Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2014, **24**, 346–348

Mendeleev Communications

Unexpected formation of substituted naphthalenes and phenanthrenes in a $GaCl_3$ mediated dimerization–fragmentation reaction of 2-arylcyclopropane-1,1-dicarboxylates

Roman A. Novikov,[a] Anna V. Tarasova,[a] Kyrill Yu. Suponitsky[b] and Yury V. Tomilov*[a]

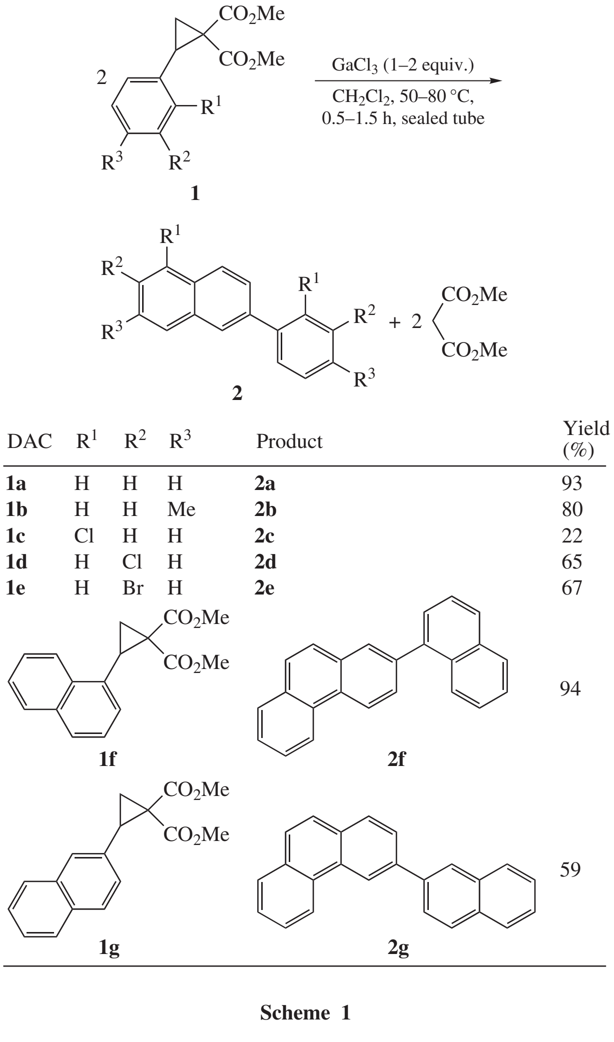
[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 6390; e-mail: tom@ioc.ac.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2014.11.011

Dimethyl 2-arylcyclopropane-1,1-dicarboxylates on heating with $GaCl_3$ undergo dimerization to afford arylnaphthalenes or phenanthrenes. A possible reaction mechanism including elimination of two dimethyl malonate molecules was proposed, dimethyl malonate gallium complex $Ga^{3+}[H_2C(CO_2Me)_2]_3(GaCl_4^-)_3$ was isolated and characterized by X-ray diffraction analysis.

Donor–acceptor cyclopropanes (DACs) containing donor and acceptor substituents in the vicinal position are widely used in present-day organic synthesis as the sources of 1,3-dipoles which are generated from them in the presence of Lewis acids.[1–5] Recently, it was shown that donor–acceptor cyclopropanes can undergo dimerization under the action of Lewis acids and organic catalysts in the absence of unsaturated substrates and other scavengers of generated 1,3-dipoles, the dimers having various origin such as arylidene malonates,[6] diarylhexenes,[6,7] cyclohexanes,[7] tetralins,[7–9] dihydroanthracenes,[7] pentaleno[1,6-*a*,*b*]indoles,[10] polysubstituted cyclopentanes[6,8] and 2-oxabicyclo[3.3.0]octanes.[11] Among the discovered DAC transformations, attention should be focused on the dimerization of 2-arylcyclopropane-1,1-dicarboxylates **1** to polysubstituted cyclopentanes and/or tetralins under the action of anhydrous $GaCl_3$,[8,9,12] the ratio of the products being dependent only on the reaction temperature and the amount of gallium trichloride used.

We studied the behaviour of phenylcyclopropane dicarboxylate **1a** with $GaCl_3$ under conditions different from those used previously:[8,9] the reaction temperature was raised to 80 °C and the amount of $GaCl_3$ was 1–2 equiv. Under these conditions, a new route of DAC transformation occurred with the unexpected formation of 2-phenylnaphthalene **2a**, whose molecule did not contain ester groups (Scheme 1, R = H).[†] Unlike the previously described products of donor–acceptor cyclopropanes dimerization,[6–11] compound **2a** is not a true dimer, although it is formed from two cyclopropane dicarboxylate molecules. In the course of this reaction, two malonic ester molecules are eliminated, and the formation of **2a** formally corresponds to the dimerization of phenylacetylene, which was not observed earlier. Other Lewis acids, *e.g.*, $EtAlCl_2$ or scandium and ytterbium triflates, do not provide compounds like **2a**. Thus, the application of anhydrous $GaCl_3$ is a unique procedure for performing fragmentation processes under the conditions of DAC dimerization.



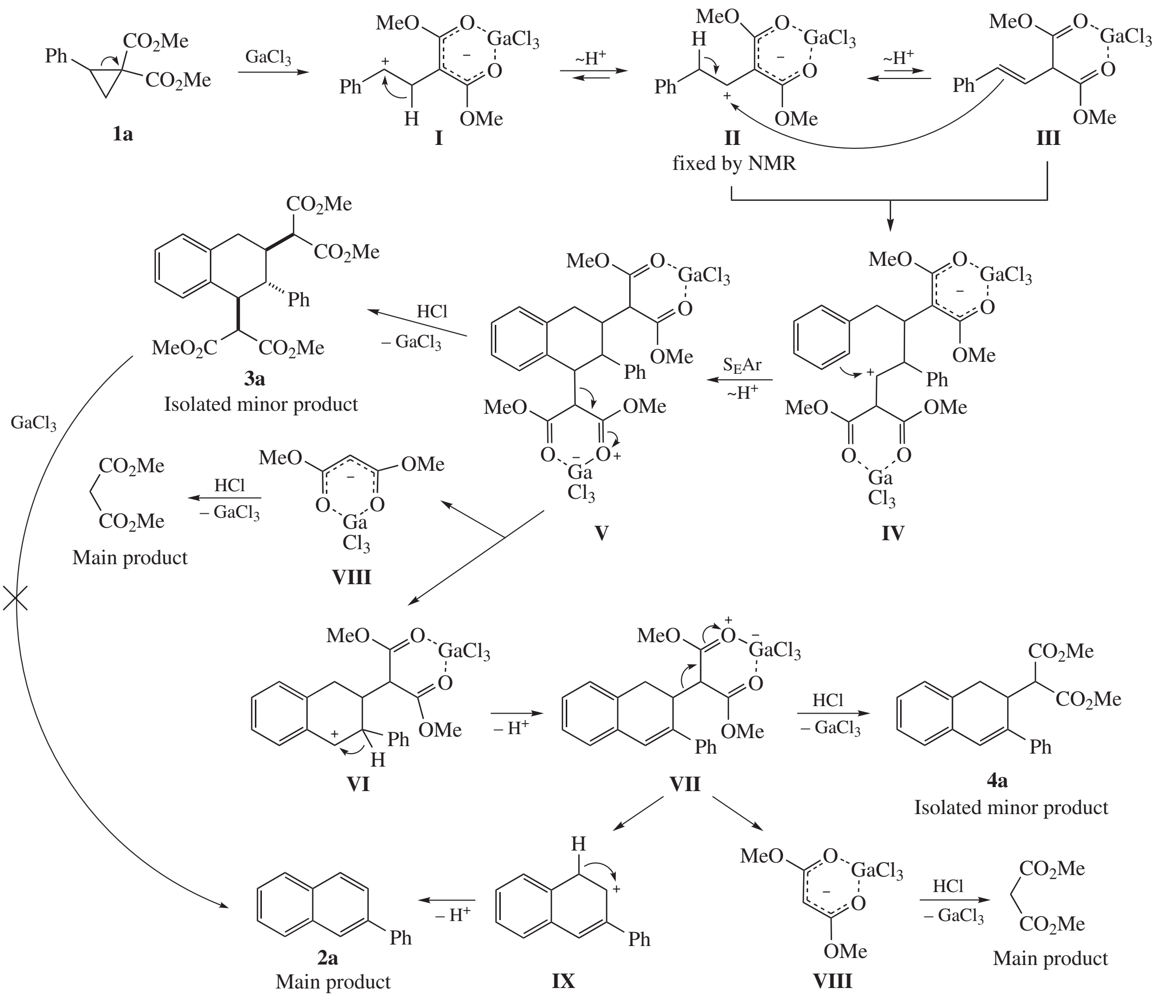
DAC	R^1	R^2	R^3	Product	Yield (%)
1a	H	H	H	**2a**	93
1b	H	H	Me	**2b**	80
1c	Cl	H	H	**2c**	22
1d	H	Cl	H	**2d**	65
1e	H	Br	H	**2e**	67
1f				**2f**	94
1g				**2g**	59

Scheme 1

[†] ^1H and ^{13}C NMR spectra were recorded on Bruker AMX-III 400 (400.1 and 100.6 MHz, respectively) and Bruker AVANCE II 300 (300 and 75 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% TMS as the internal standard. Assignments of ^1H and ^{13}C signals were made with the aid of 1D DEPT-135 and 2D COSY, NOESY, HSQC and HMBC spectra.

Compounds **2** (*general procedure*). Solid $GaCl_3$ (0.45–0.75 mmol, 150 mol%) was added in one portion to a solution of cyclopropane **1** (0.3–0.5 mmol) in 4 ml of dry CH_2Cl_2 in dry argon atmosphere at room temperature under vigorous stirring. The mixture was heated to 80 °C under slight pressure in sealed tube and was stirred for 1 h. Then aqueous 5% HCl solution was added at room temperature to reach pH 3, and the mixture was extracted with CH_2Cl_2 (3×10 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (benzene–EtOAc, 20 : 1) to afford pure compounds **2** in yields specified in Scheme 1.

2-Phenylnaphthalene **2a**: yield 93%, colourless crystals, mp 97–98 °C. NMR spectra correspond to published data.[14]



Scheme 2

The conditions found were successfully extended on other aryl-substituted cyclopropane dicarboxylates **1**. In this case, dimerization–fragmentation reactions effectively occurred with cyclopropanes containing phenyl, *p*-tolyl and 1-naphthyl substituents, whereas cyclopropanes **1c**–**e** with halogen atoms in the *ortho* and *meta* positions of the benzene ring, were found less reactive. Interestingly, cyclopropanes with halogen atoms in the *para* position of the benzene ring did not form similar products.

The possible mechanism of this process is outlined on Scheme 2. Under the action of $GaCl_3$, cyclopropane **1** undergoes ring opening to afford 1,2-dipolar intermediate **II** after a number of consecutive reactions.[13] This is a key intermediate in the dimerization of cyclopropanes **1** into tetralins **3**.[9] However, this reaction does not reach the formation of tetralins **3** as a result of an elevated reaction temperature and the use of a larger amount of $GaCl_3$. Under these conditions dimeric intermediate **V** undergoes the elimination of a malonyl fragment induced by the Ga atom, which possesses considerable Lewis acidity, like an acid-catalyzed retro-aldol reaction. As a result, intermediate **VI** is generated, which is converted into intermediate **VII** and the gallium enolate of malonic ester **VIII** after proton migration. Similarly to intermediate **V**, intermediate **VII** eliminates the second malonyl fragment and gives a naphthalene fragment as a result of aromatization.

To rationalize the stepwise mechanism of the elimination of malonyl fragments from the DAC dimerization products, one should note that tetralins **3** are formed as minor reaction products; in the case of cyclopropane **1a**, monoelimination product **4a** was isolated in a yield of ~1%.[‡] It is likely that the energetically favourable aromatization of a six-membered ring is the driving force of the main process observed. However, it requires the rupture of two C–C bonds, which, in turn, requires the use of

---

7-Methyl-2-(4-methylphenyl)naphthalene **2b**: yield 80%, colourless crystals, mp 134–136 °C. ^{1}H NMR, δ: 2.41 (s, 3H, C$^{4'}$Me), 2.52 (s, 3H, C^{7}Me), 7.24–7.32 (m, 2H, *m*-H), 7.30 (dd, 1H, C^{6}H, ^3J 8.3 Hz, ^4J 1.6 Hz), 7.58–7.64 (m, 2H, *o*-H), 7.64 (br. s, 1H, C^{8}H), 7.66 (dd, 1H, C^{3}H, ^3J 8.4 Hz, ^4J 1.6 Hz), 7.74 (d, 1H, C^{5}H, ^3J 8.3 Hz), 7.84 (d, 1H, C^{4}H, ^3J 8.4 Hz), 7.92 (br. s, 1H, C^{1}H). ^{13}C NMR, δ: 21.2 and 21.8 (2Me), 124.8, 124.9, 127.2, 127.5, 128.12 and 128.16 (6CH), 127.3 and 129.6 (*o*-C, *m*-C), 130.9, 134.1, 135.9, 137.1, 138.5 and 138.6 (6C). Found (%): C, 92.85; H, 6.73. Calc. for $C_{18}H_{16}$ (%): C, 93.06; H, 6.94.

1-Chloro-6-(2-chlorophenyl)naphthalene **2c**: yield 22%, colourless crystals, mp 46–48 °C. IR ($CHCl_3$, ν/cm^{-1}): 3020, 2975, 2923, 1646, 1520, 1466, 1419. ^{1}H NMR, δ: 7.34 (ddd, 1H, C$^{4'}$H or C$^{5'}$H, ^3J 7.4 and 7.3 Hz, ^4J 2.0 Hz), 7.37 (ddd, 1H, C$^{4'}$H or C$^{5'}$H, ^3J 7.4 and 7.3 Hz, ^4J 2.0 Hz), 7.42 (dd, 1H, C^{3}H, ^3J 8.3 and 7.4 Hz), 7.44 (dd, 1H, C$^{3'}$H or C$^{6'}$H, ^3J 7.3 Hz, ^4J 2.0 Hz), 7.52 (dd, 1H, C$^{3'}$H or C$^{6'}$H, ^3J 7.3 Hz, ^4J 2.0 Hz), 7.60 (dd, 1H, C^{2}H, ^3J 7.4 Hz, ^4J 1.1 Hz), 7.71 (dd, 1H, C^{7}H, ^3J 8.7 Hz, ^4J 1.7 Hz), 7.81 (br. d, 1H, C^{4}H, ^3J 8.3 Hz), 7.91 (d, 1H, C^{5}H, ^4J 1.7 Hz), 8.33 (br. d, 1H, C^{8}H, ^3J 8.7 Hz). ^{13}C NMR, δ: 124.3 (C^8), 126.3 (C^3), 126.6 (C^2), 127.1 and 129.1 (C$^{4'}$ and C$^{5'}$), 127.5 (C^4), 128.8 (C^5), 129.0 (C^7), 130.2 and 131.7 (C$^{3'}$ and C$^{6'}$), 130.3 (C^{8a}), 132.0 (C$^{2'}$), 132.1 (C^1), 134.5 (C^{4a}), 138.1 (C^6), 140.2 (C$^{1'}$). MS, *m*/*z* (%): 272 (96) [M]$^+$ for ^{35}Cl, 232 (18), 202 (65), 149 (39), 100 (36), 83 (30), 59 (43), 57 (88), 43 (100). Found (%): C, 70.87; H, 3.80. Calc. for $C_{16}H_{10}Cl_2$ (%): C, 70.35; H, 3.69.

2-(1-Naphthyl)phenanthrene **2f**: yield 94%, thick colourless oil. NMR spectra correspond to published data.[15]

3-(2-Naphthyl)phenanthrene **2g**: yield 59%, colourless crystals, mp 122–123 °C. NMR spectra correspond to published data.[16]

For characteristics of compounds **2d**,**e**, see Online Supplementary Materials.

severe reaction conditions. It is obvious that the elimination of the second malonyl fragment proceeds much more rapidly than that of the first one because aromatization occurs at this step, as observed experimentally; that is, the reaction does almost not stop with the formation of monoelimination products **4**. Note that dimeric tetralins **3** do not give even the traces of compounds **2** on the interaction with $GaCl_3$ under the conditions of fragmentation. This is likely due to the fact that a complex with $GaCl_3$ (like compound **V**) should be formed for the elimination of a malonyl fragment; however, it was found previously[13] that substituted malonates do not produce stable complexes on the interaction with $GaCl_3$. This complex can be formed only indirectly through the dimerization of complex **II** and its fragmentation described above. In all cases, the above transformations occur with very high regioselectivity. Thus, cyclopropanes **1d**,**e**,**g**, which can react at both *ortho* positions of the aromatic ring, form only one regioisomer. However, the mechanism of this electrophilic substitution remains unclear.

Note that Ga enolate **VIII** converted into new complex **5**, whose structure was determined by X-ray diffraction analysis (Figure 1), in a matter of several days. This complex includes three fragments of malonic ester and four gallium atoms, three of which exist in the form of the $GaCl_4^-$ anions.[§]

Thus, we found a new uncommon reaction of 2-arylcyclopropane-1,1-dicarboxylates with anhydrous $GaCl_3$ on heating resulting in the regiospecific formation of substituted naphthalenes and phenanthrenes in good yields. In this case, the dimeric intermediate formed from two DAC molecules undergoes fragmentation with the elimination of two malonyl fragments as dimethyl malonate.

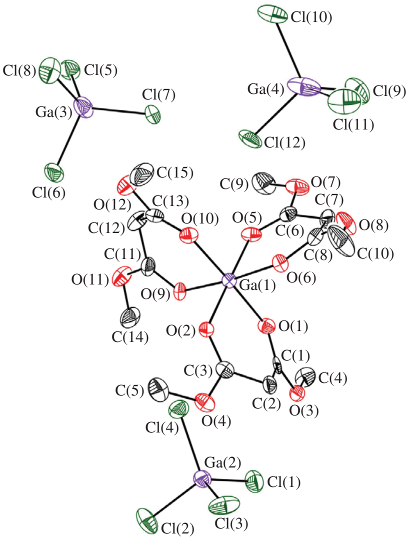


Figure 1 X-ray structure of a molecule of **5** in the representation of atoms as thermal ellipsoids ($p = 50\%$).

This work was supported by the Russian Science Foundation (grant no. 14-13-01054).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.11.011.

References

1 H. U. Reissig and R. Zimmer, *Chem. Rev.*, 2003, **103**, 1151.

2 (*a*) M. Yu and B. L. Pagenkopf, *Tetrahedron*, 2006, **61**, 321; (*b*) F. de Simone and J. Waser, *Synthesis*, 2009, **20**, 3353; (*c*) M. J. Campbell, J. S. Johnson, A. T. Parsons, P. D. Pohlhaus and S. D. Sanders, *J. Org. Chem.*, 2010, **75**, 6317.

3 M. Ya. Mel'nikov, E. M. Budynina, O. A. Ivanova and I. V. Trushkov, *Mendeleev Commun.*, 2011, **21**, 293.

4 M. A. Cavitt, L. H. Phun and S. France, *Chem. Soc. Rev.*, 2014, **43**, 804.

5 (*a*) T. F. Schneider, J. Kaschel and D. B. Werz, *Angew. Chem. Int. Ed.*, 2014, **53**, 5504; (*b*) S. Chakrabarty, I. Chatterjee, B. Wibbeling, C. G. Daniliuc and A. Studer, *Angew. Chem. Int. Ed.*, 2014, **53**, 5964; (*c*) F. de Nanteuil, E. Serrano, D. Perrotta and J. Waser, *J. Am. Chem. Soc.*, 2014, **136**, 6239; (*d*) M. K. Ghorai, R. Talukdar and D. P. Tiwari, *Org. Lett.*, 2014, **16**, 2204; (*e*) M. Zhu, J. Liu, J. Yu, L. Chen, C. Zhang and L. Wang, *Org. Lett.*, 2014, **16**, 1856; (*f*) W. D. Mackay, M. Fistikci, R. M. Carris and J. S. Johnson, *Org. Lett.*, 2014, **16**, 1626.

6 A. O. Chagarovskiy, O. A. Ivanova, E. M. Budynina, I. V. Trushkov and M. Ya. Melnikov, *Tetrahedron Lett.*, 2011, **52**, 4421.

7 O. A. Ivanova, E. M. Budynina, A. O. Chagarovskiy, I. V. Trushkov and M. Ya. Melnikov, *J. Org. Chem.*, 2011, **76**, 8852.

8 R. A. Novikov, V. A. Korolev, V. P. Timofeev and Yu. V. Tomilov, *Tetrahedron Lett.*, 2011, **52**, 4996.

9 R. A. Novikov, A. V. Tarasova, V. A. Korolev, V. P. Timofeev and Yu. V. Tomilov, *Angew. Chem. Int. Ed.*, 2014, **53**, 3187.

10 O. A. Ivanova, E. M. Budynina, A. O. Chagarovskiy, E. R. Rakhmankulov, I. V. Trushkov, A. V. Semeykin, N. L. Shimanovskii and M. Ya. Melnikov, *Chem. Eur. J.*, 2011, **17**, 11738.

11 R. A. Novikov, V. P. Timofeev and Yu. V. Tomilov, *J. Org. Chem.*, 2012, **77**, 5993.

12 R. A. Novikov, Yu. V. Tomilov and O. M. Nefedov, *Mendeleev Commun.*, 2012, **22**, 181.

13 R. A. Novikov, D. O. Balakirev, V. P. Timofeev and Yu. V. Tomilov, *Organometallics*, 2012, **31**, 8627.

14 T. E. Storr and M. F. Greaney, *Org. Lett.*, 2013, **15**, 1410.

15 S. Y. Lee, H. N. Shin, Y. J. Cho, H. J. Kwon, B. O. Kim, S. M. Kim and S. S. Yoon, *US Patent 2009230852*, 2009.

16 C. W. Ong and C. Y. Yu, *Tetrahedron*, 2003, **59**, 9677.

Received: 16th June 2014; Com. 14/4395

[‡] *Compounds* **3a** *and* **4a**. Solid $GaCl_3$ (113 mg, 0.64 mmol, 100 mol%) was added in one portion to a solution of cyclopropane **1a** (150 mg, 0.64 mmol) in dry CH_2Cl_2 (4 ml) under dry argon at 40 °C and the mixture was stirred at the same temperature for 30 min. Then an aqueous HCl solution (5%) was added at room temperature to reach pH 3 and the mixture was extracted with CH_2Cl_2 (3×10 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was separated by column chromatography on silica gel (benzene–EtOAc, 50 : 1 to 10 : 1) to afford 118 mg (79%) of known[9] tetralin **3a** as a thick colourless oil and a small fraction containing compound **4a**. This fraction was additionally purified on a Silufol chromatographic plate (20×20 cm) to afford ~1.5 mg of 2-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-3-phenyl-1,2-dihydronaphthalene-2 **4a**. IR ($CHCl_3$, ν/cm^{-1}): 3020, 2956, 2926, 2853, 1732 (O=C–O), 1659, 1519, 1468, 1423. ^{1}H NMR, δ: 2.71–2.87 (m, 2H, C^{1}H$_2$), 3.30–3.38 and 4.10–4.18 (2m, 2×1H, C^{2}H and C$^{2'}$H), 3.69 and 3.72 (2s, 2×3H, 2OMe), 7.04–8.00 (m, 10H, C^{4}H–C^{8}H, Ph). ^{13}C NMR, δ: 34.5 (C^{1}H$_2$), 48.9 and 52.7 (C^{2}H and C$^{2'}$H), 50.2 (2OMe), 125.7, 126.0, 126.9, 127.5, 128.2, 128.5, 128.8 and 129.0 (C^4–C^8, 5C$_{\text{Ph}}$), 132.7, 132.8, 141.1 and 143.3 (C^3, C^{4a}, C^{8a} and *i*-C), 169.9 (2COO). MS, *m/z* (%): 336 (6) [M]$^+$, 306 (100), 291 (13), 276 (12), 215 (22), 204 (33), 115 (23), 91 (32), 59 (46).

[§] *Crystallographic data for* **5**. Crystals of $C_{16}H_{26}Cl_{14}Ga_4O_{12}$ ($M = 1185.55$) are orthorhombic, space group $P2_12_12_1$, at $T = 100(2)$ K: $a = 13.8249(10)$, $b = 14.8020(11)$ and $c = 20.4605(15)$ Å, $V = 4187.0(5)$ Å^3, $Z = 4$, $F(000) = 2320$, $d_{\text{calc}} = 1.881$ g cm^{-3}, $\mu = 3.485$ mm^{-1}. Intensities of 38 393 reflections were measured on an automated SMART 1000 CCD diffractometer [λ(MoKα) radiation, graphite monochromator, φ and ω-scanning techniques, $\theta_{\max} = 28°$]. The structure was solved by direct methods and refined by a full-matrix least-squares method against F^2 in the anisotropic–isotropic approximation. The positions of the hydrogen atoms were calculated geometrically. The final *R* factors were as follows: $R_1 = 0.0625$ for 10 086 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1334$ for all 7723 independent reflections, GOF = 1.270. All calculations were carried out using the SHELXTL PLUS software (Version 5.0).

CCDC 1024005 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.