OEt}* or Tp′; X = Cl, N_3, Br or NCS. [b] Bond lengths are given in pm, bond angles in degrees and estimated standard deviations in parentheses. [c] Ge–L_{eq} is the mean value of the two equatorial Ge–L bond lengths, L_{eq}–Ge–X the mean value of the two L_{eq}–Ge–X bond angles, and L_{ax}–Ge–L_{eq} the mean value of the two L_{ax}–Ge–L_{eq} bond angles. [d] Two crystallographically independent molecules are found in the crystal structure; the listed bond lengths and angles are the average values for the two molecules.

D becomes zero in ionic derivatives, such as [L_{OEt}*Ge][SCN] [average Ge–O 191.8(3) pm] and [Tp′Ge][$InCl_4$] [average Ge–N 200.0(7) pm], which contain trigonal pyramidal cations with an idealized C_{3v} molecular symmetry.[9] It is also larger in $L_{OR}Ge^{II}$ compounds (*e.g.* **3**) than Tp′Ge^{II} derivatives (*e.g.* **5**) suggesting that the former have a more covalent Ge–X bond. In fact, the Ge–O_{ax} bond of **2** and **3** is by 57.1 and 66.4 pm longer than the mean Ge–O_{eq} bond (Table 3) and also longer than the Ge–O donor–acceptor bond of $GeCl_2(C_4H_8O_2)$ [240.9(3) pm].[17] The Ge–O_{eq} distances in **2** and **3** are similar to those of other germanium(II) compounds (Table 3) or germanium(IV) derivatives bearing an L_{OR} ligand [*e.g.*, **4**, average Ge–O 189.3(6) pm (Table 4); L_{OEt}*$Ge(N_3)_3$, average Ge–O 190.8(6) pm; $L_{OEt}GeCl_3$·$CHCl_3$, average Ge–O 192.1(3) pm][9] and correspond to Ge–O single bonds. They are however slightly longer than those of two-co-ordinate germanium(II) compounds [*e.g.* $Ge(OC_6H_2Me\text{-}4\text{-}^tBu_2\text{-}2,6)_2$: average Ge–O 180.7(8) pm],[33] in which pπ–pπ bonding interactions are expected to shorten the Ge–O bonds, and also longer than that calculated for a Ge(sp^3)–O single bond (177 pm)[24,34] probably due to the lower s character of the Ge–O_{eq} bonds.

The germanium(II) azides **3** and **5** are useful starting materials for the synthesis of hitherto unknown six-co-ordinate triazidogermanium(IV) compounds. Thus, treatment of **3** with more than two equivalents of HN_3 resulted in the formation of **4**, which was isolated as a yellow solid in 63% yield (eqn. 1).

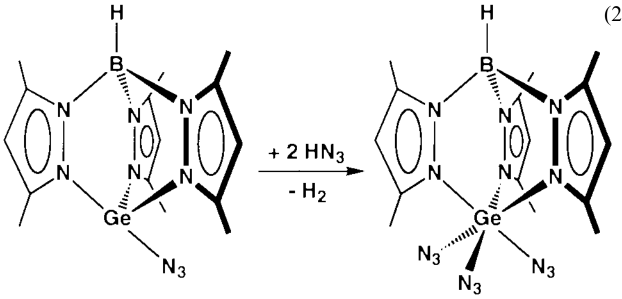


(1)

3 **4**

Similarly, the oxidation of **5** with two equivalents of HN_3 afforded the triazidogermanium(IV) derivative **6**, which was isolated as a white, microcrystalline solid in 72% yield (eqn. 2). Both compounds are soluble in MeCN, CH_2Cl_2 and THF, sparingly soluble in Et_2O and insoluble in pentane, the L_{OEt} derivative **4** being in general more soluble than the Tp′ derivative **6**. They show remarkable thermal stability decomposing upon heating at 235 and 224 °C, respectively.

Another conceivable synthesis of compounds **4** and **6** could involve the salt metathesis reaction of the trichlorogermanium(IV) congeners $L_{OEt}GeCl_3$ and Tp′$GeCl_3$ with NaN_3. In order to test the suitability of this method, $L_{OEt}GeCl_3$ was selectively prepared by oxidation of **2** with $PhICl_2$, and Tp′$GeCl_3$ by chloride substitution from $GeCl_4$ and KTp′.[9] The compound Tp′$GeCl_3$ proved to be quite unreactive towards NaN_3. For example, only a very slow and uncomplete conversion of this compound was observed in refluxing THF or MeCN in the presence of an excess of NaN_3, whereas decomposition occurred in refluxing toluene.



(2)

5 **6**

Compounds **4** and **6** were fully characterized. Thus, the IR spectrum of **4** shows in CH_2Cl_2 two absorptions for the $\nu_{asym}(N_3)$ vibrations at 2114 and 2095 cm^{-1} (Table 1). This indicates at first glance a C_{3v} symmetric $Ge(N_3)_3$ fragment.[35] However, this fragment has approximately C_s symmetry in the solid state (Figs. 6 and 8), which implies the existence of three $\nu_{asym}(N_3)$ absorptions, two of them overlapping to give the strong band at 2095 cm^{-1}. In comparison, the IR spectrum of **6** in THF displays four $\nu_{asym}(N_3)$ absorptions (Table 1) suggesting the presence of at least two conformers in solution, whereas the azide groups of **6** adopt in the solid state a C_1 symmetric conformation (Figs. 7 and 8). The $\nu_{asym}(N_3)$ absorptions of **4** and **6** appear at higher wavenumbers than those of the germanium(II) azides **3** and **5** indicating a higher covalent character of the Ge–N_{azide} bonds in **4** and **6** or in terms of the valence bond model a stronger contribution of the resonance formula **A** to the Ge–N_{azide} bond (Fig. 5). This is supported by the structural data of these compounds (Table 6, see below). Furthermore a comparison of the IR spectra in KBr of $L_{OEt}GeCl_3$ with **4** and of Tp′$GeCl_3$ with **6** allows a tentative assignment of the absorption at 1297 cm^{-1} (**4**) and the absorptions at 1292 and 1285 cm^{-1} (**6**) to the $\nu_{sym}(N_3)$ vibrations. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of **4** and **6** show a single set of resonances for the phosphonato and pyrazolyl groups as expected for compounds with an idealized C_{3v} symmetry. In addition, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4** in $CDCl_3$ shows one singlet resonance for the equivalent phosphonato groups, which appears at lower field (δ 113.8) than that of **3** (δ 110.3).

The solid-state structures of compounds **4** and **6** were determined by single-crystal X-ray diffraction. Suitable single crystals of **4** were obtained upon slow diffusion of diethyl ether into a THF solution of **4** in a glove-box and single crystals of **6** were grown upon evaporation of a CD_2Cl_2 solution over weeks at ambient temperature. ZORTEP plots of the molecular structures of **4** and **6** with the atom-labeling schemes adopted are

Table 4 Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for $L_{OEt}Ge(N_3)_3$ **4**

Ge–O(3)	188.5(6)	O(3)–Ge–O(6)	91.4(3)	O(6)–Ge–N(7)	175.4(3)
Ge–O(6)	188.4(5)	O(3)–Ge–O(9)	89.7(3)	O(9)–Ge–N(1)	176.2(3)
Ge–O(9)	190.9(6)	O(6)–Ge–O(9)	88.5(3)	O(9)–Ge–N(4)	91.3(3)
Ge–N(1)	193.5(8)	N(1)–Ge–N(4)	92.4(3)	O(9)–Ge–N(7)	90.1(4)
Ge–N(4)	192.6(7)	N(1)–Ge–N(7)	89.0(4)	Ge–N(1)–N(2)	121.5(6)
Ge–N(7)	196.0(9)	N(4)–Ge–N(7)	94.3(4)	Ge–N(4)–N(5)	121.1(6)
N(1)–N(2)	116.6(10)	O(3)–Ge–N(1)	86.5(3)	Ge–N(7)–N(8)	118.6(9)
N(2)–N(3)	109.1(12)	O(3)–Ge–N(4)	178.2(3)	N(1)–N(2)–N(3)	174.1(9)
N(4)–N(5)	116.3(11)	O(3)–Ge–N(7)	84.2(4)	N(4)–N(5)–N(6)	176.6(8)
N(5)–N(6)	114.9(12)	O(6)–Ge–N(1)	92.1(3)	N(7)–N(8)–N(9)	171.9(14)
N(7)–N(8)	116.3(14)	O(6)–Ge–N(4)	90.1(3)		
N(8)–N(9)	111.6(16)				

Table 5 Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for $Tp'Ge(N_3)_3$ **6**

Ge–N(1)	203.1(3)	N(1)–Ge–N(3)	87.97(9)	N(3)–Ge–N(13)	176.75(9)
Ge–N(3)	204.4(3)	N(1)–Ge–N(5)	85.82(11)	N(5)–Ge–N(7)	177.05(9)
Ge–N(5)	202.3(3)	N(3)–Ge–N(5)	87.51(10)	N(5)–Ge–N(10)	91.99(11)
Ge–N(7)	195.4(3)	N(7)–Ge–N(10)	89.79(12)	N(5)–Ge–N(13)	90.29(10)
Ge–N(10)	193.9(3)	N(7)–Ge–N(13)	92.04(11)	Ge–N(7)–N(8)	120.4(2)
Ge–N(13)	193.7(3)	N(10)–Ge–N(13)	90.91(11)	Ge–N(10)–N(11)	118.4(2)
N(7)–N(8)	121.2(4)	N(1)–Ge–N(7)	92.38(11)	Ge–N(13)–N(14)	116.1(2)
N(8)–N(9)	114.2(4)	N(1)–Ge–N(10)	177.78(10)	N(7)–N(8)–N(9)	176.7(3)
N(10)–N(11)	122.0(4)	N(1)–Ge–N(13)	89.49(10)	N(10)–N(11)–N(12)	176.5(3)
N(11)–N(12)	114.1(4)	N(3)–Ge–N(7)	90.09(10)	N(13)–N(14)–N(15)	175.6(3)
N(13)–N(14)	122.1(4)	N(3)–Ge–N(10)	91.55(10)		
N(14)–N(15)	114.1(4)				

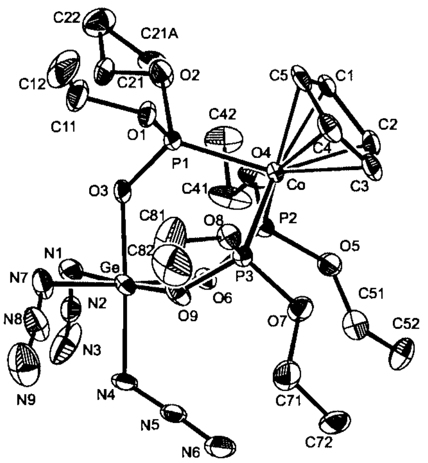


Fig. 6 ZORTEP plot of the molecular structure of compound **4** with thermal ellipsoids drawn at 15% probability level. Hydrogen atoms are omitted for clarity.

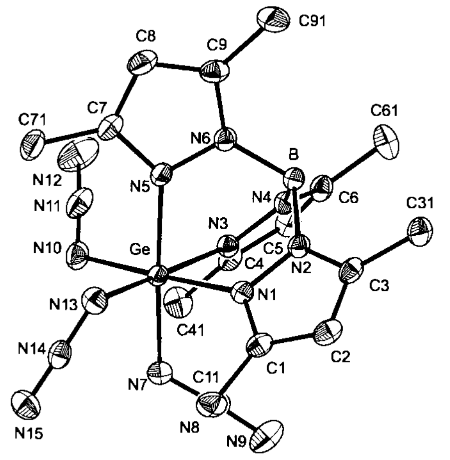


Fig. 7 ZORTEP plot of the molecular structure of compound **6** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

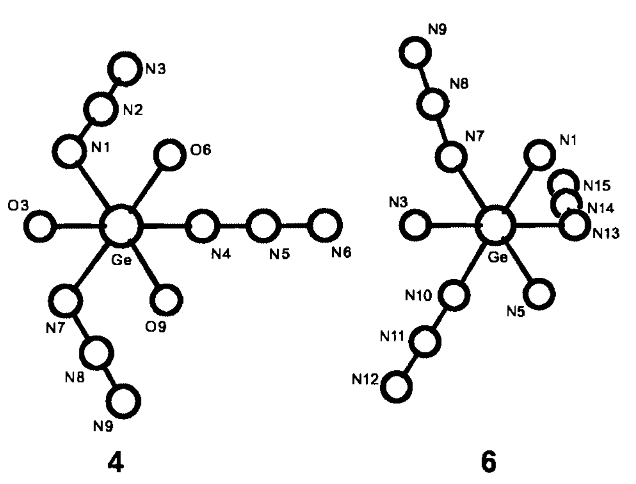


Fig. 8 View of the molecule of compound **4** down the Co–Ge axis and of **6** down the B–Ge axis. Only the co-ordination sphere of the germanium atom and the azide groups are depicted.

depicted in Figs. 6 and 7, respectively. Selected bond lengths and angles are listed in Tables 4 and 5.

Compounds **4** and **6** are rare examples of six-co-ordinate germanium compounds with an octahedral GeN_6 framework. The only other known compounds of this type are to our knowledge $K_2[Ge(NCS)_6]$[36] and $Ge(por)(N_3)_2$ [por = tptp, tmtp or oep; tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2−), tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate(2−), oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−)].[28a] Compound **4** has an idealized C_s molecular symmetry, the symmetry plane passing through the atoms Co, P(1), O(3), Ge, N(4), N(5) and N(6) (Figs. 6 and 8), whereas **6** is C_1 symmetric due to the *gauche* conformation adopted by the azide group N(13)–N(14)–N(15) (Figs. 7 and 8).

The mean $Ge–N_{azide}$ bond length of compound **4** [194.0(8) pm] and of **6** [194.3(3) pm] compares well with that of other octahedral germanium(IV) polyazides (Table 6). It is however larger than that of tetrahedral organogermanium(IV) azides, *e.g.* $Ge[N(SiMe_3)_2][N(SiMe_3)Ph]_2N_3$ [$Ge–N_{azide}$ 186.9(4) pm],[22] and shorter than that of the germanium(II) azides **3** [Ge–N

Table 6 Structural parameters of azide groups in various six-co-ordinate germanium(IV) azides

Compound	Ge–N[a]	N_α–N_β[a]	N_β–N_γ[a]	Ge–N_α–N_β[a]	ΔNN[b]	Ref.
$L_{OEt}Ge(N_3)_3$ **4**	194.0(8)	116.4(12)	111.9(13)	120.4(7)	4.5	This work
$L_{OEt}*Ge(N_3)_3$	192.1(11)	119.5(15)	116.8(16)	117.0(11)	2.7	9
$Tp'Ge(N_3)_3$ **6**	194.3(3)	121.8(4)	114.1(4)	118.3(2)	7.7	This work
$TpGe(N_3)_3$	193.4(3)	121.1(4)	114.3(5)	120.0(3)	6.8	9
$[N(PPh_3)_2]_2[Ge(N_3)_6]$	197.4(2)	121.2(3)	114.7(3)	119.81(17)	6.5	9
$Ge(tptp)_2(N_3)_2$	196.3(4)	116.0(8)	115.4(13)	124.8(1)	0.6	28(*a*)

[a] Mean bond lengths are given in pm, mean bond angles in degrees and estimated standard deviations in parentheses. [b] The difference between the mean N_α–N_β and N_β–N_γ bond lengths of the azide groups in pm.

209.4(7) pm] and **5** [Ge–N_{azide} 226.2(4) pm] (see above). This trend is predicted by the delocalized molecular orbital model used to describe the bonding in six-co-ordinate compounds of main-group elements such as **4** and **6**.[37] The above mentioned model offers also an explanation for the long Ge–O bonds of **4** [average Ge–O 189.3(6) pm] and the long Ge–N_{pz} bonds of **6** [average Ge–N 203.3(3) pm] considering the calculated length of a Ge–O [177 pm] and a Ge–N single bond [184 pm].[24] In addition, the difference ΔNN between the mean N_α–N_β and N_β–N_γ bond lengths of the azide groups has a value of 4.5 (**4**) and 7.7 pm (**6**), which is close to that found for most six-co-ordinate germanium(IV) azides (Table 6), but is larger than that of the germanium(II) azides **3** and **5**. All these structural data suggest that the covalent character of the Ge–N_{azide} bond decreases in the series four-co-ordinate germanium(IV) azides > six-co-ordinate germanium(IV) azides > four-co-ordinate germanium(II) azides.

Conclusion

Cyclopentadienyltris(diethylphosphonato-*P*)cobaltate(1−) is a useful tripod ligand for the stabilization of metastable germanium(II) compounds as shown by the synthesis of the azide $L_{OEt}GeN_3$ **3**. Spectroscopic and structural data of **3** and of related germanium(II) azides indicate the presence of a polar Ge–N_{azide} bond. This is supported by the solvent-dependent dissociation equilibrium between **3** and the ions $[L_{OEt}Ge]^+$ and N_3^- observed in solution. The oxidation of germanium(II) azides with HN_3 offers a unique route to hitherto unknown six-co-ordinate germanium(IV) triazides, such as $L_{OEt}Ge(N_3)_3$ and $Tp'Ge(N_3)_3$, having an octahedral GeN_6 framework.

Experimental

General

Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane over CaH_2, Et_2O and THF over Na/benzophenone, CH_2Cl_2 over Sicapent and Na/Pb alloy, $CHCl_3$ over Sicapent, MeCN over Sicapent and predried K_2CO_3), distilled under argon and stored over 4 or 3 Å (MeCN) molecular sieves prior to use; DMF was dried as described in ref. 38 and stored over 4 Å molecular sieves. The compounds $GeCl_2(C_4H_8O_2)$, NaL_{OEt} and a solution of HN_3 in diethyl ether were prepared according to literature procedures.[39–41] The ether solution of HN_3 was dried over P_4O_{10} and recondensed *in vacuo*. Its concentration was determined by titration with an aqueous 0.1 M solution of NaOH. The compound NaN_3 was finely ground and dried for 15 h at 109 °C in a vacuum of 10^{-2} mbar. All other chemicals were commercially available. Sicapent was purchased from Merck.

Elemental analyses were obtained from the Central Analytical Group of the Department of Chemistry of the Humboldt-Universität zu Berlin. Solution IR spectra were recorded in the region of 2600–1500 cm^{-1} on a Bruker IFS-55 spectrometer using a NaCl or CaF_2 cell, ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectra on a Bruker AM-300 spectrometer in dry deoxygenated methylene-d_2 chloride, chloroform-d_1 or toluene-d_8 at 20 °C. The ^1H and ^{13}C-{^1H} NMR spectra were calibrated against the internal residual proton or natural abundance ^{13}C resonances of the deuteriated solvent (methylene-d_2 chloride, δ_H 5.32 and δ_C 53.8; chloroform-d_1, δ_H 7.24 and δ_C 77.0; toluene-d_8, $\delta(CD_2H)$ 2.09 and $\delta(CD_2H)$ 20.4) and the ^{31}P-{^1H} NMR spectra against an external 85% H_3PO_4 aqueous solution. Temperature calibration was carried out by measuring the difference in chemical shift of the two ^1H NMR signals of a 4% CH_3OH solution in CD_3OD. The standard deviation for the temperature values was found to be ±3.5 K. Mass spectra were obtained with a Hewlett Packard 5995A spectrometer; *m*/*z* values are given relative to the ^{74}Ge and ^{35}Cl isotopes. Melting points were determined using a Büchi 530 melting point apparatus and are not corrected. The samples were sealed in capillary tubes *in vacuo* and heated with a rate of 3 K min^{-1} to a temperature 10 K lower than that of melting. Heating was then continued with a rate of 0.5 K min^{-1} until the sample melted. IR spectra of the heated samples of **3**, **4** and **6** were recorded and compared with those of authentic samples to determine whether the compounds had decomposed.

Syntheses

$L_{OEt}GeCl$ 2. The compound $GeCl_2(C_4H_8O_2)$ **1** (213 mg, 0.92 mmol) and 508 mg (0.91 mmol) of NaL_{OEt} were weighted in a Schlenk tube and the mixture dissolved in 30 ml of THF at −78 °C. The solution was allowed to warm to ambient temperature and stirred for 3 h. During this time the yellow solution became cloudy and a white, fine granular precipitate formed. The suspension was filtered and the filtrate evaporated to dryness. The residue was treated with 150 ml of pentane, the yellow pentane solution filtered and the filtrate concentrated *in vacuo* to a few milliliters and cooled overnight to −78 °C. The resulting yellow, microcrystalline precipitate was separated from the supernatant solution and dried *in vacuo*. Yield 556 mg (95% relative to NaL_{OEt}). mp 122 °C (decomp.) (Found: C, 32.49; H, 5.60; Cl, 5.37%. Calc. for $C_{17}H_{35}ClCoGeO_9P_3$: C, 31.74; H, 5.48; Cl, 5.51%). IR (KBr, cm^{-1}): 3129vw, 3112vw, 2976m, 2926w, 2900w, 2864vw, 1481vw, 1440w, 1425w, 1386w, 1370vw, 1156m, 1133s [ν(P=O)], 1101m, 1031vs, 1014vs (sh), 982s, 948vs, 936vs, 859w, 843m, 778m, 742w, 721w (sh), 628m, 600s and 571s. ^1H NMR (toluene-d_8, 300 MHz, 297 K): δ 1.17 (t, ^3J(HH) = 7.1, 18H, 6 CH_3), 4.14 (m, 12H, 6 CH_2) and 4.89 (q, ^3J(PH) = 0.5 Hz, 5H, C_5H_5). ^{13}C-{^1H} NMR (toluene-d_8, 75.5 MHz, 297 K): δ 16.7 (m, ^3J(PC) + ^5J(PC) = 6.0 Hz, CH_3), 61.8 (m, CH_2) and 89.9 (q, ^2J(PC) = 1.7 Hz, C_5H_5). ^{31}P-{^1H} NMR (toluene-d_8, 121.5 MHz, 297 K): δ 110.4. ^1H NMR (toluene-d_8, 300 MHz, 175 K): δ 1.16, 1.28 (br, 12:6, 18H, 6 CH_3), 4.07, 4.19, 4.44, 4.69 (br, 6:2:2:2, 12H, 6 CH_2) and 4.84 (s, 5H, C_5H_5). ^{13}C-{^1H} NMR (toluene-d_8, 75.5 MHz, 175 K): δ 16.5, 16.7 (br, 4:2, 6CH_3), 60.3, 62.1, 62.4 (br, 2:2:2, 6CH_2) and 89.7 (C_5H_5). ^{31}P-{^1H} NMR (toluene-d_8, 121.5 MHz, 175 K): δ 97.1 (t, ^2J(PP) = 135, 1P) and 120.1 (d, ^2J(PP) = 135 Hz, 2P). ^1H NMR ($CDCl_3$, 300 MHz, 297 K): δ 1.27 (t, ^3J(HH) = 7.1 Hz, 18H, 6 CH_3), 4.13 (m, 12 H, 6 CH_2) and 5.17 (s, 5H, C_5H_5). ^{13}C-{^1H} NMR ($CDCl_3$, 75.5 MHz, 297 K): δ 16.4 (m, ^3J(PC) + ^5J(PC) = 6.4, CH_3), 62.5 (^2J(PC) + ^4J(PC) = 9.2, CH$_2$) and 90.2 (q, ^2J(PC) = 1.6 Hz, C$_5$H$_5$). ^{31}P-{^{1}H} NMR (CDCl$_3$, 121.5 MHz, 297 K): δ 112.1. EI-MS (70 eV), *m/z* (rel. intensity in %) 609 (14, [M − Cl]$^+$), 580 (4, [M − Cl − Et]$^+$), 552 (33, [M − Cl − Et − C$_2$H$_4$]$^+$), 488 (16, [M − Cl − Et − P(O)(OEt)]$^+$), 460 (8, [M − Cl − Et − C$_2$H$_4$ − P(O)(OEt)]$^+$), 396 (8, [M − Cl − Et − 2 P(O)(OEt)]$^+$), 380 (10, [M − Cl − Et − P(O)$_2$(OEt) − P(O)(OEt)]$^+$), 368 (12, [M − Cl − Et − C$_2$H$_4$ − P(O)$_2$(OEt) − P(O)(OEt)]$^+$), 288 (15, [M − Cl − Et − P(O)$_2$(OEt) − 2 P(O)(OEt)]$^+$), 139 (30, [CpGe]$^+$) and 124 (100%, [CpCo]$^+$).

L$_{\mathrm{OEt}}$GeN$_3$ 3. Compound **2** (440 mg, 0.68 mmol) and 117 mg (1.8 mmol) of NaN$_3$ were weighed in a Schlenk tube and the mixture suspended at ambient temperature in 50 ml of THF. IR monitoring of the reaction revealed a continuous increase in intensity of the ν_{asym}(N$_3$) absorption of the product in THF at 2053 cm^{-1}. After 24 h stirring at ambient temperature no change in intensity of this absorption was detectable and the suspension was evaporated to dryness. The yellow residue was dried *in vacuo* and extracted three times with 40 ml of pentane. The extracts were filtered from insoluble material, combined and concentrated *in vacuo* to a few milliliters resulting in the precipitation of a yellow, microcrystalline solid. The supernatant solution was rejected and the solid dried *in vacuo* for several hours. Yield 355 mg (80%). mp 98 °C (decomp.) (Found: C, 31.41; H, 5.41; Cl, 0; N, 6.29%. Calc. for C$_{17}$H$_{35}$CoGeN$_3$O$_9$P$_3$: C, 31.34; H, 5.42; N, 6.29%). IR (cm^{-1}): (CH$_2$Cl$_2$) 2055vs, 2005vw [ν_{asym}(N$_3$)]; (THF) 2053vs [ν_{asym}(N$_3$)]; (Et$_2$O) 2058vs [ν_{asym}(N$_3$)]; (pentane) 2063vs [ν_{asym}(N$_3$)]; (KBr) 3118vw, 3097vw, 2978m, 2928w, 2901w, 2866vw, 2049vs [ν_{asym}(N$_3$)], 1479vw, 1442w, 1421vw, 1387w, 1365vw, 1325vw, 1279vw [ν_{sym}(N$_3$)], 1164m, 1139s [ν(P=O)], 1100m, 1042vs, 1023vs, 978s, 945vs, 923vs, 843m, 837m, 777m, 758m, 746m, 721m, 630w, 604s, 567s, 500vw and 454vw. ^{1}H NMR (toluene-d_8, 300 MHz, 297 K): δ 1.17 (t, ^3J(HH) = 7.1 Hz, 18H, 6 CH$_3$), 4.10 (m, 12H, 6 CH$_2$) and 4.88 (5H, C$_5$H$_5$). ^{13}C-{^{1}H} NMR (toluene-d_8, 75.5 MHz, 297 K): δ 16.7 (m, ^3J(PC) + ^5J(PC) = 6.0, CH$_3$), 61.6 (m, CH$_2$) and 89.9 (q, ^2J(PC) = 1.6 Hz, C$_5$H$_5$). ^{31}P-{^{1}H} NMR (toluene-d_8, 121.5 MHz, 297 K): δ 109.3. ^{1}H NMR (toluene-d_8, 300 MHz, 168 K): δ 1.12, 1.18, 1.26 (br, 6 : 6 : 6, 18H, 6 CH$_3$), 4.04, 4.23, 4.29, 4.48 (br, 6 : 2 : 2 : 2, 12H, 6 C*H*$_2$), 4.82 (s, 5H, C$_5$*H*$_5$). ^{13}C-{^{1}H} NMR (toluene-d_8, 75.5 MHz, 168 K): δ 16.4, 16.7 (br, 4 : 2, 6 CH$_3$), 60.2, 62.0 (br, 2 : 4, 6 CH$_2$) and 89.7 (C$_5$H$_5$). ^{31}P-{^{1}H} NMR (toluene-d_8, 121.5 MHz, 168 K): δ 95.8 (t, ^2J(PP) = 135, 1P) and 120.1 (d, ^2J(PP) = 135 Hz, 2P). ^{1}H NMR (CDCl$_3$, 300 MHz, 297 K): δ 1.26 (t, ^3J(HH) = 7.1 Hz, 18H, 6 CH$_3$), 4.12 (m, 12H, 6 CH$_2$) and 5.09 (s, 5H, C$_5$H$_5$). ^{13}C-{^{1}H} NMR (CDCl$_3$, 75.5 MHz, 297 K): δ 16.5 (m, ^3J(PC) + ^5J(PC) = 5.6, CH$_3$), 61.7 (m, ^2J(PC) + ^4J(PC) = 9.2, CH$_2$) and 90.1 (q, ^2J(PC) = 1.5 Hz, C$_5$H$_5$). ^{31}P-{^{1}H} NMR (CDCl$_3$, 121.5 MHz, 297 K): δ 110.3. EI-MS (70 eV), *m/z* (rel. intensity in %): 609 (26, [M − N$_3$]$^+$), 580 (3, [M − N$_3$ − Et]$^+$), 535 (2, [M − N$_3$ − Et − OEt]$^+$), 488 (10, [M − N$_3$ − Et − P(O)OEt]$^+$), 396 (4, [M − N$_3$ − Et − 2 P(O)(OEt)]$^+$), 380 (5, [M − N$_3$ − Et − P(O)$_2$(OEt) − P(O)(OEt)]$^+$), 288 (11, [M − N$_3$ − Et − P(O)$_2$(OEt) − 2 P(O)(OEt)]$^+$), 139 (17, [CpGe]$^+$), 124 (83, [CpCo]$^+$) and 29 (100, [C$_2$H$_5$]$^+$).

L$_{\mathrm{OEt}}$Ge(N$_3$)$_3$ 4. A solution of 290 mg (0.45 mmol) of compound **3** in 40 ml of CH$_2$Cl$_2$ was treated at ambient temperature with 0.93 ml (1.14 mmol) of a 1.23 M solution of HN$_3$ in diethyl ether and stirred for 26 h. IR monitoring of the reaction revealed a gradual replacement of the ν_{asym}(N$_3$) absorption of HN$_3$ at 2137 cm^{-1} and of **3** at 2055 cm^{-1} by those of the product at 2114 and 2095 cm^{-1}. The cloudy yellow solution was evaporated to dryness. The residue was washed three times with 5 ml of pentane to remove some starting material and extracted with 10 ml and then 5 ml of CH$_2$Cl$_2$. The combined extracts were concentrated to approximately 0.5 ml and treated with 1 ml of diethyl ether and then 10 ml of pentane to precipitate the product. The supernatant pale yellow solution was rejected and the precipitate washed with 5 ml of pentane and dried *in vacuo* for 4 h to afford **4** as a pale yellow solid. Yield 206 mg (63%). mp 235 °C (decomp.) (Found: C, 27.70; H, 4.83; N, 16.76%. Calc. for C$_{17}$H$_{35}$CoGeN$_9$O$_9$P$_3$: C, 27.82; H, 4.81; N, 17.17%). IR (cm^{-1}): (KBr) 3377vw, 3118vw, 3097vw, 2986w, 2978w, 2930vw, 2909vw, 2113s [ν_{asym}(N$_3$)], 2090vs [ν_{asym}(N$_3$)], 1475vw, 1443vw, 1425vw, 1390w, 1297m [ν_{sym}(N$_3$)], 1162w, 1103m, 1064s [ν(P=O)], 1039vs, 1012m, 943s, 852w, 785w and 609m; (CH$_2$Cl$_2$) 2114s, 2095vs [ν_{asym}(N$_3$)]; (Et$_2$O) 2114s, 2096vs [ν_{asym}(N$_3$)]. ^{1}H NMR (CDCl$_3$, 300 MHz, 297 K): δ 1.31 (t, ^3J(HH) 7.1, 18H, 6 CH$_3$), 4.26 (m, 12H, 6 CH$_2$) and 5.17 (q, 5H, ^3J(PH) = 0.3 Hz, C$_5$H$_5$). ^{13}C-{^{1}H} NMR (CDCl$_3$, 75.5 MHz, 297 K): δ 16.4 (m, ^3J(PC) + ^5J(PC) = 6.6, CH$_3$), 63.6 (m, ^2J(PC) + ^4J(PC) = 10.3, CH$_2$) and 90.1 (q, ^2J(PC) = 1.5 Hz, C$_5$H$_5$). ^{31}P-{^{1}H} NMR (CDCl$_3$, 121.5 MHz, 297 K): δ 113.8. EI-MS (70 eV), *m/z* (rel. intensity in %): 693 (12, [M − N$_3$]$^+$), 609 (3, [M − 3N$_3$]$^+$), 488 (3, [M − 3 N$_3$ − Et − P(O)OEt]$^+$), 139 (10, [CpGe]$^+$), 124 (37, [CpCo]$^+$) and 28 (100 [C$_2$H$_4$]$^+$).

Tp′Ge(N$_3$)$_3$ 6. To a stirred colourless solution of 277 mg (0.67 mmol) of compound **5** in 40 ml of CH$_2$Cl$_2$ was added at −70 °C 1.25 ml (1.56 mmol) of a 1.23 M solution of HN$_3$ in diethyl ether. The mixture was allowed to warm to ambient temperature and monitored by IR spectroscopy. This revealed a slow decrease in intensity of the ν_{asym}(N$_3$) absorption of HN$_3$ at 2137 cm^{-1} and of **5** at 2041 cm^{-1} as well as a concomitant increase in intensity of the ν_{asym}(N$_3$) absorptions of the product at 2110, 2098 and 2092 cm^{-1}. After 43 h the reaction was complete and the cloudy, colourless solution was evaporated to dryness. The residue was washed with 20 ml of pentane–CH$_2$Cl$_2$ (20 : 1) and the wash solution discarded. The residue was dried *in vacuo* and then extracted twice with 10 ml of CH$_2$Cl$_2$. The white, water soluble, extraction residue was rejected and the combined colourless extracts were concentrated at reduced pressure to approximately 1 ml. The resulting suspension was treated in portions with 20 ml of pentane to complete precipitation of the product and the supernatant solution was discarded. The white solid was treated with 1 ml of CH$_2$Cl$_2$ and the product reprecipitated with 10 ml of pentane. The precipitate was washed with 10 ml of pentane and heated *in vacuo* for 1 h at 60 °C to remove adhesive CH$_2$Cl$_2$. White, microcrystalline solid, yield 240 mg (72%). mp 224 °C (decomp.) (Found: C, 36.38; H, 4.46; Cl, <1; N, 42.18. Calc. for C$_{15}$H$_{22}$BGeN$_{15}$: C, 36.33; H, 4.47; N, 42.37%). IR (cm^{-1}): (KBr) 3362vw, 3127vw, 2934vw, 2561w [ν(BH)], 2110s [ν_{asym}(N$_3$)], 2096vs [ν_{asym}(N$_3$)], 2085vs [ν_{asym}(N$_3$)], 1545s, 1452m, 1418w, 1386w, 1368w, 1303vw, 1292m [ν_{sym}(N$_3$)], 1285s [ν_{sym}(N$_3$)], 1209m, 1188w, 1071s, 869w, 811m, 688w, 645w, 596vw, 481w, 439w and 414w; (CH$_2$Cl$_2$) 2563vw [ν(BH)], 2117s, 2098vs, 2092vs [ν_{asym}(N$_3$)] and 1547m [ν(CN)]; (THF) 2559vw [ν(BH)], 2115s, 2111m (sh), 2097vs, 2089vs [ν_{asym}(N$_3$)] and 1547m [ν(CN)]. ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 297 K): δ 2.40 (s, 9H, 3 CH$_3$), 2.67 (s, 9H, 3 CH$_3$) and 5.97 (s, 3H, 3 CH). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz, 297 K): δ 12.4 (CH$_3$), 12.8 (CH$_3$), 107.7 (CH), 145.1 (*C*CH$_3$) and 150.9 (*C*CH$_3$). EI-MS (70 eV), *m/z* (rel. intensity in %): 455 (37, [M − N$_3$]$^+$), 371 (27, [M − 3 N$_3$]$^+$), 275 (6, [M − 3 N$_3$ − 3,5-Me$_2$pzH]$^+$), 169 (49, [M − 3 N$_3$ − HB(3,5-Me$_2$pz)$_2$]$^+$), 128 (27, [M − 3 N$_3$ − HB(3,5-Me$_2$pz)$_2$ − MeCN]$^+$) and 96 (100, [3,5-Me$_2$pzH]$^+$).

Crystal structure determinations of compounds 2, 3, 4 and 6

A summary of the crystal data, data collection and refinement for compounds **2**, **3**, **4** and **6** is given in Table 7. Data collection for **2** and **3** was performed on a STOE IPDS area detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were integrated and converted into a SHELX *hkl* file with the STOE IPDS software.[42] Data collection for **4** and **6** was performed on a STOE STADI4 four circle diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073

Table 7 Summary of crystallographic data for the complexes **2**, **3**, **4** and **6**

	2	**3**	**4**	**6**
Empirical formula	$C_{17}H_{35}ClCoGeO_9P_3$	$C_{17}H_{35}CoGeN_3O_9P_3$	$C_{17}H_{35}CoGeN_9O_9P_3$	$C_{15}H_{22}BGeN_{15}$
M_r	643.35	649.93	733.97	495.90
Crystal colour	Yellow	Yellow	Maroon	Colourless
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1 2_1 2_1$ (no. 19)	$P2_1/n$ (no. 14)	Cc (no. 9)	$P2_1/c$ (no.14)
a/Å	12.219(3)	8.4580(12)	17.1284(14)	11.378(7)
b/Å	14.260(3)	17.226(2)	12.0633(10)	10.918(13)
c/Å	15.304(3)	18.673(4)	14.6659(8)	17.719(9)
β/°	—	93.29(2)	97.283(8)	101.04(4)
V/Å^3	2666.7(13)	2716.1(8)	3005.9(4)	2160(3)
Z	4	4	4	4
$\mu_{\text{Mo-K}\alpha}$/mm^{-1}	2.010	1.882	1.771	1.403
T/K	180(2)	180(2)	180(2)	180(2)
Measured/independent reflections	27383/5227	7342/4391	7938/5339	6301/4234
R(int) ($I > 2\sigma I$)	0.0554	0.0477	0.0383	0.0403
$R1$ ($I > 2\sigma I$)	0.0248	0.0425	0.0522	0.0413
$wR2$ ($I > 2\sigma I$)	0.0455	0.0845	0.1360	0.1135

Å). Intensity data were corrected for Lorentz-polarization effects. The input files for the SHELX programs were prepared with the program UTILITY.[43] Structure solution was performed with Direct Methods (SHELXS 86)[44] and subsequent Fourier-difference synthesis (SHELXL 97).[45] Refinement on F^2 was carried out by full-matrix least squares techniques (SHELXL 97). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model. Geometrical calculations were performed with PLATON[46] and illustrations with ZORTEP.[47]

In the final stages of refinement, data for compound **6** were corrected for secondary extinction effects. A split atom model was successfully employed in **2** for one ethyl group with the atoms C(21) and C(22) attached to atom O(2) leading to a ratio of 1 : 1. Atoms C(21), C(22), C(21A) and C(22A) could be refined anisotropically. In **4** one ethyl group showed some disorder for atom C(21) attached to O(2) and the same procedure was used as for **2**.

CCDC reference number 186/1929.

See http://www.rsc.org/suppdata/dt/b0/b001198n/ for crystallographic files in .cif format.

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