

3-Germyl-3,3-dimethylpropionic acid  
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Received 26 August 2004

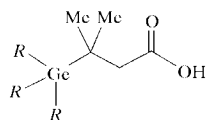
Accepted 25 November 2004

Online 18 December 2004

The crystal structures of 3,3-dimethyl-3-(trichlorogermyl)propionic acid, [Ge(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)Cl<sub>3</sub>], 3,3-dimethyl-3-(triphenylgermyl)propionic acid, [Ge(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)], and 3,3-dimethyl-3-(tri-*p*-tolylgermyl)propionic acid, [Ge(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)], have slightly distorted tetrahedral geometries about the Ge atoms. All the structures form dimers *via* strong O—H···O hydrogen bonds, resulting in eight-membered rings that can be best described in terms of graph-set notation  $R_2^2(8)$ .

## Comment

Organotin carboxylates have been studied extensively because of their richness in structural motifs, biological activities, commercial values and potential as antitumor agents (Davis & Smith, 1982). It is well known that the biological activities and selectivities of trialkyltin derivatives depend mainly on the alkyl groups attached to the Sn atom. Organogermanium is another class of compound that has a wide range of biological activity (Lukevics, 1992). The first organogermanium pharmaceutical, propagermanium, was launched in Japan in 1994; its biological activity spectrum modulates protection against

(I)  $R = \text{Cl}$ (II)  $R = \text{C}_6\text{H}_5$ (III)  $R = p\text{-MeC}_6\text{H}_4$ 

viruses, immunostimulation and hepatoprolation (William *et al.*, 1997; Kakimoto *et al.*, 1985; Lukevics *et al.*, 1992, 1998). In this paper, we report the crystal structures of 3,3-dimethyl-3-germylpropionic acid derivatives 3,3-dimethyl-3-(trichlorogermyl)propionic acid, (I), 3,3-dimethyl-3-(triphenylgermyl)propionic acid, (II), and 3,3-dimethyl-3-(tri-*p*-tolylgermyl)propionic acid, (III).

Compound (I) contains two independent molecules in the asymmetric unit; these molecules form dimers *via* strong O—H···O hydrogen bonds, resulting in eight-membered rings that can be best described in terms of graph-set notation  $R_2^2(8)$  (Bernstein *et al.*, 1994) (Fig. 1). Details of the hydrogen-bonding geometry are given in Table 2. The geometry around the Ge atoms is slightly distorted tetrahedral. The Ge—Cl distances (Table 1) in both molecules are essentially identical within  $3\sigma$  limits and lie within a narrow range. The Ge—C distances are also identical. These distances agree with the corresponding distances reported for trichlorogermyl complexes in the Cambridge Structural Database, with refcodes BOSBIU01, CUBMUH, CUBYUT, DADKEY, JIRLOL and SIWZON (CSD; Version 5.25, 2003 release; Allen, 2002).

Compound (II) also contains two independent molecules in the asymmetric unit; these molecules form dimers (Fig. 2) as in (I), resulting in eight-membered  $R_2^2(8)$  rings. Details of the hydrogen-bonding geometry are given in Table 4. The geometry around the Ge atoms is slightly distorted tetrahedral. The Ge—C<sub>aromatic</sub> distances (Table 3) in both molecules are essentially identical within  $3\sigma$  limits. The Ge—C<sub>aliphatic</sub> distances are also identical and are significantly longer than the Ge—C<sub>aromatic</sub> distances, as expected. These distances agree with the corresponding distances reported for a handful of triarylgemyl complexes contained in the CSD, with refcodes ATPGER, IHELIQ, IHELOW, SUZOF, TPENGE, XUQZOY and ZAHKIC.

Unlike (I) and (II), compound (III) contains one molecule in the asymmetric unit (Fig. 3); these molecules form dimers about inversion centers, resulting in eight-membered  $R_2^2(8)$  rings, as observed in (I) and (II). Details of the hydrogen-bonding geometry are given in Table 6. The geometry around the Ge atoms is slightly distorted tetrahedral. The Ge—C<sub>aromatic</sub> and Ge—C<sub>aliphatic</sub> distances (Table 5) show the same pattern as observed in the structure of (II). The fact that the Ge—C<sub>aliphatic</sub> distances in (I) are significantly shorter than those in (II) and (III) may be attributed to the Cl atoms bonded to the Ge atom in (I).

In all three structures, the carboxyl groups adopt the more prevalent synplanar conformation. However, the rings formed by the intermolecular interactions between carboxyl groups in

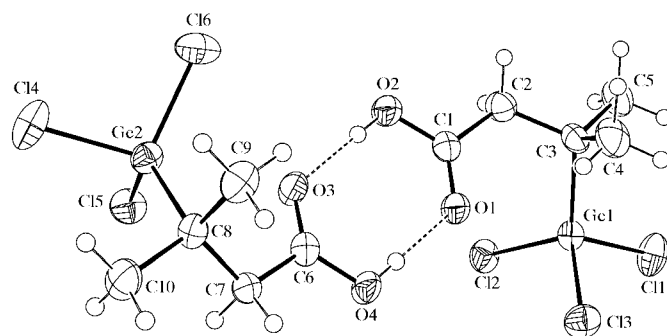
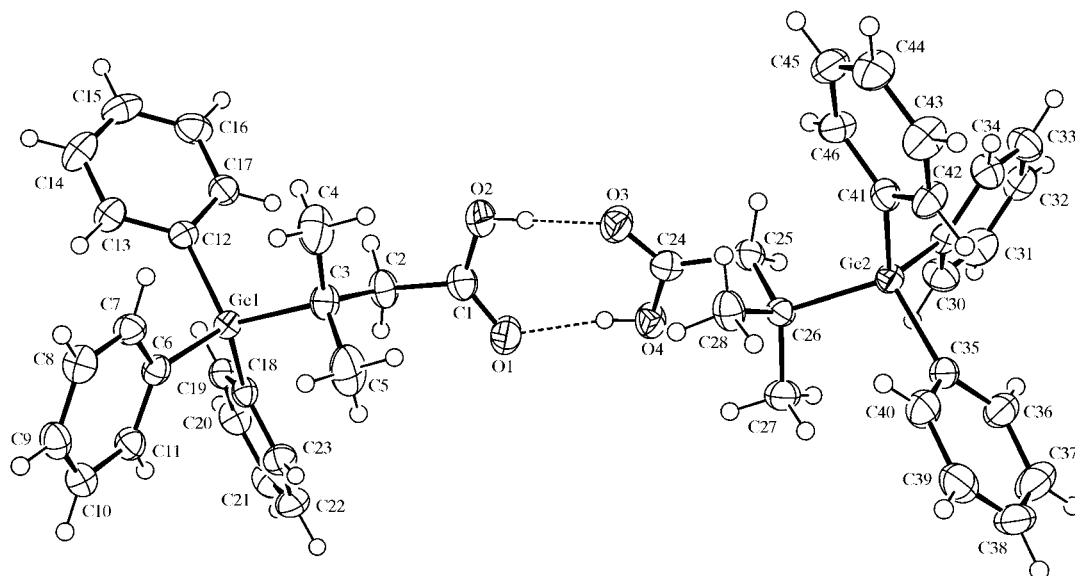
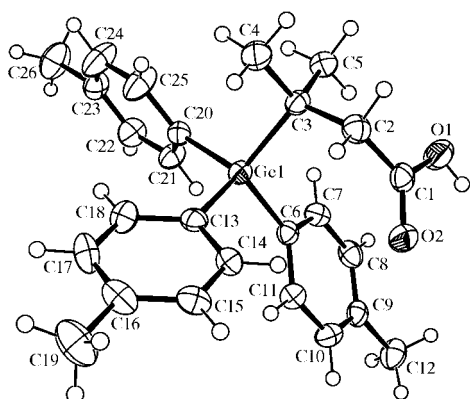


Figure 1

An ORTEP (Johnson, 1976) drawing showing the two hydrogen-bonded molecules in the asymmetric unit of (I), with displacement ellipsoids plotted at the 50% probability level.


**Figure 2**

An ORTEP (Johnson, 1976) drawing showing the two hydrogen-bonded molecules in the asymmetric unit of (II), with displacement ellipsoids plotted at the 50% probability level.


**Figure 3**

An ORTEP (Johnson, 1976) drawing of (III), with displacement ellipsoids plotted at the 50% probability level.

(I) and (III) are more or less planar [the maximum deviation of any atom from the plane defined by four O and two C atoms being 0.054 (2) and 0.010 (2) Å, respectively], in contrast to the ring in (II), which is substantially twisted [the maximum deviation is 0.224 (2) Å]. Moreover, the propyl and carboxyl groups in the two molecules of (I) are oriented at 12.4 (3) and 30.2 (2)°, compared with 78.6 (3) and 80.6 (2)° in (II), and 70.0 (2)° in (III). The differences in the orientations of these groups appear to influence the O...O interactions, which are somewhat longer in (I) than in (II) and (III), and have also been observed in the germyl complexes mentioned above.

## Experimental

Compounds (I), (II) and (III) were synthesized following the methods described by Choudhary *et al.* (2001). Suitable crystals were isolated for X-ray analyses by dissolving the respective compound (0.5 g) in chloroform (5.0 ml) to which a few drops of acetone had been added. Slow evaporation of the solvent at room temperature over a period of several days yielded fine crystals, which were

subsequently washed with acetone. For (I), IR (cm<sup>-1</sup>): 3100–3500 (*b*, OH), 1699 (*s*, CO), 563 (*w*, GeC); <sup>1</sup>H NMR (p.p.m.): 2.75 (*s*, 2H, CH<sub>2</sub>), 1.47 (*s*, 6H, CH<sub>3</sub>), 10.81 (*s*, 1H, OH); <sup>13</sup>C NMR (p.p.m.): 46.58 (CH<sub>2</sub>), 45.48 (C), 25.83 (CH<sub>3</sub>). For (II), IR (cm<sup>-1</sup>): 3000–3410 (*b*, OH), 1695 (*s*, CO), 621 (*w*, Ge–C); <sup>1</sup>H NMR (p.p.m.): 2.55 (*s*, 2H, CH<sub>2</sub>), 1.35 (*s*, 6H, CH<sub>3</sub>), 7.25–7.81 (*m*, 15H, C<sub>6</sub>H<sub>5</sub>); <sup>13</sup>C NMR (p.p.m.): 48.72 (CH<sub>2</sub>), 42.61 (C), 27.20 (CH<sub>3</sub>), 136.21, 135.98, 128.13, 131.42 (C<sub>6</sub>H<sub>5</sub>Ge). For (III), IR (cm<sup>-1</sup>): 3100–3480 (*b*, OH), 1711 (*s*, CO), 629 (*w*, Ge–C); <sup>1</sup>H NMR (p.p.m.): 2.64 (*s*, 2H, CH<sub>2</sub>), 1.45 (*s*, 6H, CH<sub>3</sub>), 1.18 (*d*, 9H, *J* = 6.9 Hz, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C NMR (p.p.m.): 38.51 (CH<sub>2</sub>), 34.10 (C), 29.57 (CH<sub>3</sub>), 21.71 (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 139.45, 134.08, 128.90, 133.86 (C<sub>6</sub>H<sub>4</sub>Ge).

## Compound (I)

### Crystal data

[Ge(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)Cl<sub>3</sub>]  
*M<sub>r</sub>* = 280.06  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 15.526 (4) Å  
*b* = 11.521 (4) Å  
*c* = 11.828 (6) Å  
 $\beta$  = 98.423 (15)°  
*V* = 2092.9 (14) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.778 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 4514 reflections  
 $\theta$  = 2.6–27.5°  
 $\mu$  = 3.65 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Block, colorless  
 0.22 × 0.18 × 0.15 mm

### Data collection

Nonius KappaCCD diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1997)  
*T<sub>min</sub>* = 0.501, *T<sub>max</sub>* = 0.611  
 8438 measured reflections  
 4760 independent reflections

3200 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.037  
 $\theta_{max}$  = 27.6°  
*h* = -20 → 20  
*k* = -13 → 14  
*l* = -15 → 15

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.034  
*wR*(*F*<sup>2</sup>) = 0.079  
*S* = 1.00  
 4760 reflections  
 201 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.5P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.35 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.50 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °) for (I).

Ge1—C3	1.978 (3)	Ge2—C8	1.971 (3)
Ge1—Cl3	2.1356 (12)	Ge2—Cl6	2.1330 (12)
Ge1—Cl1	2.1431 (10)	Ge2—Cl5	2.1422 (11)
Ge1—Cl2	2.1446 (10)	Ge2—Cl4	2.1525 (10)
O1—C1	1.227 (4)	O3—C6	1.222 (3)
O2—C1	1.308 (3)	O4—C6	1.305 (3)
C3—Ge1—Cl3	117.63 (10)	C8—Ge2—Cl6	118.47 (10)
C3—Ge1—Cl1	110.73 (9)	C8—Ge2—Cl5	113.62 (9)
Cl3—Ge1—Cl1	101.64 (4)	Cl6—Ge2—Cl5	110.02 (4)
C3—Ge1—Cl2	114.30 (10)	C8—Ge2—Cl4	108.92 (9)
Cl3—Ge1—Cl2	107.77 (4)	Cl6—Ge2—Cl4	100.61 (5)
Cl1—Ge1—Cl2	103.09 (4)	Cl5—Ge2—Cl4	103.27 (4)

**Table 2**  
Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2···O3	0.84	1.83	2.665 (3)	179
O4—H4···O1	0.84	1.81	2.649 (3)	176

**Compound (II)**

*Crystal data*

[Ge(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)]  
*M<sub>r</sub>* = 405.01  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 7.785 (1) Å  
*b* = 15.678 (2) Å  
*c* = 32.703 (5) Å  
 $\beta$  = 96.668 (5)°  
*V* = 3964.5 (9) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.357 Mg m<sup>-3</sup>

*Data collection*

Nonius KappaCCD diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1997)  
*T<sub>min</sub>* = 0.789, *T<sub>max</sub>* = 0.835  
 16 723 measured reflections  
 9032 independent reflections

Mo *K*α radiation  
 Cell parameters from 16 723 reflections  
 $\theta$  = 1.4–27.5°  
 $\mu$  = 1.56 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Block, colorless  
 0.16 × 0.14 × 0.12 mm

**Table 3**  
Selected geometric parameters (Å, °) for (II).

Ge1—C6	1.953 (3)	Ge2—C41	1.955 (3)
Ge1—C18	1.954 (3)	Ge2—C35	1.956 (3)
Ge1—C12	1.955 (3)	Ge2—C29	1.960 (3)
Ge1—C3	1.998 (3)	Ge2—C26	2.005 (3)
O1—C1	1.231 (3)	O3—C24	1.246 (3)
O2—C1	1.297 (3)	O4—C24	1.295 (3)
C6—Ge1—C18	109.98 (11)	C41—Ge2—C35	110.01 (12)
C6—Ge1—C12	108.89 (11)	C41—Ge2—C29	109.00 (11)
C18—Ge1—C12	108.22 (11)	C35—Ge2—C29	110.49 (11)
C6—Ge1—C3	108.92 (11)	C41—Ge2—C26	109.49 (10)
C18—Ge1—C3	110.07 (11)	C35—Ge2—C26	106.35 (11)
C12—Ge1—C3	110.75 (11)	C29—Ge2—C26	111.48 (11)

**Table 4**  
Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2···O3	0.84	1.82	2.645 (3)	169
O4—H4···O1	0.84	1.81	2.638 (3)	170

*Refinement*

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.040  
*wR* (*F*<sup>2</sup>) = 0.093  
*S* = 1.01  
 9032 reflections  
 475 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 1.542P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 0.59 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{Å}^{-3}$

**Compound (III)**

*Crystal data*

[Ge(C<sub>7</sub>H<sub>7</sub>)<sub>3</sub>(C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>)]  
*M<sub>r</sub>* = 447.09  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 20.041 (3) Å  
*b* = 9.370 (2) Å  
*c* = 12.816 (5) Å  
 $\beta$  = 108.436 (9)°  
*V* = 2283.1 (11) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.301 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 9035 reflections  
 $\theta$  = 3.0–27.4°  
 $\mu$  = 1.36 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Block, colorless  
 0.20 × 0.16 × 0.10 mm

*Data collection*

Nonius KappaCCD diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1997)  
*T<sub>min</sub>* = 0.773, *T<sub>max</sub>* = 0.876  
 9035 measured reflections  
 5123 independent reflections

3474 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.044  
 $\theta_{\max}$  = 27.4°  
*h* = -25 → 25  
*k* = -11 → 11  
*l* = -16 → 16

*Refinement*

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.040  
*wR* (*F*<sup>2</sup>) = 0.095  
*S* = 1.03  
 5123 reflections  
 268 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0370P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.47 \text{ e } \text{Å}^{-3}$

**Table 5**  
Selected geometric parameters (Å, °) for (III).

Ge1—C13	1.952 (3)	Ge1—C3	1.999 (2)
Ge1—C20	1.954 (3)	O1—C1	1.278 (3)
Ge1—C6	1.960 (2)	O2—C1	1.257 (3)
C13—Ge1—C20	109.50 (11)	C13—Ge1—C3	109.39 (10)
C13—Ge1—C6	108.77 (10)	C20—Ge1—C3	109.00 (10)
C20—Ge1—C6	108.18 (10)	C6—Ge1—C3	111.97 (10)

**Table 6**  
Hydrogen-bonding geometry (Å, °) for (III).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···O2 <sup>i</sup>	0.84	1.80	2.634 (3)	170

Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.

In all three structures, H atoms were located from difference Fourier syntheses and included in the refinements at idealized positions, with O—H distances of 0.84 Å, C—H distances of 0.95, 0.98 and 0.99 Å, and  $U_{\text{iso}}(\text{H})$  values of 1.5 (hydroxyl and methyl) and 1.2 (aromatic and CH<sub>2</sub>) times  $U_{\text{eq}}$  of the parent atoms.

For all compounds, data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1515). Services for accessing these data are described at the back of the journal.

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## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bernstein, J., Etter, M. C. & Leiserowitz, L. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, pp. 431–507. New York: VCH.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Choudhary, M. A., Mazhar, M., Salma, U., Ali, S., Qinglan, X. & Molloy, K. C. (2001). *Synth. React. Inorg. Met. Org. Chem.* **31**, 277–295.
- Davis, A. G. & Smith, P. J. (1982). *Comprehensive Organometallic Chemistry, The Synthesis, Reactions and Structures of Organometallic Compounds*, Vol. 2, edited by G. Wilkinson, F. G. Stone & E. W. Abel, pp. 519–527. New York: Pergamon.
- Fan, H.-F. (1991). *SAPI91*. Rigaku Corporation, Tokyo, Japan.
- Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kakimoto, N., Matsui, M., Takada, T. & Aluba, M. (1985). *Heterocycles*, **23**, 2681–2684.
- Lukevics, E. (1992). *Appl. Organomet. Chem.* **6**, 113–126.
- Lukevics, E., Arsenyan, P. & Viveries, M. (1998). *Met. Based Drugs*, **5**, 251–257.
- Lukevics, E., Germaine, S. & Ignatovich, L. (1992). *Appl. Organomet. Chem.* **6**, 543–564.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- William, R., Dalil, H., Briekaert, P., Biesemans, M., Ghys, L., Nooter, K., Devos, D., Ribot, F. & Gielen, M. (1997). *Main Group Met. Chem.* **20**, 535–542.