Organometallics **2000,** *19,* 3085−3090

Synthesis and Characterization of 1-Aza-allyl Complexes with Al−Al, Ga−Ga, and In−In Bonds[†]

Klaus S. Klimek, Chunming Cui, Herbert W. Roesky*, Mathias Noltemeyer, and Hans-Georg Schmidt

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

Received February 10, 2000

The synthesis of new compounds containing Al−Al, Ga−Ga, and In−In bonds, the 1-aza-allyl ligand R (R = $[(Me_3Si)_2C(Ph)C(Me_3Si)N]$), and halide substituents is described. The gallium(III) compound $RGaCl_2$ (**1**) was prepared by reaction of $GaCl_3$ with RLi·THF. The reduction of a mixture of $RAlI_2$ and RAlClI with potassium afforded [RIAl−AlClR] (**2**). $[RGaCl]_2$ (**3**) was synthesized by the reduction of $RGaCl_2$ with sodium/potassium alloy, while $[RInBr]_2$ (**4**) was prepared by reaction of RLi·THF with indium(I) bromide. The molecular structures of **1**, **2**, **3**, and **4** have been established by X-ray crystallography.

Introduction

Element organic compounds of aluminum, gallium, and indium with Al−Al, Ga−Ga, and In−In moieties have been investigated ($[((Me_3Si)_2CH)_2Al]_2$,[1] $[((Me_3Si)_2CH)_2Ga]_2$,[2] and $[((Me_3Si)_2CH)_2In]_2$[3]). On the other hand dialuminum and diindium compounds that feature both organic and halide substituents are not known. Only gallium compounds of this type with bulky aryl (Ar = 2,4,6-*t*-$Bu_3C_6H_2$)[4] and silyl ($(Me_3Si)_3Si$)[5] substituents are reported.

In comparison with the corresponding boron derivatives,[6] compounds of the type $[RMX]_2$ (M = Al, Ga, In; X = Cl, Br, I) could be ideal starting materials for the synthesis of novel homodinuclear derivatives of aluminum, gallium, and indium. Furthermore, there is a great interest in new polynuclear group 13 compounds. As a consequence, several reports have appeared recently that focus upon the ligand stabilization.[7] For obtaining novel gallium(I) compounds of the type Cp*Ga,[8] $[(Me_3Si)_3CGa]_4$,[9] and $[(Me_3Si)_3SiGa]_4$[10] the synthesis of new halogen precursors of the type $RGaCl_2$ (R = chelating group) for reduction is a challenge. Particularly, the use of the 1-aza-allyl ligand with its ability to chelate in a η^3 mode should allow the synthesis of solvent-free starting materials that are ideal for preparing new low-valent metal group 13 aggregates.

Experimental Section

General Considerations. All experiments were performed using standard Schlenk techniques under a dry nitrogen atmosphere due to the extreme sensitivity of the reactants and products toward air and moisture. A Braun Labmaster 130 drybox was used to store the compounds and to prepare the samples for spectroscopic characterizations. All solvents were dried over sodium/benzophenone, freshly distilled, and degassed prior to use. Chemicals were purchased from Aldrich Chemical Co. and used as received: $[(Me_3Si)_2C(Ph)C(Me_3Si)N]$-Li·THF,[11,12] $[(Me_3Si)_2C(Ph)C(Me_3Si)N]AlI_2$,[13] $GaCl_3$,[14] and InBr[15] were prepared as described in the literature. NMR spectra were recorded on a Bruker AM 200 and a Bruker AM 250. Chemical shifts are reported in ppm with reference to tetramethylsilane as external standard. EI mass spectra were obtained on Finnigan MAT 8230 or Varian MAT CH 5 instruments, and FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates or as KBr pellets in the range 4000−400 cm^{-1} (abbreviations used: vs, very strong; s, strong; m, medium). Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes and are uncorrected.

Preparation of $RGaCl_2$ (1). RLi·THF[11,12] (1.66 g, 4.0 mmol) dissolved in *n*-hexane (30 mL) was added to a stirred suspension of $GaCl_3$ (0.70 g, 4.0 mmol) in *n*-hexane (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. The reaction mixture was filtered through a column of Celite. The solvent was removed in vacuo, and the yellow residue was crystallized from toluene (30 mL) to yield compound **1** as colorless crystals (1.43 g, 3.0 mmol, 75%). Mp: 102 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.00 (s, 9 H, $NSiMe_3$), 0.24 (s, 18 H, $SiMe_3$), 6.80−6.98 (m, 3 H, Ph), 7.20 (d, 2 H, Ph). ^{13}C NMR (125.76 MHz, C_6D_6): δ 0.54 (s, $NSiMe_3$), 2.55 (s, $SiMe_3$), 49.85 (s, CSi_2), 126.37, 128.50, 130.78 (s, Ph), 139.34 (s, ipso-C), 208.83 (s, CN). ^{29}Si NMR

[†] Dedicated to Professor Max Schmidt on the occasion of his 75th birthday.

(1) Uhl, W. *Z. Naturforsch. Sect. B* **1988**, *43*, 1113.

(2) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289.

(3) Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 139.

(4) Cowley, A. H.; Decken, A.; Olazábal, C. A. *J. Organomet. Chem.* **1996**, *524*, 271.

(5) Linti, G.; Köstler, W. *Angew. Chem.* **1996,** *108*, 593; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 550.

(6) Fussstetter, H.; Nöth, H.; Winterstein, W. *Chem. Ber.* **1977**, *110*, 1931.

(7) Power, P. P. *J. Chem. Soc., Dalton Trans* **1998**, 2939.

(8) Loos, D.; Schnöckel, H. *J. Organomet. Chem.* **1993**, *463*, 37.

(9) Uhl, W.; Hiller, W.; Layh, M.; Schwarz, W. *Angew. Chem.* **1992,** *104*, 1378; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1364.

(10) Linti, G. *J. Organomet. Chem.* **1996**, *520*, 107.

(11) Hitchcock, P. B.; Lappert, M. F.; Layh, M. *Inorg. Chim. Acta* **1998**, *269*, 181.

(12) Lappert, M. F.; Layh, M. *Tetrahedron Lett.* **1998**, *39*, 4745.

(13) Cui, C.; Roesky, H. W.; Noltemeyer, M.; Lappert, M. F.; Schmidt, H.-G.; Hao, H. *Organometallics* **1999**, *18*, 2256.

(14) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie, Bd II, 3. Auflage*; Emke: Stuttgart, 1978; p 851.

(15) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie, Bd II, 3. Auflage*; Emke: Stuttgart, 1978; p 870.

10.1021/om000125c CCC: $19.00

Table 1. Summary of Crystal Data for Complexes 1, 2, 3, and 4

	1	**2**	**3**	**4**
empirical formula	$C_{17}H_{32}Cl_2GaNSi_3$	$C_{34}H_{64}Al_2Cl_{0.86}I_{1.14}N_2Si_6$	$C_{48}H_{80}Cl_2Ga_2N_2Si_6$ incl. 2 toluene	$C_{48}H_{80}Br_2In_2N_2Si_6$ incl. 2 toluene
fw	475.33	898.30	1064.02	1243.14
temp (K)	153(2)	133(2)	273(2)	150(2)
cryst size (mm)	0.80 × 0.50 × 0.50	0.50 × 0.50 × 0.20	0.70 × 0.50 × 0.50	0.60 × 0.20 × 0.20
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
space group	*Pbca*	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	16.918(3)	15.536(3)	11.025(2)	10.636(8)
b (Å)	16.149(2)	18.201(4)	15.012(4)	15.440(13)
c (Å)	17.725(3)	17.155(3)	18.943(5)	19.040(3)
α (deg)	90	90	97.46(3)	98.55(14)
β (deg)	90	108.15(3)	96.94(15)	92.11(4)
γ (deg)	90	90	105.06(14)	105.11(3)
cell vol ($Å^3$)	4842.4(13)	4610(2)	2962.4(12)	2975.0(6)
Z	8	4	2	2
d(calc) (Mg/m^3)	1.304	1.294	1.193	1.388
abs coeff (mm^{-1})	1.507	1.056	1.152	2.270
F(000)	1984	1868	1124	1268
θ range (deg)	3.56−25.02	2.41−27.78	3.55−22.53	3.68−25.03
limiting indices	$-1 \le h \le 20$	$-20 \le h \le 20$	$-11 \le h \le 11$	$-12 \le h \le 12$
	$0 \le k \le 19$	$-23 \le k \le 15$	$-16 \le k \le 16$	$-18 \le k \le 18$
	$-21 \le l \le 21$	$-22 \le l \le 22$	$-19 \le l \le 20$	$-22 \le l \le 22$
no. of reflns	4253	70 718	10 164	14 044
no of indep reflns	4249 ($R_{int} = 0.1304$)	10729 ($R_{int} = 0.1281$)	7726 ($R_{int} = 0.0358$)	10 443 ($R_{int} = 0.0845$)
no. of data/restraints/params	4242/0/226	10727/0/453	7721/355/519	10423/0/529
GOF/F^2	1.150	0.949	1.022	1.048
R indices	R1 = 0.0277	R1 = 0.0513	R1 = 0.0471	R1 = 0.0567
[$I > 2\sigma(I)$]	wR2 = 0.0635	wR2 = 0.0868	wR2 = 0.1290	wR2 = 0.1479
R indices	R1 = 0.0334	R1 = 0.1155	R1 = 0.0554	R1 = 0.0696
(all data)	wR2 = 0.0688	wR2 = 0.0985	wR2 = 0.1398	wR2 = 0.1673
largest diff peak/hole (e $Å^{-3}$)	0.434 /−0.294	0.438 /−0.399	0.746 /−0.684	1.821 /−1.654

(79.46 MHz, C_6D_6): δ −0.27 (s, $SiMe_3$), 9.87 (s, $NSiMe_3$). MS: *m*/*z* (%) 472 (M^+ − H, 20), 458 (M^+ − Me, 25), 73 (Me_3Si^+, 100). IR (Nujol mull, cm^{-1}): 1599 (m), 1577 (m), 1510 (s), 1255 (vs), 1181 (m), 1159 (m), 1082 (s), 1063 (s), 1025 (s), 1002 (m), 966 (s), 926 (m), 870 (vs), 847 (vs), 762 (vs), 714 (s), 699 (s), 686 (s), 658 (vs), 594 (m), 530 (s), 446(m), 368 (s). Anal. Calcd for $C_{17}H_{32}Cl_2GaNSi_3$ (475.33): C, 42.96; H, 6.79; N, 2.95. Found: C, 42.75; H, 6.83; N, 3.04.

Preparation of [RIAl−AlClR] (2). Me_2AlCl (3.5 mL, 1 M in *n*-hexane, 3.5 mmol) was added to a stirred suspension of RLi·THF (1.24 g, 3.0 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for an additional 15 h. The volatiles were removed in vacuo. The crude product was extracted with *n*-pentane (20 mL), and the extract was concentrated to leave a yellow oil, which was redissolved in toluene (20 mL). Iodine (I_2, 1.52 g, 6.0 mmol) was added in a single portion at room temperature. The mixture was stirred for 20 h. It was filtered to remove residual amounts of I_2 to yield a dark yellow solution. This solution was added to a suspension of finely divided potassium (0.20 g, 5.6 mmol) in toluene (10 mL), and the mixture was vigorously stirred at room temperature for 3 days and additional 1 day at 60 °C to give a deep red solution containing a large amount of precipitate. After the mixture was filtered, the deep red filtrate was evaporated to dryness and the residual solid was crystallized from diisopropyl ether at −30 °C to give bright yellow, almost orange crystals (0.20 g, 25%). Mp: 196 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.12, 0.13, 0.14 (s, 18 H, $NSiMe_3$), 0.18, 0.28, 0.29, 0.33, 0.58, 0.66 (s, 36 H, $SiMe_3$), 6.8−7.0 (m, 6 H, Ph), 7.2−7.4 (m, 4 H, Ph). ^{29}Si NMR (99.36 MHz, C_6D_6): δ −3.9, −3.7, −3.1, −0.51, −0.17, 0.24, 1.5 ($SiMe_3$), 7.9, 8.9, 9.2 ($NSiMe_3$). FI-MS: *m*/*z* (%) 722 (M^+ − Cl, − I, 1), 361 (M^+/2 − Cl, 100). EI−MS: *m*/*z* (%) 488 ($[RAlI]^+$, 52), 396 ($[RAlCl]^+$, 20), 73 (Me_3Si^+, 100). Anal. Calcd for $C_{34}H_{64}Al_2ClIN_2Si_6$ (885.73): C, 46.13; H, 7.29; Al, 6.11; N 3.17. Found: C, 45.41; H, 7.32; Al, 6.20; N, 2.85.

Preparation of $[RGaCl]_2$ (3). To a stirred suspension of a Na/K alloy obtained from sodium (0.03 g, 1.3 mmol) and potassium (0.10 g, 2.5 mmol) in toluene (20 mL) was added at room temperature a solution of $RGaCl_2$ (**1**) (1.00 g, 2.1 mmol) in toluene (30 mL). The colorless solution was stirred for 24 h at room temperature. The yellow solution was filtered through a column of Celite and concentrated to ca. 5 mL. Pure **3** was obtained as colorless crystals at 0 °C. Yield: 0.66 g (0.76 mmol, 72%). Mp: 192 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.08 (s, 9 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 0.61 (s, 9 H, $NSiMe_3$), 6.80−6.98 (m, 3 H, Ph), 7.35 (d, 2 H, Ph). ^{13}C NMR (125.76 MHz, C_6D_6): δ 2.31 (s, $NSiMe_3$), 3.92 (s, $SiMe_3$), 4.71 (s, $SiMe_3$), 59.52 (s, CSi_2), 126.14, 128.40, 130.09 (s, Ph), 142.75 (s, ipso-C), 206.44 (s, CN). ^{29}Si NMR (99.36 MHz, C_6D_6): δ −2.73 (s, $SiMe_3$), −0.37 (s, $SiMe_3$), 9.87 (s, $NSiMe_3$). MS: *m*/*z* (%) 438 (M^+/2, 8), 403 (M^+/2 − Cl, 18), 73 (Me_3Si^+, 100). IR (Nujol mull, cm^{-1}): 1508 (s), 1248 (vs), 1157(m), 1084 (s), 1070 (s), 1028 (m), 950 (s), 870 (vs), 848 (vs), 762 (s), 716 (s), 669 (m), 656 (m), 612 (m), 592 (m), 511 (s). Anal. Calcd for $C_{34}H_{64}Cl_2Ga_2N_2Si_6$ (879.73): C, 46.42; H, 7.33; N, 3.62. Found: C, 46.13; H, 7.28; N, 3.38.

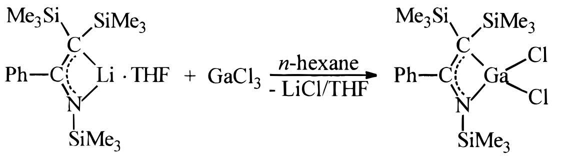
Preparation of $[RInBr]_2$ (4). To a suspension of freshly sublimed InBr (1.30 g, 10.0 mmol) in toluene (20 mL) was slowly added a solution of RLi·THF (2.10 g, 5.1 mmol) in toluene (30 mL) at −78 °C. The solution was allowed to warm to −10 °C and filtered to remove a brown precipitate that could not be characterized and metallic indium. The solvent was removed in vacuo, and the residue was crystallized from toluene (15 mL) to give **4** (1.80 g, 3.6 mmol, 70%) as colorless crystals. Mp: 132 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.11 (s, 9 H, $SiMe_3$), 0.20 (s, 9 H, $SiMe_3$), 0.41 (s, 9 H, $NSiMe_3$), 6.80−6.98 (m, 3 H, Ph), 7.25 (d, 2 H, Ph). ^{13}C NMR (125.76 MHz, C_6D_6): δ 1.54 (s, $NSiMe_3$), 2.83 (s, $SiMe_3$), 3.32 (s, $SiMe_3$), 65.85 (s, CSi_2), 126.48, 128.44, 130.95 (s, Ph), 143.62 (s, ipso-C), 166.03 (s, CN). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −9.47 (s, $SiMe_3$), −7.51 (s, $SiMe_3$), 7.55 (s, $NSiMe_3$). MS: *m*/*z* (%) 529 (M^+/2, 10), 73 (Me_3Si^+, 100). IR (KBr, cm^{-1}): 2959 (s), 2925 (m), 1682 (m), 1623 (vs), 1599 (s), 1578 (s), 1450 (s), 1400 (s), 1361 (m), 1261 (vs), 1101 (vs), 1027 (vs), 843 (vs), 806, (s), 755 (vs), 693 (s), 610 (m), 466 (m). Anal. Calcd for $C_{34}H_{64}Br_2In_2N_2Si_6$ (1058.84): C, 38.57; H, 6.09; N, 2.65. Found: C, 38.84; H, 6.09; N, 2.85.

Crystal Structure Solution and Refinement for 1−4. Data for structures **1**, **2**, **3**, and **4** were collected on a Stoe-Siemens-Huber four-circle diffractometer using Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods (SHELXS-96)[16] and refined against F^2 using SHELXS-97.[17] All heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atom. The structure parameters and refinement procedures are summarized in Table 1.

Results and Discussion

Synthesis of Al−Al, Ga−Ga, and In−In 1-Aza-allyl (R) Complexes. Our recent results highlight the synthesis of precursors of the type $RAlX_2$ (X = Me, F, Cl, Br, I)[13] and promt us to generalize the concept realized with other group 13 metals.

The reaction of $GaCl_3$ with RLi·THF in *n*-hexane affords $RGaCl_2$ (**1**) in high yield (eq 1).



1

(1)

A solvent-free product could be easily obtained by treating the crude product for a prolonged time in high vacuum at ambient temperature, as realized in the case of $RAlX_2$.[13] Exposed to air and moisture, compound **1** is readily attacked, which is indicated by an immediate color change from colorless to red.

The η^3 chelating mode of the ligand increases the coordination number of the metal, and this may make reduction of the RMX_2 compounds a favorable process.

The reductive dehalogenation of Cp^*AlX_2 (X = Cl, Br, I) using potassium or Na/K alloy affords $[Cp^*Al]_4$[18,19] (of Cp^*GaCl_2, Cp^*Ga[20,21] and of $(Me_3Si)_3CAlI_2$·THF,[22] $[(Me_3Si)_3CAl]_4$[23]). The reduction of solvent-free $RAlI_2$ by finely divided potassium in toluene did not give an identifiable product. However, when a mixture of $RAlI_2$ and RAlClI was used for the reduction, the first example of a dialuminum species [RClAl−AlIR] (**2**), which contains both organic and two different halide substituents, was obtained. The EI-MS mass spectrum clearly showed $[RAlCl]^+$ and $[RAlI]^+$ fragments. The ^1H and ^{29}Si NMR spectra of **2** are complicated probably due to the different halogens on the two aluminum atoms, which may give several species in solution (RClAl−AlClR, RIAl−AlIR, RClAl−AlIR). The formation of **2** might be explained by the simultaneous reduction of $RAlI_2$ and RAlClI. A possible pathway for the formation of RAlClI is illustrated in Scheme 1.[24] However, attempts to isolate pure RAlClI from the reaction of RAlClMe[13] and I_2 were unsuccessful.

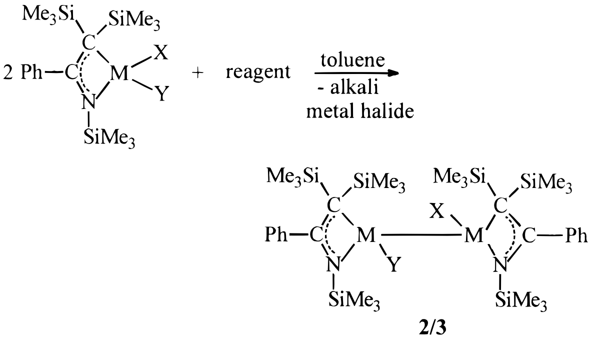
Scheme 1

$$2\,Me_2AlCl \rightleftharpoons MeAlCl_2 + Me_3Al$$

$$RAlMe_2 + 2I_2 \rightleftharpoons RAlI_2 + 2MeI$$

$$RMeAlCl + I_2 \rightleftharpoons RAlClI + MeI$$

The reaction of $RGaCl_2$ with Na/K alloy in toluene at room temperature did not lead to the expected $[RGa]_n$, but rather to the digallium compound **3**, with an organic and a halide substituent on each Ga atom. **3** is a new example of a digallane of type $[RGaCl]_2$, in addition to the known complexes $[2,4,6\text{-}t\text{-}Bu_3C_6H_2GaCl]_2$[4] and $[(Me_3Si)_3SiGaCl]_4$.[5]

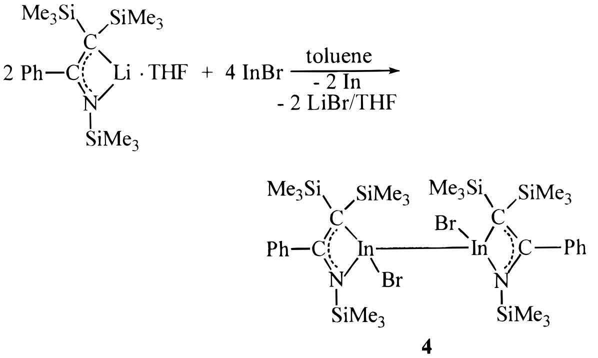


(2)

2/3

compound	reagent	M	X	Y
2	K	Al	Cl	Cl, I
3	Na/K	Ga	Cl	Cl

In another approach, the reaction between InBr and RLi·THF surprisingly delivers after workup **4** as colorless crystals (eq 3). This was unexpected. The expected product was RIn or $[RIn]_n$.



(3)

4

Compounds **1**−**4** were characterized by ^1H, ^{13}C, ^{29}Si NMR, and IR spectroscopy as well as by mass spectrometry, elemental analysis, and X-ray crystal structure analysis. Crystal data for compounds **1**−**4** are summarized in Table 1. Selected bond distances and angles are collected in Table 2. Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from toluene at 0 °C (**1**, **3**, **4**) or from *n*-pentane

---

(16) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(17) Sheldrick, G. M. *SHELXL, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(18) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem.* **1991,** *103*, 594; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564.

(19) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem.* **1993,** *105*, 1828; *Angew. Chem., Int. Ed. Engl.* **1993,** *32*, 1729.

(20) Koch, H. J. Dissertation, University of Göttingen, Göttingen, Germany, 1992.

(21) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H. G. *Organometallics* **1998**, *17*, 1305.

(22) Schnitter, C.; Klimek, K. S.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Röpken, C.; Parisini, E. *Organometallics* **1998**, *17*, 2249.

(23) Schnitter, C.; Roesky, H. W.; Röpken, C.; Herbst-Irmer, R.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **1998,** *110*, 2059; *Angew. Chem., Int. Ed.* **1998**, *37*, 1952.

(24) Schonberg, P. R.; Paine, R. T.; Campana, C. F.; Duesler, E. N. *Organometallics* **1982**, *1*, 799.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [(Me$_3$Si)$_2$C(Ph)C(Me$_3$Si)N]GaCl$_2$ (1)

Ga(1)−N(1) 2.013(2)	Ga(1)−C(2) 2.035(2)	Ga(1)−C(1) 2.405(2)
Ga(1)−Cl(2) 2.168(7)	Ga(1)−Cl(1) 2.179(7)	C(1)−C(2) 1.498(3)
C(1)−N(1) 1.303(3)	N(1)−Si(1) 1.795(2)	C(2)−Si(2) 1.906(2)
C(2)−Si(3) 1.905(2)	C(1)−C(3) 1.488(3)	
N(1)−Ga(1)−C(2) 71.09(8)	N(1)−C(1)−C(2) 114.20(2)	C(1)−N(1)−Si(1) 132.90(2)
C(2)−Ga(1)−Cl(2) 126.38(7)	N(1)−C(1)−Ga(1) 56.85(11)	Si(1)−N(1)−Ga(1) 136.15(10)
C(2)−Ga(1)−Cl(1) 122.63(6)	C(2)−C(1)−Ga(1) 57.36(11)	N(1)−Ga(1)−Cl(1) 113.68(6)
Cl(1)−Ga(1)−C(1) 124.06(5)	C(1)−C(2)−Si(2) 112.27(15)	Cl(2)−Ga(1)−Cl(1) 105.29(3)
Cl(2)−Ga(1)−C(1) 126.74(5)	N(1)−Ga(1)−Cl(2) 112.17(6)	C(1)−N(1)−Ga(1) 90.35(13)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [(Me$_3$Si)$_2$C(Ph)C(Me$_3$Si)N]$_2$Al$_2$ClI (2)

I(1)−Al(1) 2.553(3)	C(2)−Si(1) 1.897(4)	Al(2)−C(4) 2.106(4)
Cl(1)−Al(1) 2.286(11)	C(3)−C(51) 1.492(5)	N(1)−C(1) 1.322(4)
Al(1)−N(1) 1.960(3)	C(4)−Si(6) 1.904(4)	N(2)−C(3) 1.321(4)
Al(1)−C(1) 2.351(4)	I(2)−Al(2) 2.546(2)	C(1)−C(2) 1.472(5)
Al(2)−N(2) 1.939(3)	Cl(2)−Al(2) 2.347(11)	C(2)−Si(2) 1.882(4)
Al(2)−C(3) 2.354(4)	Al(1)−C(2) 2.095(4)	C(3)−C(4) 1.466(5)
C(1)−C(11) 1.488(5)	Al(1)−Al(2) 2.593(2)	C(4)−Si(5) 1902(4)
N(1)−Al(1)−C(2) 71.14(13)	C(4)−Al(2)−Al(1) 120.66(12)	C(1)−Al(1)−Al(2) 117.65(10)
C(1)−Al(1)−Cl(1) 120.7(4)	C(3)−Al(2)−Al(1) 115.12(11)	N(2)−Al(2)−C(4) 70.64(13)
N(1)−Al(1)−I(1) 113.08(12)	C(3)−N(2)−Al(2) 90.4(2)	C(4)−Al(2)−Cl(2) 122.2(3)
N(1)−Al(1)−Al(2) 113.45(10)	N(1)−C(1)−C(2) 115.2(3)	N(2)−Al(2)−I(2) 110.23(10)
Cl(1)−Al(1)−Al(2) 111.9(3)	N(2)−C(3)−C(4) 114.3(3)	N(2)−Al(2)−Al(1) 112.00(10)
I(1)−Al(1)−Al(2) 110.40(8)	N(1)−Al(1)−Cl(1) 108.6(3)	Cl(2)−Al(2)−Al(1) 113.0(3)
N(2)−Al(2)−Cl(2) 108.1(3)	Cl(1)−Al(1)−C(1) 127.2(3)	I(2)−Al(2)−Al(1) 110.76(5)
Cl(2)−Al(2)−C(3) 127.)(3)	C(2)−Al(1)−I(1) 120.06(13)	C(1)−N(1)−Al(1) 89.3(2)
C(4)−Al(2)−I(2) 123.88(11)	C(1)−Al(1)−I(1) 103.05(12)	C(3)−C(4)−Al(2) 80.2(2)
C(3)−Al(2)−I(2) 130.43(11)	C(2)−Al(1)−Al(2) 122.27(11)	C(1)−C(2)−Al(1) 80.4(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [((Me$_3$Si)$_2$C(Ph)C(Me$_3$Si)N)GaCl]$_2$ (3)

Ga (1)−N(1) 2.047(3)	Si(5)−C(4) 1.890(4)	Ga(2)−Cl(2) 2.241(14)
Ga(1)−Cl(1) 2.236(14)	Si(6)−C(4) 1.905(4)	N(1)−C(1) 1.309(5)
Ga(1)−Ga(2) 2.445(9)	C(1)−C(2) 1.486(6)	N(2)−C(3) 1.308(5)
Ga(2)−C(4) 2.092(4)	C(3)−C(34) 1.496(6)	Si(2)−C(2) 1.898(4)
Ga(2)−C(3) 2.435(4)	Ga(1)−C(2) 2.097(4)	Si(3)−C(2) 1.898(4)
N(1)−Si(1) 1.785(3)	Ga(1)−C(1) 2.444(4)	C(1)−C(14) 1.487(6)
N(2)−Si(4) 1.775(4)	Ga(2)−N(2) 2.05(3)	C(3)−C(4) 1.483(6)
N(1)−Ga(1)−C(2) 69.07(15)	Si(1)−N(1)−Ga(1) 138.20(2)	C(1)−N(1)−Ga(1) 90.70(2)
C(2)−Ga(1)−Cl(1) 117.60(12)	C(3)−N(2)−Ga(2) 90.00(2)	Si(4)−N(2)−Ga(2) 138.50(2)
N(1)−Ga(1)−Ga(2) 114.04(14)	N(1)−Ga(1)−Cl(1) 108.68(10)	N(2)−C(3)−C(4) 115.20(4)
Cl(1)−Ga(1)−Ga(2) 107.64(5)	C(2)−Ga(1)−Ga(2) 130.94(11)	N(1)−C(1)−C(2) 114.20(4)
N(2)−Ga(2)−C(4) 69.33(14)	C(1)−Ga(1)−Ga(2) 124.99(10)	C(1)−C(2)−Ga(1) 84.20(2)
C(4)−Ga(2)−Cl(2) 118.02(12)	N(2)−Ga(2)−Cl(2) 107.06(11)	C(3)−C(4)−Ga(2) 84.00(2)
N(2)−Ga(2)−Ga(1) 115.47(10)	Cl(2)−Ga(2)−C(3) 121.34(11)	C(1)−N(1)−Si(1) 131.10(3)
Cl(2)−Ga(2)−Ga(1) 107.13(5)	C(4)−Ga(2)−Ga(1) 131.01(12)	C(3)−Ga(2)−Ga(1) 126.58(10)

at −30 °C (**2**). The molecular structures are shown in Figures 1−4.

Compound **1** crystallizes as a colorless solid in the orthorhombic space group *Pbca* and adopts a distorted tetrahedral structure (Figure 1). The core angle N(1)−Ga(1)−C(2) is acute (71.09(8)°), which is compensated for by opening of the N−Ga−Cl and C−Ga−Cl angles. The structure of **1** is similar to that of 1-aza-allyl RAlCl$_2$[13] and PhC(NSiMe$_3$)$_2$AlCl$_2$.[25] However the core angle of **1** is slightly smaller than N−Al−N (72.9(2)°) in PhC(NSiMe$_3$)$_2$AlCl$_2$ and N(1)−Al(1)−C(2) (73.68(10)°) in RAlCl$_2$. The long C(1)−C(2) and short N(1)−C(1) bond distances in **1** indicate delocalization of the electrons in the N(1)−C(1)−C(2) unit. The Ga−Cl bond distances (2.168(7) Å) are somewhat longer than those in 2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$H$_3$C$_6$GaCl$_2$ (2.124(3) Å).[26]

The structure of compound **2** is shown in Figure 2. Selected bond lengths and angles are summarized in Table 3. The two R groups are bonded to the aluminum atoms in η^3 fashion in trans conformation, leading to four-coordinated Al centers with distorted tetrahedral geometry. The Al(1)−Al(2) bond distance (2.593(2) Å) is the shortest one reported so far for neutral Al

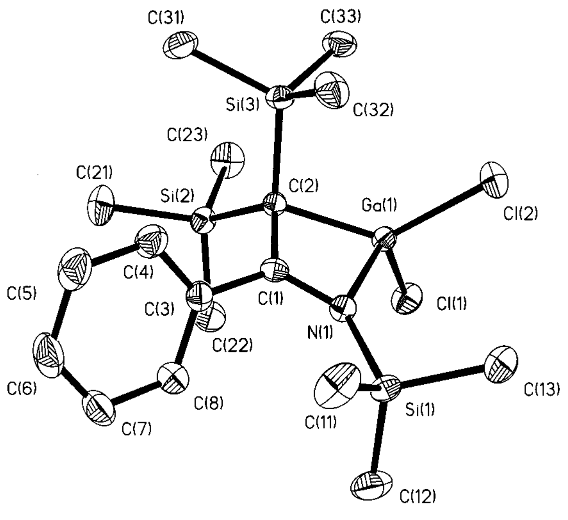


Figure 1. Molecular structure of **1** in the crystal (50% probability). Hydrogen atoms have been omitted for clarity.

---

(25) Ergezinger, C.; Weller, F.; Dehnicke, K. *Z. Naturforsch., Sect. B* **1988**, *43*, 1621.

(26) Twamley, B.; Power, P. P. *Chem. Commun.* **1999**, 1805.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[((Me_3Si)_2C(Ph)C(Me_3Si)N)InBr]_2$ (4)

In(1)−N(1) 2.254(5)	Si(3)−C(2) 1.898(6)	In(1')−N(1') 2.251(5)
In(1)−Br(1) 2.567(4)	Si(3')−C(2') 1.885(6)	In(1')−Br(1') 2.561(2)
In(1)−In(1') 2.728(4)	C(1')−N(1') 1.295(8)	Si(1)−N(1) 1.774(5)
In(1')−C(2') 2.279(6)	C(1')−C(2') 1.497(8)	Si(1')−N(1') 1.776(5)
In(1')−C(1') 2.635(6)	C(1)−C(3) 1.503(9)	N(1)−C(1) 1.297(8)
Si(2)−C(2) 1.889(6)	In(1)−C(2) 2.281(6)	C(1')−C(3') 1.491(8)
Si(2')−C(2') 1.889(7)	In(1)−C(1) 2.633(6)	C(1)−C(2) 1.482(8)
N(1)−In(1)−C(2) 63.1(2)	Br(1)−In(1)−C(1) 124.5(2)	N(1')−C(1')−C(2') 116.9(5)
C(2)−In(1)−Br(1) 121.9(2)	C(2)−In(1)−In(1') 129.5(2)	N(1)−C(1)−C(3) 121.2(5)
N(1)−In(1)−In(1') 113.5(2)	C(1)−In(1)−In(1') 122.6(2)	C(1')−N(1')−In(1') 92.0(4)
Br(1)−In(1)−In(1') 106.8(10)	N(1')−In(1')−Br(1') 105.4(14)	C(1)−N(1)−In(1) 91.7(3)
N(1')−In(1')−C(2') 63.4(2)	Br(1')−In(1')−C(1') 119.9(14)	N(1')−C(1')−C(3') 121.8(5)
C(2')−In(1')−Br(1') 119.6(2)	C(2')−In(1')−In(1) 131.2(2)	N(1)−C(1)−C(2) 117.2(5)
N(1')−In(1')−In(1) 117.4(2)	C(1')−In(1')−In(1) 126.4(2)	Si(1')−N(1')−In(1') 136.3(3)
Br(1')−In(1')−In(1) 107.4(10)	C(1)−N(1)−Si(1) 132.3(4)	C(1)−C(2)−In(1) 86.1(3)
N(1)−In(1)−Br(1) 110.2(2)	Si(1)−N(1)−In(1) 135.8(3)	C(1')−C(2')−In(1') 85.9(3)

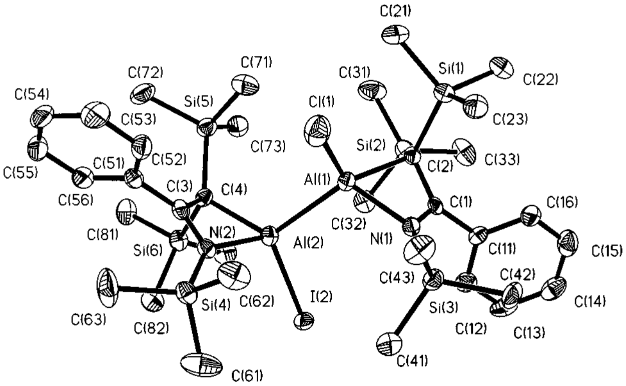


Figure 2. Molecular structure of **2** in the crystal (50% probability). Hydrogen atoms have been omitted for clarity.

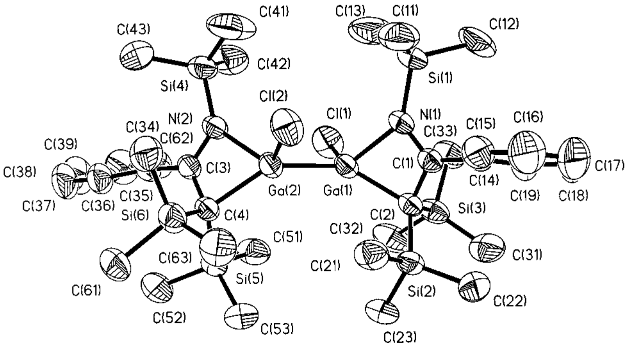


Figure 3. Molecular structure of **3** in the crystal (50% probability). Hydrogen atoms have been omitted for clarity.

compounds (Table 6). The Al−Cl bond length (2.347(11) Å) is longer by ca. 0.2 Å than those in the Al(III) compound $RAlCl_2$ (average 2.13(10) Å).

Compounds **3** and **4** crystallize as colorless solids in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The molecules are generated by a center of symmetry located at the midpoint of the Ga−Ga (Figure 3) and the In−In bonds (Figure 4), respectively.

The Ga−Ga bond distance in compound **3** (2.445(9) Å) is slightly longer than in $[2,4,6\text{-}t\text{-}Bu_3C_6H_2GaCl]_2$[4] (2.438(6) Å) and shorter than those in $[(Me_3Si)_3SiGaCl]_4$[5] (2.509(12) Å), $[((Me_3Si)_2CH)_2Ga]_2$[2] (2.541(1) Å), $[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2Ga]_2$[27] (2.513(3) Å), and $[(2,4,6\text{-}(CF_3)_3C_6H_2)_2Ga]_2$[28] (2.479(1) Å) (Table 6). Presumably, the reason for this shortening stems from the fact that **3** features two rather than four bulky substituents. The geometry of the gallium centers is that of a distorted tetrahedron. The angle C(1)−N(1)−Ga(1) (90.7(2)°) in **3** is comparable with that of **1** (90.4(13)°), and the Ga(1)−N(1) (2.047(3) Å), Ga(1)−C(1) (2.444(4) Å), and Ga (1)−C(2) (2.097(4) Å) bond lengths in **3** are somewhat longer than those in **1**: Ga(1)−N(1) (2.013(2) Å), Ga(1)−C(1) (2.405(2) Å), Ga (1)−C(2) (2.035(2) Å). This is caused by the steric demand of the second ligand.

The In−In bond distance of **4** (2.728(4) Å) is shorter than those reported in $[((Me_3Si)_2CH)_2In]_2$[3] (2.828(1) Å), $[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2In]_2$[29] (2.775(2) Å), $[(2,4,6\text{-}(CF_3)_3C_6H_2)_2\text{-}$

---

[27] He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem.* **1993,** *105*, 761; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717.

[28] Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070.

[29] Brothers, P. J.; Hübler, K.; Hübler, U.; Noll, B. C.; Olmstead, M. M.; Power, P. P. *Angew. Chem.* **1996,** *108*, 2528; *Angew. Chem., Int. Ed. Engl.* **1996,** *35*, 2355.

[30] Wiberg, N.; Amelunxen, K.; Nöth, H.; Schmidt, H.; Schwenk, H. *Angew. Chem.* **1996,** *108*, 110; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 65.

[31] Gabbaï, F. P.; Schier, A.; Riede, J.; Schichl, D. *Organometallics* **1996**, *15*, 4119.

[32] Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983.

[33] Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J. *Organometallics* **1998**, *17*, 5431.

[34] Purath, A.; Dohmeier, C.; Ecker, A.; Schnöckel, H.; Amelunxen, K.; Passler, T.; Wiberg, N. *Organometallics* **1998**, *17*, 1894.

[35] Purath, A.; Schnöckel, H. *J. Organomet. Chem.* **1999**, *579*, 373.

[36] Uhl, W.; Graupner, R.; Hahn, I.; Spies, T.; Frank, W. *Eur. J. Inorg. Chem.* **1998**, 355.

[37] Linti, G.; Frey, R.; Schmidt, M. *Z. Naturforsch., Sect. B* **1994**, *49*, 958.

[38] Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421.

[39] Haubrich, S.; Power, P. P. Unpublished work.

[40] Wiberg, N.; Amelunxen, K.; Nöth, H.; Schwenk, H.; Kaim, W.; Klein, A.; Scheiring, T. *Angew. Chem.* **1997**, *109*, 1258; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1213.

[41] Loos, D.; Baum, E.; Ecker, A.; Schnöckel, H.; Downs, A. J. *Angew. Chem.* **1997**, *109*, 894; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860.

[42] Uhl, W.; Jantschak, A. *J. Organomet. Chem.* **1998**, *555*, 263.

[43] Schnepf, A.; Weckert, E.; Linti, G.; Schnöckel, H. *Angew. Chem.* **1999,** *111*, 3578; *Angew. Chem., Int. Ed.* **1999**, *38*, 3381.

[44] Beachley, Jr., O. T.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346.

[45] Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1.

[46] Uhl, W.; Jantschak, A.; Saak, W.; Kaupp, M.; Wartchow, R. *Organometallics* **1998**, *17*, 5009.

[47] Wiberg, N.; Blank, T.; Purath, A.; Stösser, G.; Schnöckel, H. *Angew. Chem.* **1999,** *111*, 2745; *Angew. Chem., Int. Ed.* **1999**, *38*, 2563.

[48] Wiberg, N.; Blank, T.; Nöth, H.; Ponikwar, W. *Angew. Chem.* **1999,** *111*, 887; *Angew. Chem., Int. Ed.* **1999**, *38*, 839.

[49] Henkel, S.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem.* **1994,** *106*, 721; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 681.

[50] Uhl, W.; Keimling, S. U.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem.* **1997,** *109*, 64; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 64.

Table 6. Metal−Metal Bond Lengths of Structurally Characterized Group 13 Tetraorganodimetallanes and Related Species

compound	M−M/Å	M−C/Å	ref
$[((Me_3Si)_2CH)_2Al]_2$	2.660(1)	1.982(3)	1
$[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2Al]_2$	2.647(3)	1.996(3)	32
$[(t\text{-}Bu_3Si)_2Al]_2$	2.751(2)	2.717(1)^c	33
$[(Me_3Si)_2C(Ph)C(Me_3Si)N]_2Al_2ClI$	2.593(2)	2.095(4), 1.960(3)^d	
$[Cp^*Al]_4$	2.773(4)	2.292(13)	18
$[(Me_3Si)_3CAl]_4$	2.747(2)	2.027(5)	23
$[t\text{-}Bu_3SiAl]_4$	2.600(12)	2.501(10)^c	34
$[(Me_3Si)_3SiAl]_4$	2.592(2)	2.447(12)^c	35
$[((Me_3Si)_2CH)_2Ga]_2$	2.541(1)	1.995(5)	2
$[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2Ga]_2$	2.515(3)	2.008(7)	27
$[(Me_3Si)_3SiGaCl]_4$	2.505(4)	2.395(5)^c	5
$[((Me_3Si)_2CH)_2(DPPD)_2Ga]_2{}^a$	2.440(1)	1.995(5)	36
$[(TMP)_2Ga]_2{}^b$	2.525(1)	1.901(4)^d	37
$[(t\text{-}BuNCH{=}CHNt\text{-}Bu)Ga]_2$	2.333(1)	1.836(4)^d	38
$[((Me_3Si)_2C(Ph)C(Me_3Si)N)GaCl]_2$	2.445(9)	2.097(4), 2.047(3)^d	
$[(2,4,6\text{-}(CF_3)_3C_6H_2)_2Ga]_2$	2.479(1)		28
$[2,6\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3GaI]_2$	2.511(3)	1.994(9)	39
$[(t\text{-}Bu_3Si)Ga\text{-}Ga(Sit\text{-}Bu_3)_2]$	2.420(1)		40
$[Cp^*Ga]_6$	4.073(2), 4173(3)	2.380(9)	41
$[(Me_3Si)_3CGa]_4$	2.678(4)	2.060(2)	9
$[(EtMe_2Si)_3CGa]_4$	2.709(1)	2.102(8)	42
$[(Me_3Si)_3SiGa]_4$	2.567(2)	2.406(2)^c	10
$[(Me_3Si)_3Si]_8Ga_{22}$	2.942(5), 2.867(7), 2.673(6)	2.426(5)^c	43
$[((Me_3Si)_2CH)_2In]_2$	2.828(1)	2.194(5)	3
$[((Me_3Si)_2C(Ph)C(Me_3Si)N)InBr]_2$	2.728(4)	2.281(6), 2.254(5)^d	
$[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2In]_2$	2.775(2)	2.184(7)	29
$[(2,4,6\text{-}(CF_3)_3C_6H_2)_2In]_2$	2.744(2)	2.210(1)	28
$[(t\text{-}Bu_3Si)_2In]_2$	2.922(1)	2.778(4)^c	30
$[Cp^*In]_6$	3.943(1)	2.586(4)	44
$[(Me_3Si)_3CIn]_4$	3.002(1)	2.257(7)	45
$[(EtMe_2Si)_3CIn]_4$	3.004(1)	2.270(1)	46
$[(i\text{-}PrMe_2Si)_3CIn]_4$	3.145(1)	2.299(8)	46
$(t\text{-}Bu_3Si)_6In_8$	2.770(1)−3.303(1)	2.615(1),^{c} 2.665(2),^{c} 2.683(1)^c	47
$(t\text{-}Bu_3Si)_8In_{12}$	2.814(2)−3.307(2)	2.668(3),^{c} 2.685(3)^c	48
$[(t\text{-}Bu_3Si)_2Tl]_2$	2.966(2)	2.789(12)^c	30
$[((Me_3Si)_3Si)_2Tl]_2$	2.914(5)	2.675(2)^c	49
$[(Me_3Si)_3CTl]_4$	3.322(1)	2.380(1)	50

[a] DPPD = 1,3-diphenylpropane-1,3-dionate. [b] TMP = 2,2,6,6-tetramethylpiperidine. [c] M−Si distances. [d] M−N distances.

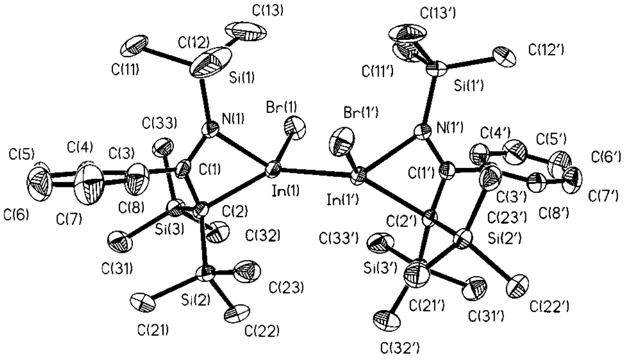


Figure 4. Molecular structure of **4** in the crystal (50% probability). Hydrogen atoms have been omitted for clarity.

$In]_2$[28] (2.744(2) Å), and $[(t\text{-}Bu_3Si)_2In]_2$[30] (2.922(1) Å) (Table 6). The reason for the shorter In−In bond of **4** could be the same as given for compound **3**. The In−Br bond distance (2.567(4) Å) is in good agreement with that in $[o\text{-}C_6H_4(InBr(THF)_2)]_2$[31] (2.547(1) Å). Both indium atoms in **4** adopt the geometry of a distorted tetrahedron. The torsion angle between the metal−halogen planes of compounds **2**, **3**, and **4** increases from Br(1)−In(1)−In(1′)−Br(1′) (129.4°), to Cl(1)−Ga(1)−Ga(2)−Cl(2) (133.9°), to I(1)−Al(1)−Al(2)−Cl(2) (145.9°). Metal−metal and metal−carbon/silicon bond lengths of structurally characterized group 13 tetraorganodimetallanes and related species are summarized in Table 6.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften.

Supporting Information Available: Listings of crystal data, atom coordinates, and equivalent isotropic displacement parameters for all non-hydrogen atoms, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and angles for compounds **1**, **2**, **3**, and **4** are given. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000125C