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Synthesis, Characterization, and Molecular Structures of Supermesitylgallium and Supermesitylindium Dihalides

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Compounds sMesMX$_2$ (sMes = 2,4,6-*t*-BuC$_6$H$_2$; X = Cl, Br; M = Ga, In) were prepared from MX$_3$ and sMesLi. X-ray structure determinations prove that this species are the first gallium and indium dihalides which are monomeric even in the solid state.

Introduction

The synthesis and structural characterization of monosubstituted gallium(III) and indium(III) compounds has attracted considerable attention, as these compounds are used as precursors for III–V-semiconductor thin-layered films in MOCVD methods or for the preparation of reduced Ga(I) and In(I) derivatives. It is noteworthy that all compounds stable at room temperature of Al, Ga, and In in oxidation state I have bulky substituents (Cp$^*_4$Al$_4$,[1] CpIn,[2] Cp*In,[3] (PhCH$_2$)$_5$C$_5$In,[4] [(η^6-Mesityl)$_2$Ga]GaCl$_4$[5]). The steric demand of bulky substituents stabilizes these compounds in low oxidation state by reducing their Lewis acidity.[6] We were interested in preparing monoorgano gallium and indium dihalides with a sterically demanding substituent. We chose the sMes ligand which has been successfully used stabilizing the first diphosphene[7] as well as iminoboranes.[8] sMesBF$_2$ was reacted with sodium–potassium alloy to afford an isomeric mixture of a bis(benzo[1]borolo) derivative of diborane(6).[9] In this paper we describe the synthesis and characterization of sMesGaX$_2$ and sMesInX$_2$ (X = Cl, Br), the first structurally characterized monomeric organogallium and -indium dihalides.

Experimental Section

All compounds described are sensitive to oxygen and moisture. All manipulations were performed under an inert atmosphere of dry nitrogen gas. GaCl$_3$ and InCl$_3$ were prepared according to the literatures.[10,11] GaBr$_3$ and InBr$_3$ were purchased from Heraeus and Fluka. sMesLi was prepared from sMesBr according to standard literature methods.[12] The solvents were dried using Na. Infrared spectra of Nujol films between CsI plates were recorded using a Perkin-Elmer 735 B spectrometer. Absorption intensities are reported with abbreviations m (medium), s (strong), and vs (very strong). ^{1}H and ^{13}C NMR spectra were recorded at 250 and 62.9 MHz using a Bruker AM 250. Chemical shifts are reported in δ units (ppm) and are referenced to SiMe$_4$ at δ 0.00 and benzene at 7.15. NMR tubes were sealed under vacuum. In the ^{13}C NMR spectra signals of the M-bonded C atoms have not been observed due to quadrupolar relaxation (^{69}Ga and ^{71}Ga, $I = ^3/_2$; ^{115}In, $I = ^9/_2$). Mass spectra were obtained with a Finnigan MAT 8230.

sMesGaCl$_2$ (1). A solution of GaCl$_3$ (8.80 g, 50 mmol) in 50 mL of hexane was added dropwise with stirring to a suspension of 12.62 g (50 mmol) of sMesLi in 300 mL of hexane at −78 °C. The suspension formed was slowly warmed to room temperature with continued stirring, hexane was evaporated under reduced pressure, and **1** was extracted from the residue with pentane. Crystals of mp 137 °C were obtained by 2-fold recrystallization from pentane at −20 °C in 47% yield (9.1 g).

^{1}H NMR (C$_6$D$_6$): 1.25 (s, 9H, *p-t*-Bu–H); 1.39 (s, 18H, *o-t*-Bu–H); 7.42 (s, 2H, aromatic-H). ^{13}C NMR (C$_6$D$_6$): 31.3 (s, p-C–*Me*$_3$); 32.9 (s, *o*-C–*Me*$_3$); 35.0 (s, p-*C*-Me$_3$); 37.2 (s, *o*-*C*-Me$_3$); 122.1 (s, *m*-aromatic-C); 153.0 (s, *p*-aromatic-C); 156.1 (s, *o*-aromatic-C).

MS (70eV), *m*/*z* (%): 386 (4), [M]$^+$; 371 (4), [M − Me]$^+$; 333 (15), [M − Me − HCl]$^+$; 315 (11), [M − Cl − HCl]$^+$; 245 (81), [sMes]$^+$; 57 (100), [C$_4$H$_9$]$^+$.

Anal. Calcd. for C$_{18}$H$_{29}$Cl$_2$Ga (M_r = 386.06): C, 56.0; H, 7.6; Cl, 18.4. Found: C, 56.0; H, 7.6; Cl, 18.3.

sMesGaBr$_2$ (2). A diethyl ether solution (30 mL) of sMesLi (0.50 g, 2 mmol) was added dropwise at −78 °C to a solution of GaBr$_3$ (0.62 g, 2 mmol) in diethyl ether. The solution was stirred for 20 h during which time the temperature was allowed to warm up to room temperature and a white precipitate of LiBr was formed. After removal of diethyl ether by vacuum distillation, the white solid was extracted with pentane. Reduction of the volume under reduced pressure to 15 mL and storage of the solution at −78 °C gave 0.68 g of **2** (1.4 mmol, 72% yield), mp 192 °C.

^{1}H NMR (benzene): 1.24 (s, 9H, *p-t*-Bu–H); 1.41 (s, 18H, *o-t*-Bu–H); 7.40 (s, 2H, aromatic-H); ^{13}C NMR (benzene): 31.2 (s, *p*-C–*Me*$_3$); 33.2 (s, *o*-C–*Me*$_3$); 35.0 (s, *p*-*C*–Me$_3$); 37.7 (s, *o*-*C*–Me$_3$); 122.2 (s, *m*-aromatic-C); 152.9 (s, *p*-aromatic-C); 156.1 (s, *o*-aromatic-C).

MS (70 eV), *m*/*z* (%): 474 (6), [M]$^+$; 459 (5), [M − Me]$^+$; 379 (6), [M − Me − Br]$^+$; 313 (5), [M − HBr − Br]$^+$; 245 (100), [sMes]$^+$.

IR (Nujol, CsI) [cm^{-1}]: 1591 (s), 1365 (s), 1246 (m), 1100 (m), 879 (s), 806 (s), 741 (m), 650 (m), 577 (s), 477 (m), 397 (m), 360 (m).

Anal. Calcd. for C$_{18}$H$_{29}$Br$_2$Ga (M_r = 474.96): C, 45.5; H, 6.1. Found: C, 46.6; H, 6.7.

sMesInCl$_2$ (3). To 8.85 g (40 mmol) of InCl$_3$ dissolved in 300 mL of THF was added a solution of 10.09 g (40 mmol) of sMesLi in 200 mL of THF dropwise with stirring at −78 °C. After the reaction mixture was slowly warmed to ambient temperature, THF was evaporated at reduced pressure. From the residue a mixture of **3** and InCl$_3$·2THF was extracted with pentane which both formed colorless crystals at −20 °C. The single crystal for the X-ray structure determination was selected from the crystal mixture; mp 141 °C.

^{1}H NMR (C$_6$D$_6$): 1.24 (s, 9H, *p-t*-Bu–H); 1.27 (s, 18H, *o-t*-Bu–H); 7.42 (s, 2H, aromatic-H). ^{13}C NMR (C$_6$D$_6$): 31.3 (s, *p*-C–*Me*$_3$); 32.5 (s, *o*-C–*Me*$_3$); 35.0 (s, *p*-*C*–Me$_3$); 36.4 (s, *o*-*C*–Me$_3$); 122.5 (s, *m*-aromatic-C); 152.6 (s, *p*-aromatic-C); 156.2 (s, *o*-aromatic-C).

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Table I. Crystallographic Data for **1**–**4**

	1	**2**	**3**	**4**
formula	$C_{18}H_{29}Cl_2Ga$	$C_{18}H_{29}Br_2Ga$	$C_{18}H_{29}Cl_2In$	$C_{18}H_{29}Br_2In$
MW	386.03	474.95	431.13	520.05
data collcn *T* (°C)	–183	–120	–120	–80
cryst. size (mm)	0.5 × 0.4 × 0.3	0.6 × 0.2 × 0.1	0.5 × 0.5 × 0.4	0.6 × 0.4 × 0.4
space group	$P2_1/n$	$C2/c$	$P2_1/n$	$C2/c$
a (pm)	1248.2(3)	1438.7(6)	1256.4(2)	1422.8(2)
b (pm)	1498.9(3)	1245.5(4)	1515.2(3)	1260.6(1)
c (pm)	2144.3(4)	1216.9(4)	2152.6(3)	1207.2(1)
β (deg)	106.81(1)	110.86(5)	106.41(1)	111.27(1)
V (nm^3)	3.840(1)	2.038(1)	3.931(1)	2.018(1)
Z	8	4	8	4
ρ (Mg/m^3)	1.335	1.548	1.457	1.712
μ (mm^{-1})	1.704	5.266	1.468	5.126
2θ range (deg)	8–50	6–55	8–45	6–55
no. of measd reflcns	7418	3110	5474	3745
no. of unique reflcns	6783	2350	5149	2023
no. of reflcns used	6780	2350	5123	2022
wR_2 (for all data)	0.1057	0.1855	0.2001	0.0796
$R1$ (for $F > 4\sigma F$)	0.0412	0.0601	0.0623	0.0357
no. of refined params	397	114	397	114

MS (70 eV), m/z (%): 430 (2), $[M]^+$; 395 (3), $[M - Cl]^+$; 245 (18), $[Mes]^+$; 57 (100), $[C_4H_9]^+$.

$C_{18}H_{29}Cl_2In$ ($M_r = 431.16$): no elemental analysis (crystal mixture).

sMesInBr₂ (4). $InBr_3$ (0.71 g, 2 mmol) was dissolved in 30 mL of diethyl ether. A diethyl ether solution of sMesLi (0.50 g, 2 mmol) was added dropwise at –78 °C. The resulting solution was stirred for 2 h before being allowed to warm up to room temperature. After the mixture was stirred for 20 h, the diethyl ether was removed by vacuum distillation. The resulting white solid was extracted with pentane. At –78 °C 0.74 g (1.4 mmol, 72%) of **4** were obtained as a white solid, mp 194 °C.

^{1}H NMR (benzene): 1.24 (s, 9H, *p-t*-Bu–H); 1.28 (s, 18H, *o-t*-Bu–H); 7.43 (s, 2H, aromatic-H); ^{13}C NMR (benzene): 31.7 (s, *p*-C-*Me*₃); 33.1 (s, *o*-C-*Me*₃); 35.4 (s, *p*-*C*-Me₃); 37.2 (s, *o*-*C*-Me₃); 122.8 (s, *m*-aromatic-C); 152.7 (s, *p*-aromatic-C); 156.3 (s, *o*-aromatic-C).

MS (70 eV), m/z (%): 520 (5), $[M]^+$; 439 (20), $[M - HBr]^+$; 245 (100), $[sMes]^+$.

IR (Nujol, CsI) [cm^{-1}]: 1586 (m), 1366 (s), 1214 (m), 1193 (m), 878 (s), 804 (s), 575 (m), 478 (m), 392 (m), 241 (vs).

Crystal Growth and X-ray Structure Determination. Suitable single crystals of **1**, **2**, and **4** were grown over a period of 2 weeks by slow evaporation of a pentane solution of **1** and **2**, and a hexane solution of **4**, respectively; a crystal of **3** was selected from the mixture with $InCl_3 \cdot 2THF$. Details of the structure determinations are given in Table I. The crystals were oil-coated shock-cooled at the tip of a glass fibre. The data were collected on a Stoe Siemens AED four-circle diffractometer using graphite-monochromated Mo Kα (λ = 71.073 pm) radiation. A semiempirical absorption correction was applied for **2**–**4**. All structures were solved by direct methods[13] and refined on F^2 by full-matrix least-squares techniques.[14] All non-hydrogen atoms were refined anisotropically. In **2** and **4** the *p-t*-Bu group is disordered due to the 2-fold axis. For **2** distance restraints for the 1–2 and the 1–3 distances and the rigid bond restraint[15–17] were applied on this group. In **3** relatively high residual electron density (about 2 $e^-/10^6\ pm^3$) is found caused by problems during the measurement. For the same reason rigid bond[15–17] restraints are used for one *p-t*-Bu group. All hydrogen atoms were refined using a riding model with fixed isotropic displacement parameters.

Results and Discussion

The supermesitylgallium and -indium dihalides $sMesMX_2$ (M = Ga, In; X = Cl, Br) were prepared according to eq 1. While

$$MX_3 + sMesLi \xrightarrow[-LiX]{} sMesMX_2$$

$$M = Ga, In;\ X = Cl, Br$$

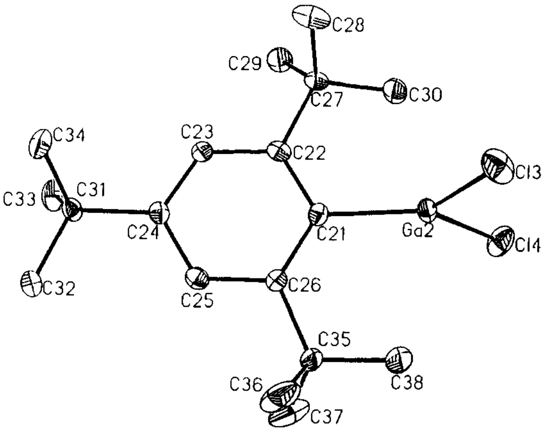

Figure 1. Structure of one molecule of **1** showing 50% displacement ellipsoids. Selected mean bond distances (pm) and angles (deg) are as follows: Ga–Cl(mean) = 215.7(1), Ga–C(mean) = 193.5(4); Cl–Ga–Cl(mean) = 106.9(1), Cl–Ga–C(mean) = 126.5(1).

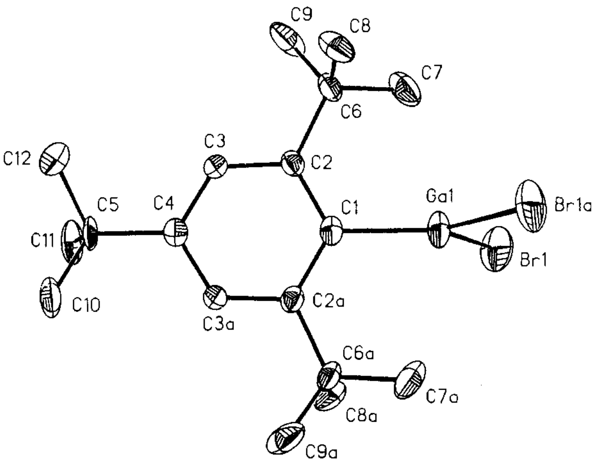

Figure 2. Structure of one molecule of **2** showing 50% displacement ellipsoids. Selected bond distances (pm) and angles (deg) are as follows: Ga–Br = 233.1(2), Ga–C = 197.5(8); Br–Ga–Br = 109.5(1), Br–Ga–C = 125.3(1).

the $sMesMBr_2$ (M = Ga, In) compounds **2** and **4** were obtained in good yields (72%), the corresponding chlorides obviously are more sensitive. This is shown by the fact that, in the presence of unreacted sMesBr (from the preparation of sMesLi), Cl is exchanged by Br and sMesMBrCl can be observed in the mass spectra. The products are isolated as colorless crystals, sensitive to moisture. In the case of **3** a mixture with $InCl_3 \cdot 2THF$ was

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Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) of **1**[a]

	x	*y*	*z*	*U*(eq)
Ga(1)	3080.0(3)	4583.2(3)	1279.9(2)	17.1(2)
Cl(1)	3308.6(8)	3801.1(7)	2155.1(5)	29.9(5)
Cl(2)	2858.5(8)	3643.1(7)	490.9(5)	29.4(5)
C(1)	3043(3)	5874(2)	1238(2)	14(2)
C(2)	4014(3)	6360(2)	1249(2)	16(2)
C(3)	3951(3)	7282(2)	1193(2)	15(2)
C(4)	2965(3)	7752(2)	1136(2)	16(2)
C(5)	2031(3)	7261(2)	1152(2)	16(2)
C(6)	2039(3)	6338(2)	1190(2)	16(2)
C(7)	5166(3)	5945(2)	1294(2)	19(2)
C(8)	5424(3)	6085(3)	643(2)	32(2)
C(9)	6083(3)	6382(3)	1845(2)	24(2)
C(10)	5231(3)	4955(3)	1434(3)	42(2)
C(11)	2944(3)	8767(2)	1058(2)	17(2)
C(12)	1775(3)	9158(3)	950(2)	24(2)
C(13)	3728(3)	9195(3)	1671(2)	27(2)
C(14)	3330(3)	9008(3)	466(2)	25(2)
C(15)	945(3)	5879(2)	1203(2)	19(2)
C(16)	−78(3)	6341(3)	741(3)	41(2)
C(17)	852(5)	5903(5)	1888(2)	69(3)
C(18)	861(3)	4917(3)	965(3)	43(2)
Ga(2)	6945.1(3)	8141.5(3)	3601.4(2)	16.5(2)
Cl(3)	7229.4(9)	8915.6(7)	4480.6(5)	31.8(5)
Cl(4)	6700.9(8)	9066.2(7)	2801.1(5)	29.0(5)
C(21)	6938(3)	6852(2)	3608(2)	14(2)
C(22)	5953(3)	6387(2)	3622(2)	15(2)
C(23)	6002(3)	5471(2)	3716(2)	16(2)
C(24)	6975(3)	4980(2)	3779(2)	14(2)
C(25)	7915(3)	5439(2)	3738(2)	17(2)
C(26)	7927(3)	6365(2)	3666(2)	14(2)
C(27)	4813(3)	6839(2)	3555(2)	17(2)
C(28)	4603(3)	6849(3)	4219(2)	32(2)
C(29)	3865(3)	6325(3)	3069(2)	24(2)
C(30)	4747(3)	7792(3)	3294(2)	29(2)
C(31)	6982(3)	3969(2)	3896(2)	16(2)
C(32)	8139(3)	3560(3)	4002(2)	24(2)
C(33)	6160(3)	3524(3)	3308(2)	28(2)
C(34)	6615(3)	3780(3)	4507(2)	25(2)
C(35)	9043(3)	6769(2)	3643(2)	18(2)
C(36)	9988(3)	6485(3)	4235(2)	40(2)
C(37)	9322(4)	6432(3)	3026(2)	40(2)
C(38)	9068(4)	7775(3)	3613(3)	46(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) of **2**[a]

	x	*y*	*z*	*U*(eq)
Ga(1)	0	7050.2(7)	2500	33.0(6)
Br(1)	1087.5(7)	8130.9(6)	1956.7(9)	58.7(6)
C(1)	0	5465(6)	2500	23(4)
C(2)	−709(4)	4899(5)	1550(5)	22(3)
C(3)	−691(4)	3772(5)	1596(5)	24(3)
C(4)	0	3188(6)	2500	24(4)
C(5)	0	1947(6)	2500	34(5)
C(6)	−1511(5)	5439(5)	495(5)	26(3)
C(7)	−1246(6)	6590(6)	220(7)	44(4)
C(8)	−2493(5)	5489(6)	743(6)	37(3)
C(9)	−1675(7)	4813(6)	−662(6)	48(5)
C(10)	246(11)	1484(8)	3745(9)	54(12)
C(11)	761(9)	1506(8)	1997(12)	41(5)
C(12)	−1033(8)	1493(9)	1741(11)	54(5)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) of **3**[a]

	x	*y*	*z*	*U*(eq)
In(1)	3064.2(5)	4551.2(4)	1294.6(3)	20.8(4)
Cl(1)	3376(2)	3636(2)	2215.5(13)	38.0(15)
Cl(2)	2766(2)	3500(2)	461.8(12)	32.2(14)
C(1)	3048(7)	5938(6)	1276(4)	16(4)
C(2)	4017(7)	6412(6)	1260(4)	17(5)
C(3)	3947(8)	7326(6)	1203(4)	21(5)
C(4)	2990(7)	7776(5)	1180(4)	13(4)
C(5)	2062(7)	7316(6)	1180(4)	20(5)
C(6)	2057(7)	6400(6)	1225(4)	19(5)
C(7)	5148(7)	6009(6)	1291(5)	24(5)
C(8)	5413(8)	6171(7)	659(5)	31(6)
C(9)	6060(8)	6414(8)	1352(5)	38(6)
C(10)	5227(9)	5004(7)	1390(6)	39(6)
C(11)	2994(7)	8815(5)	1107(4)	17(5)
C(12)	1816(9)	9191(7)	989(6)	35(6)
C(13)	3755(10)	9231(8)	1713(6)	46(7)
C(14)	3379(10)	9047(7)	507(6)	40(7)
C(15)	963(8)	5969(7)	1255(4)	27(5)
C(16)	30(9)	6316(8)	637(6)	48(6)
C(17)	658(11)	6270(9)	1835(6)	52(9)
C(18)	889(10)	4986(7)	1175(9)	63(7)
In(2)	6935.8(5)	8249.9(4)	3635.2(3)	19.8(4)
Cl(3)	7249(2)	9191(2)	4535.3(12)	38(2)
Cl(4)	6655(2)	9247(2)	2769.1(13)	37(2)
C(21)	6939(7)	6861(6)	3667(4)	15(5)
C(22)	5970(7)	6395(6)	3662(4)	19(5)
C(23)	6032(7)	5481(6)	3733(4)	20(5)
C(24)	6993(7)	5002(6)	3801(4)	18(5)
C(25)	7921(7)	5481(6)	3755(4)	19(5)
C(26)	7932(7)	6396(6)	3690(4)	17(5)
C(27)	4821(8)	6817(6)	3610(5)	26(5)
C(28)	4592(9)	6696(9)	4273(5)	45(6)
C(29)	3916(8)	6371(7)	3067(5)	27(5)
C(30)	4746(9)	7797(7)	3444(7)	46(6)
C(31)	6997(7)	3989(6)	3827(5)	25(3)
C(32)	8166(8)	3612(7)	4007(6)	38(3)
C(33)	6240(9)	3578(8)	3291(5)	40(4)
C(34)	6626(9)	3792(7)	4485(5)	36(5)
C(35)	9028(7)	6816(6)	3674(4)	19(5)
C(36)	9953(9)	6535(9)	4253(7)	55(6)
C(37)	9310(10)	6503(10)	3064(6)	54(8)
C(38)	9085(9)	7807(8)	3664(7)	51(6)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

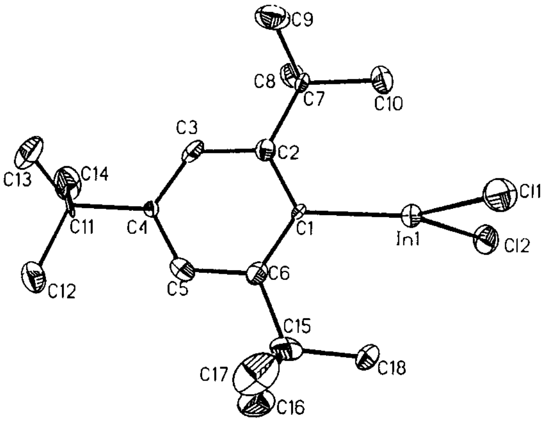

Figure 3. Structure of one molecule of **3** showing 50% displacement ellipsoids. Selected mean bond distances (pm) and angles (deg) are as follows: In–Cl(mean) = 235.1(3), In–C(mean) = 210.4(8); Cl–In–Cl(mean) = 101.9(1), Cl–In–C(mean) = 129.1(3).

obtained (even when the stoichiometry of the reactants was changed), and the crystal of **3** for the X-ray structure determination had to be selected from this mixture. However no difficulties arised in the assignment of the NMR and mass spectra of **3**.

Crystal Structures of 1–4. The crystals of **1**–**4** consist of monomeric molecules of which the structures are shown in Figures 1–4. Atomic parameters are given in Tables II–V. Compounds **1** and **3** as well as **2** and **4**, respectively, are isostructural. In **1** and **3** there are two independent molecules, while in the other structures the molecule lies on a crystallographic 2-fold axis. The geometry around the metal atoms in all structures is trigonally planar. The metal–halide bond lengths agree well with values found in the Cambridge Crystallographic Data File.[18] The Ga–C (193.5 (**1**), 197.5 pm (**2**)) and the In–C (210.4 (**3**), 211.6 pm (**4**))

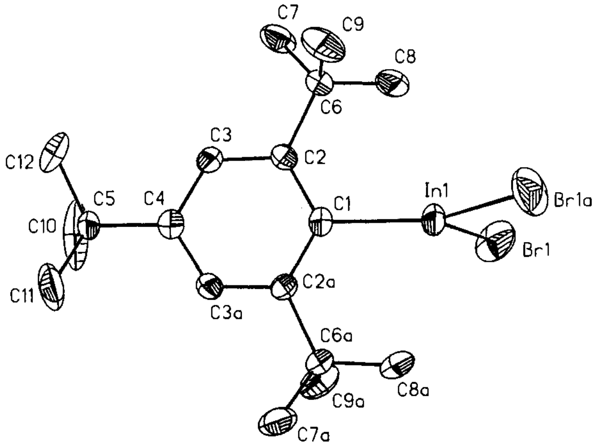

Figure 4. Structure of one molecule of **4** showing 50% displacement ellipsoids. Selected bond distances (pm) and angles (deg) are as follows: In–Br = 247.0(1), In–C = 211.6(5); Br–In–Br = 107.7(1), Br–In–C = 126.2(2).

distances correspond well with values found in $GaCl_2Mes$ (197 and 194 pm)[6] and $[InClMes_2]_2$ (214.6 pm).[19] The C–M–X–X units (M = Ga, In; X = Cl, Br) are nearly perpendicular to the sMes ring plane (84.7 and 85.3° (**1**); 79.1° (**2**); 86.8 and 86.1° (**3**); 77.8° (**4**)). Due to the steric requirement of the *tert*-butyl groups in the ortho positions of the sMes ring, only one of the methyl groups is pointing to the metal, while the two others are above and below the ring plane. *Note made upon revision of the manuscript*: The crystal structures of **1** and **3** have also been recently published by Power et al.[20] In contrast to their results we found these compounds to be isostructural. The resulting structures are essentially the same. However, the structure determinations reported in this paper are of significantly better quality. The configuration of the *tert*-butyl groups mentioned before has been attributed to methyl–hydrogen long-range interaction by the same authors.[20]

Table V. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) of **4**[a]

	x	*y*	*z*	*U*(eq)
In(1)	5000	7109.7(3)	2500	32.6(3)
Br(1)	6181.4(5)	8265.7(5)	1983.0(5)	69.8(5)
C(1)	5000	5431(4)	2500	24(3)
C(2)	4300(3)	4885(3)	1548(3)	24(2)
C(3)	4303(3)	3781(3)	1587(3)	27(2)
C(4)	5000	3211(4)	2500	28(3)
C(5)	5000	1989(4)	2500	32(3)
C(6)	3484(3)	5414(3)	472(3)	28(2)
C(7)	3340(4)	4793(4)	−668(4)	48(3)
C(8)	3733(4)	6531(4)	205(4)	48(3)
C(9)	2504(3)	5438(4)	702(4)	48(2)
C(10)	5773(13)	1629(8)	2017(18)	89(13)
C(11)	5250(14)	1543(8)	3738(9)	69(13)
C(12)	3965(10)	1540(8)	1701(13)	72(8)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Conclusion

The presence of the sMes substituent stabilizes **1**–**4** as monomeric molecules. By contrast $MesGaCl_2$[6] is polymeric and $[Mes_2InCl]_2$[17] is a dimer. The ortho *t*-Bu groups of the sMes ligand protect the metal atom better than the *o*-methyl groups of the Mes ligand.[20]

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Supplementary Material Available: Listings of crystallographic data, and bond distances and angles for $GaCl_2C_{18}H_{29}$, $GaBr_2C_{18}H_{29}$, $InCl_2C_{18}H_{29}$ and $InBr_2C_{18}H_{29}$ (8 pages). Ordering information is given on any current masthead page.

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