BINOL Compounds of Group 13

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The reaction of $GaMe_3$ with 1 equiv of (*S*)-BINOL ((*S*)-(−)-2,2′-dihydroxy-1,1′-binaphthyl) in toluene at reflux conditions gave after recrystallization from THF the chiral organogallium alkoxide $[(THF)MeGa((S)\text{-BINOLate})]_2$ (**1**). In contrast treatment of $PhCH_2InCl_2$ with 1 equiv of $Li_2((S)\text{-BINOLate})$ in THF at reflux and recrystallization from DME led not to the desired organoindium alkoxide but to $[\{(DME)Li\}_3\{In((S)\text{-BINOLate})_3\}]\cdot 2DME$ (**2**·2DME). The similar salt $[\{(DME)Li\}_3\{In((S)\text{-BINOLate})_3\}]\cdot 0.75THF$ (**2**·0.75THF) was obtained by direct synthesis of $InCl_3$ with 3 equiv of $Li_2((S)\text{-BINOLate})$ in THF at 65 °C and recrystallization from DME. The compounds **1** and **2** are readily soluble only in donor solvents, while the potassium derivative $[\{(toluene)_2K\}_3\{In((S)\text{-BINOLate})_3\}]\cdot 2toluene$ (**3**·2toluene), obtained in the reaction of $InCl_3$ with 3 equiv of $K_2((S)\text{-BINOLate})$ in toluene, is very soluble in toluene and *n*-hexane. **1**−**3** have been characterized by their NMR, IR, and MS spectra as well as by X-ray analyses. Compound **1** is dimeric with a Ga_2O_2 four-membered ring. **2** consists of a tetranuclear InO_6Li_3 skeleton in which every Li^+ ion is coordinated by one additional DME ligand. The basic structural motif in **3**, an InO_6K_3 core, is comparable to the skeleton in **2**. However, the coordinated toluene molecules of every K^+ ion in **3** are bound by mainly electrostatic metal−π-electron interactions.

BINOLate complexes of a variety of metals are very valuable and effective catalysts and reagents for enantioselective synthesis.[1−6] Important for the understanding of the respective mechanism is a knowledge of the structure of the BINOLate−metal complexes. Therefore, a number of structural investigations were performed, for example, with Al[1], Ga, In,[7] Ln,[5] Cr, and Fe.[8] For all of these complexes tetrahedral or octahedral coordination of the central metal was found. For some metals both types are known. It is worth mentioning that at least one coordination site at the central metal should be vacant for a successful enantioselective reaction.[1] However, there are examples as in the enantioselective transfer of MeLi to aldehydes in the presence of $[\{(THF)_2Li\}_3\{Ln(BINOLate)_3\}]$[5] where the Ln center possesses coordination number 6. So it is not clear whether the coordination number 4 of the central metal is essential or not.

We report here a new organometallic gallium−BINOLate species and three tetranuclear complexes with M_3O_6In cores (M = Li, K), and we focus on the synthesis and structures of the compounds, not on the application in organic synthesis.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Purification and drying of the solvents were performed using standard methods.[9] $GaMe_3$ was donated by the group of Prof. Dr. J. Lorberth. (*S*)-(−)-BINOL was purchased from Merck-Schuchardt. $PhCH_2InCl_2$ was prepared according to literature procedures.[10] Solvent-free $Li_2((S)\text{-BINOLate})$ was prepared by treatment of BINOL with ^nBuLi in *n*-hexane/THF. The solvent was removed in vacuo (structures, solvated with THF, are given in ref 11).

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer (^1H, 200.135 MHz; ^{13}C, 50.324 MHz). The standard is TMS (external) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}; polyethylene disks for the range 500−100 cm^{-1}). For the EI mass spectra, a Varian CH7a mass spectrometer (70 eV) was used. The melting points were measured with a Dr. Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected).

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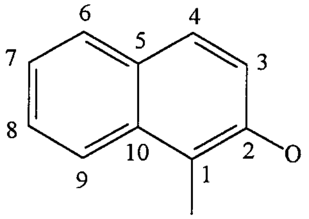

Synthesis of [(THF)MeGa((*S*)-BINOLate)]$_2$, 1. To 0.55 g (4.8 mmol) of $GaMe_3$ in 20 mL of toluene was added 1.37 g (4.8 mmol) of (*S*)-BINOL in 20 mL of toluene. The reaction mixture was heated at reflux with evolution of methane for 3 h. The solution was concentrated under vacuum to 20 mL. THF (10 mL) was added to the resulting suspension. The solution was stored at 5 °C. Colorless crystals of **1** precipitated (1.8 g, 86% yield, mp 330 °C (dec)). ^{1}H NMR (THF-d_8; ppm): −0.19 (s, 6 H, GaC*H*$_3$), 1.63 (m, 8 H, C*H*$_2$, THF), 3.51 (m, 8 H, OC*H*$_2$, THF), 6.91−8.16 (m, 24 H, BINOLate-*H*). ^{13}C NMR (THF-d_8; ppm): −1.3 (*C*H$_3$), 23.9 (*C*H$_2$, THF), 66.0 (O*C*H$_2$, THF), 122.0 (C^1), 123.5 (C^3), 124.2 (C^6), 125.5 (C^8), 127.4 (C^7), 128.2 (C^5), 128.7 (C^{10}), 129.0 (C^4), 134.3 (C^9), 153.4 (C^2). IR (Nujol, cm^{-1}): 3053 (w), 2727 (w), 1944 (vw), 1618 (s), 1590 (s), 1504 (vs), 1423 (m), 1366 (s), 1336 (s), 1272 (s), 1260 (s), 1243 (s), 1210 (vs), 1143 (s), 1126 (m), 1072 (m), 1029 (w), 988 (m), 962 (m), 947 (w), 935 (m), 863 (m), 817 (vs), 748 (vs), 695 (w), 667 (m), 632 (m), 581 (m, νGaC), 561 (m, νGaO_6), 534 (m, νGaO_6), 523 (w), 508 (w), 485 (m, br), 421 (m, br), 334 (m, br), 228 (m, br). EIMS (*m*/*z* (relative intensity), fragment): 630 (1) (M − 2THF − Me − C_7H_7)$^+$; 343 (100) (M/2 − THF − C_2H_2)$^+$; 207 (28) (BINOLate − C_6H_5)$^+$; 72 (10) (THF)$^+$. Anal. Calcd: C, 68.06; H, 5.26; Ga, 15.80. Found: C, 67.94; H, 5.09; Ga, 15.66.

Synthesis of [{(DME)Li}$_3${In((*S*)-BINOLate)$_3$}]·2DME (2·2DME). To 1.09 g (3.7 mmol) of Li$_2$(*S*)-BINOLate in 20 mL of THF was added a solution of 1.02 g (3.7 mmol) of $PhCH_2InCl_2$ in 20 mL of THF at 20 °C. The reaction mixture was heated at reflux for 2 h, the solvent was removed under vacuum almost completely, and the residue was taken up in 25 mL of toluene. After filtration, the solvent was removed under vacuum. To the residue were added 15 mL of THF and 10 mL of DME. During storage at 20 °C for 30 days, a colorless solid, **2**·2DME, crystallized (2.26 g, 43% yield, mp > 300 °C). ^{1}H NMR (THF-d_8; ppm): 3.13 (s, 30 H, OC*H*$_3$, DME), 3.26 (s, 20 H, OC*H*$_2$, DME), 6.68−7.66 (m, 36 H, BINOLate-*H*). ^{13}C NMR (THF-d_8; ppm): 57.5 (O*C*H$_3$, DME), 71.3 (O*C*H$_2$, DME), 119,8 (C^1), 120.1 (C^3), 123.5 (C^6), 125.6 (C^8), 126.1 (C^7), 127.0 (C^5), 127.1 (C^{10}), 127.5 (C^4), 134.5 (C^9), 160.3 (C^2). IR (Nujol, cm^{-1}): 3046 (m), 1614 (m), 1590 (s), 1556 (w), 1501 (s), 1423 (s), 1341 (vs), 1266 (vs), 1248 (vs), 1209 (w), 1194 (w), 1121 (m), 1087 (vs), 1028 (s), 998 (m), 956 (m), 938 (w), 822 (s), 801 (m), 740 (s), 694 (vw), 666 (m), 594 (vw), 576 (m), 554 (vw), 520 (vw), 472 (s, br, νInO_6), 420 (w), 395 (w), 325 (m, br, νLiO), 289 (w), 244 (w), 218 (vw), 153 (w), 112 (w). EI-MS (*m*/*z* (relative intensity), fragment): 343 (1) (InBINOLate − C_4H_8)$^+$; 286 (1) (BINOL)$^+$; 90 (32) (DME)$^+$; 45 (100) (OC_2H_5)$^+$. Anal. Calcd: C, 66.77; H, 6.02; Li, 1.45. Found: C, 66.55; H, 5.76; Li, 1.32.

Synthesis of [{(DME)Li}$_3${In((*S*)-BINOLate)$_3$}]·075THF (2·0.75THF). To a solution of 1.0 g (3.4 mmol) of Li$_2$(*S*)-BINOLate in 20 mL of THF was added a solution of 0.25 g (1.1 mmol) of $InCl_3$ in 10 mL of THF at 20 °C. The solution was heated at reflux for 2 h. The resulting solution was concentrated to 5 mL, and 10 mL of DME was added. During 30 days of storage at 20 °C colorless plates of **2**·0.75THF crystallized (1.2 g, 81% yield, mp > 300 °C). ^{1}H NMR (THF-d_8; 300 K; ppm): 1.68 (m, 6 H, C*H*$_2$, THF), 3.15 (s, 30 H, OC*H*$_3$, DME), 3.28 (s, 20 H, OC*H*$_2$, DME), 3,51 (m, 6 H, OC*H*$_2$, THF), 6.71−7,70 (m, 36 H, BINOLate-*H*). ^{1}H NMR (THF-d_8; 260 K; ppm): 1.77 (m, 6 H, C*H*$_2$, THF), 3.17 (s, 30 H, OC*H*$_3$, DME), 3.27 (m, 20 H, OC*H*$_2$, DME, center of a AA′BB′ spin system), 3.59 (m, 6 H, OC*H*$_2$, THF), 6.63−7.79 (m, 36 H, BINOLate-*H*). ^{13}C NMR (THF-d_8; ppm): 24.5 (*C*H$_2$, THF), 57.3 (O*C*H$_3$, DME), 66.6 (O*C*H$_2$, THF), 71.0 (O*C*H$_2$, DME), 120.0 (C^1), 120.3 (C^3), 123.7 (C^6), 125.7 (C^8), 126.3 (C^7), 127.3 ($C^{5/10}$), 127.7 (C^4), 134.6 (C^9), 160.5 (C^2). IR (Nujol, cm^{-1}): 3043 (m), 1617 (m), 1591 (s), 1553 (w), 1499 (s), 1422 (s), 1346 (vs), 1264 (vs), 1252 (vs), 1210 (w), 1191 (w), 1118 (m), 1080 (vs), 1025 (s), 1000 (m), 951 (m), 936 (w), 824 (s), 799 (m), 745 (s), 662 (m), 578 (m), 555 (vw), 524 (vw), 475 (s, br, νInO_6), 417 (w), 393 (w), 330 (m, br, νLiO), 287 (w), 240 (w), 222 (vw), 157 (w). EI-MS (*m*/*z* (relative intensity), fragment): 343 (1) (InBINOLate − C_4H_8)$^+$; 286 (3) (BINOL)$^+$; 90 (40) (DME)$^+$; 72 (23) (THF)$^+$; 45 (100) (OC_2H_5)$^+$. Anal. Calcd: C, 68.61; H, 5.53; Li, 1.48. Found: C, 68.45; H, 5.63; Li, 1.38.

Synthesis of [{(toluene)$_2$K}$_3${In((*S*)-BINOLate)$_3$}]·2-toluene (3·2toluene). To a suspension of 1.0 g (3.5 mmol) of (*S*)-BINOL in 40 mL of toluene was added 0.28 g (7.0 mmol) of KH at 20 °C. Evolution of hydrogen was observed. The solution was stirred for 3 h at 20 °C, and 0.26 g (1.2 mmol) of $InCl_3$ in 20 mL of THF was added. The mixture was heated at reflux for 3 h. The resulting yellow solution was concentrated in a vacuum to 5 mL. Forty milliliters of toluene was added, and the suspension was filtrated. The filtrate was concentrated to 10 mL and stored at 5 °C. Colorless needles of **3**·2toluene crystallized (1.22 g, 56% yield, mp > 300 °C). ^{1}H NMR (THF-d_8; ppm): 2.19 (s, 18 H, C*H*$_3$, toluene), 6.66−8.10 (m, 66 H, BINOLate-*H*; phenyl-*H*, toluene). ^{13}C NMR (THF-d_8; ppm): 22.0 (*C*H$_3$, toluene), 118.1 (C^1), 122.0 (C^3), 124.2 (C^6), 125.5 (C^8), 125.7 (C^4, toluene), 127.3 (C^7), 128.5 ($C^{3/5}$, toluene), 128.7 ($C^{5/10}$), 129.0 (C^4), 129.5 ($C^{2/6}$, toluene), 133.9 (C^9), 138.0 (C^1, toluene), 153.4 (C^2). IR (Nujol, cm^{-1}): 1609 (m), 1586 (s), 1549 (m), 1497 (s), 1421 (s), 1340 (vs), 1264 (vs), 1281 (s), 1265 (s), 1235 (s), 1175 (m), 1150 (m), 1120 (m), 1097 (m), 1067 (m), 1026 (s), 994 (s), 952 (s), 934 (m), 860 (w), 826 (vs), 696 (m), 663 (m), 632 (w), 596 (w), 569 (m), 553 (vw), 526 (vw), 496 (m), 455 (s, br, νInO_6), 408 (m), 391 (m), 321 (m), 280 (w), 225 (vw), 157 (vw), 135 (w). EI-MS (*m*/*z* (relative intensity), fragment): 578 (1) [KIn(BINOLate)$_2$ − BINOLate/2 − 2H]$^+$; 503 (7) [KIn(BINOLate)$_2$ − 1/2BINOLate − C_6H_5 + 2H]$^+$; 429 (9) [KIn(BINOLate)$_2$ − BINOLate/2 − 2C_6H_5 + 5H]$^+$; 355 (16) [KIn(BINOLate) − OC_5H_7]$^+$; 342 (15) [In(BINOLate) − OC_3H_5]$^+$; 284 (52) (BINOLate)$^+$, 207 (100) (BINOLate − C_6H_5)$^+$. Anal. Calcd: C, 76.46; H, 5.53; K, 6.44. Found: C, 76.51; H, 5.41; K, 6.35.

X-ray Structure Determination of 1, 2·2DME, 2·0.75THF, and 3·2toluene. The crystals were covered with a perfluorinated polyether and mounted at the top of a glass capillary under a flow of cold gaseous nitrogen. The reflections were collected with two IPDS instruments (Stoe; $\lambda = 0.71073$ Å).

The intensities were corrected for Lorentz and polarization effects (for absorption correction, cell parameters, and collecting of the intensities, see Table 1). The structures were solved by direct methods (**1**, **2**·2DME; SHELXS-97[12]) or by the Patterson method (**3**·2toluene; SHELXTL-Plus[13]). For **2**·0.75THF the coordinates of the isotypical Ga compound were used.[7] Refinement was performed against F^2 by full-matrix least squares with the program SHELXL-97.[14] The positions of the H atoms were calculated for an ideal geometry and refined with a common displacement parameter. The calculation of the bond lengths, bond angles, and U_{eq} values was performed with the program PLATON.[15] Strong disorder phenomena were detected in **2**·0.75THF: The site of the free THF molecule is occupied only with 25%. The molecule is

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Table 1. Crystallographic Data for the Compounds 1, 2·2DME, 2·0.75THF, and 3·2toluene

	1	**2**·2DME	**2**·0.75THF	**3**·2toluene
instrument	IPDS I (Stoe)	IPDS I	IPDS II	IPDS I
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
formula	$C_{50}H_{46}Ga_2O_6$	$C_{80}H_{86}InLi_3O_{16}$	$C_{75}H_{72}InLi_3O_{12.75}$	$C_{116}H_{100}InK_3O_6$
fw	882.35	1439.19	1313.02	1822.17
cryst size (mm)	0.19 × 0.19 × 0.18	0.21 × 0.065 × 0.06	0.5 × 0.3 × 0.2	1.0 × 0.15 × 0.1
a (Å)	22.880(2)	11.188(1)	24.487(1)	19.386(1)
b (Å)	11.022(1)	13.335(1)		10.543(1)
c (Å)	8.763(1)	14.971(2)		24.057(1)
α (deg)		63.63(1)		
β (deg)	109.47(1)	68.41(1)		103.54(1)
γ (deg)		75.70(1)		
V ($Å^3$)	2083.5(4)	1851.4(3)	14683(1)	4780.3(6)
cryst syst	monoclinic	triclinic	cubic	monoclinic
space group	$C2$	$P1$	$I432$	$P2_1$
no.[33]	5	1	211	4
Z	2	1	8	2
ρ_{calcd} (g/cm^3)	1.406	1.291	1.188	1.266
temp (K)	193	153	193	193
abs corr	numerical	numerical	numerical	numerical
μ (cm^{-1})	13.4	3.9	3.8	4.3
$2\theta_{max}$ (deg)	51.84	52.62	52.54	51.87
h, k, l values	$-28 \le h \le 28$	$-13 \le h \le 13$	$-23 \le h \le 30$	$-23 \le h \le 23$
	$-13 \le k \le 13$	$-16 \le k \le 16$	$-30 \le k \le 30$	$-12 \le k \le 12$
	$-10 \le l \le 10$	$-18 \le l \le 18$	$-30 \le l \le 30$	$-28 \le l \le 28$
no. of reflns	8195	27 113	41 811	33 313
no. of unique reflns (R_{int})	4041 (0.096)	14 196 (0.0557)	2494 (0.039)	16 577 (0.0748)
no. of reflns with $F_o > 4\sigma(F_o)$ for R_1	2196	11 905	1800	9929
no. of params	263	881	149	933
Flack param	0.00(2)	−0.01(2)	−0.04(6)	−0.03(3)
R_1[a]	0.0465	0.0463	0.0323	0.0651
wR_2 (all data)[b,c]	0.0831	0.0931	0.0767	0.1585
weight factor[a]	0	0.039	0.0452	0.0694
weight factor[b]	0	0	0	0
max/min resid electron density (e/Å^3)	0.4/−0.4	0.59/−0.38	0.34/−0.55	1.82/−0.8

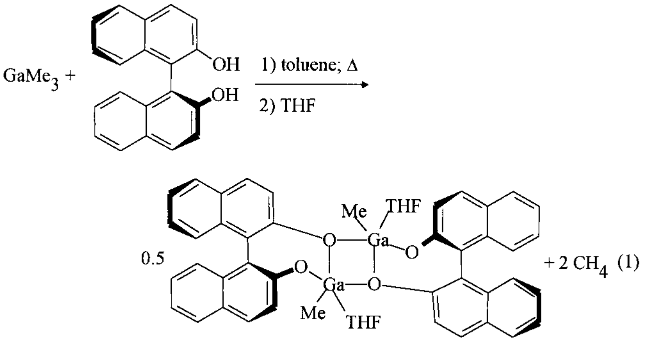
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_c|$. [b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

disordered around a C_2 axis (occupation parameters: O(3) 0.125; C(14), C(15) 0.25).

Selected bond lengths and angles of **1**−**3**·2toluene are listed in Table 2.

Results and Discussion

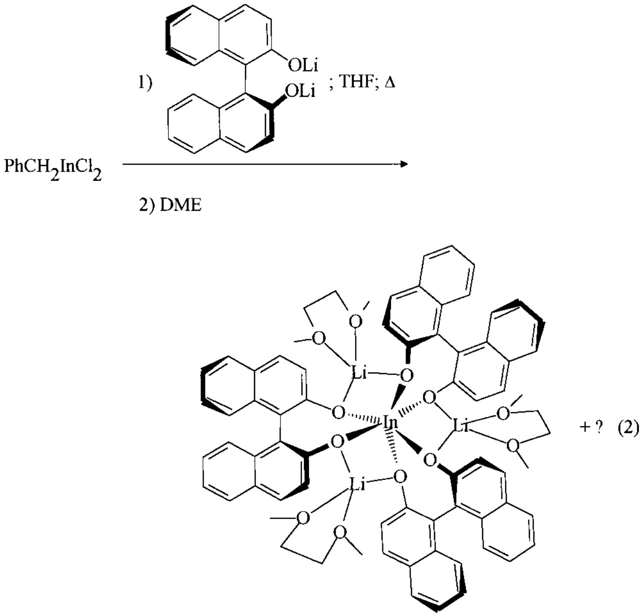
The reaction of $GaMe_3$ and (*S*)-BINOL at 105 °C in toluene led, under evolution of methane, to a poorly soluble white solid, which was recrystallized from THF to give the dimer [(THF)MeGa((*S*)-BINOLate)]$_2$ (**1**) (eq 1).



1

The poor solubility of the initial product in toluene suggests the presence of a coordination polymer of the type [MeGa((*S*)-BINOLate)]$_n$, which was broken up by the donor solvent THF.

In contrast to eq 1 the treatment of $PhCH_2InCl_2$ with the nucleophile Li_2((S)-BINOLate) did not give the desired product $PhCH_2In$((*S*)-BINOLate) but rather the tetranuclear complex [{(DME)Li}$_3${In((*S*)-BINOLate)$_3$}]·2DME (**2**·2DME) (eq 2). The reason for that lies in the instability of the MCH_2Ph unit (M = Ga, In). A typical decomposition product from thermal treatment is $PhCH_2$-CH_2Ph.[16] Ligand redistribution is also one of the important processes. The displacement of the benzyl ligand with formation of a tetranuclear complex had already been observed by us in the case of the corresponding Ga compound [{(DME)Li}$_3${Ga((*S*)-BINOLate)$_3$}].[7]



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Complex **2** can also be prepared by the reaction of $InCl_3$ with 3 equiv of Li_2((*S*)-BINOLate) (eq 3).

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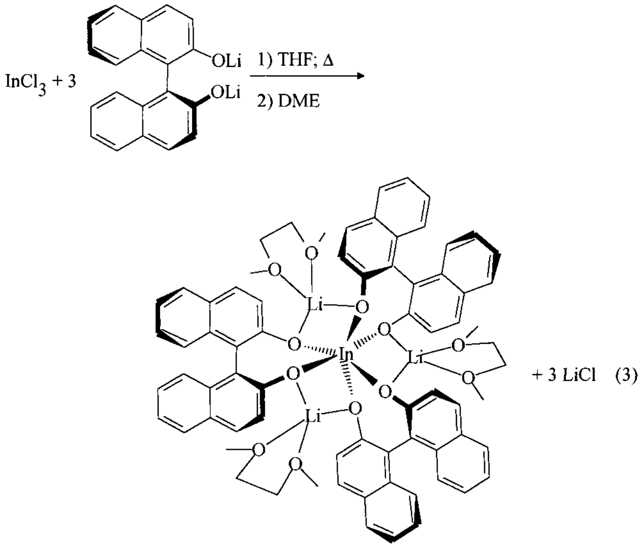
Table 2. Selected Bond Lengths (Å) and Angles (deg) of 1, 2·2DME, 2·0.75THF, and 3·2toluene

Compound **1**					
Ga(1)−O(1)	1.834(6)	O(1)−Ga(1)−O(2)	89.6(2)	Ga(1)−O(1)−C(2)	127.0(4)
Ga(1)−O(2)	2.072(4)	O(1)−Ga(1)−O(3)	89.1(2)	Ga(1)−O(2)−C(12)	116.9(3)
Ga(1)−O(2a)	1.916(4)	O(1)−Ga(1)−C(21)	121.5(3)	Ga(1)−O(2)−Ga(1a)	105.8(2)
Ga(1)−O(3)	2.122(5)	O(1)−Ga(1)−O(2a)	120.7(2)	C(12)−O(2)−Ga(1a)	135.7(3)
Ga(1)−C(21)	1.929(9)	O(2)−Ga(1)−O(3)	157.4(2)		
		O(2)−Ga(1)−C(21)	102.4(3)		
		O(2)−Ga(1)−O(2a)	72.6(2)		
		O(3)−Ga(1)−C(21)	97.5(3)		
		O(3)−Ga(1)−O(2a)	88.7(2)		
		C(21)−Ga(1)−O(2a)	117.5(3)		
Compound **2**·2DME					
In(1)−O(1)	2.154(4)	O(1)−In(1)−O(2)	86.3(2)	O(3)−Li(1)−O(7)	148.4(6)
In(1)−O(2)	2.135(4)	O(1)−In(1)−O(3)	100.6(2)	O(3)−Li(1)−O(8)	103.0(5)
In(1)−O(3)	2.138(4)	O(1)−In(1)−O(4)	170.7(2)	O(7)−Li(1)−O(8)	82.8(4)
In(1)−O(4)	2.142(4)	O(1)−In(1)−O(5)	95.4(2)	O(4)−Li(2)−O(5)	87.7(4)
In(1)−O(5)	2.150(4)	O(1)−In(1)−O(6)	77.3(2)	O(4)−Li(2)−O(9)	102.9(5)
In(1)−O(6)	2.155(4)	O(2)−In(1)−O(3)	77.4(2)	O(4)−Li(2)−O(10)	152.9(6)
Li(1)−O(2)	1.922(9)	O(2)−In(1)−O(4)	101.1(2)	O(5)−Li(2)−O(9)	151.6(6)
Li(1)−O(3)	1.93(1)	O(2)−In(1)−O(5)	171.3(2)	O(5)−Li(2)−O(10)	100.3(5)
Li(1)−O(7)	1.97(1)	O(2)−In(1)−O(6)	100.9(2)	O(9)−Li(2)−O(10)	82.3(4)
Li(1)−O(8)	1.97(1)	O(3)−In(1)−O(4)	86.7(2)	O(1)−Li(3)−O(6)	88.3(5)
Li(2)−O(4)	1.93(1)	O(3)−In(1)−O(5)	93.9(2)	O(1)−Li(3)−O(11)	154.2(6)
Li(2)−O(5)	1.972(9)	O(3)−In(1)−O(6)	177.4(2)	O(1)−Li(3)−O(12)	104.3(5)
Li(2)−O(9)	1.995(9)	O(4)−In(1)−O(5)	78.2(2)	O(6)−Li(3)−O(11)	100.8(5)
Li(2)−O(10)	1.98(1)	O(4)−In(1)−O(6)	95.6(2)	O(6)−Li(3)−O(12)	149.0(6)
Li(3)−O(1)	1.976(9)	O(5)−In(1)−O(6)	87.8(2)	O(11)−Li(3)−O(12)	80.1(5)
Li(3)−O(6)	1.89(1)	O(2)−Li(1)−O(3)	87.7(4)		
Li(3)−O(11)	2.05(1)	O(2)−Li(1)−O(7)	107.4(5)		
Li(3)−O(12)	1.94(1)	O(2)−Li(1)−O(8)	141.3(6)		
Compound **2**·0.75THF					
In(1)−O(1)	2.142(1)	O(1)−In(1)−O(1a)	97.01(6)	O(1)−Li(1)−O(2)	97.6(2)
Li(1)−O(1)	1.948(5)	O(1)−In(1)−O(1c)	175.56(6)	O(1)−Li(1)−O(1d)	89.7(2)
Li(1)−O(2)	1.990(5)	O(1)−In(1)−O(1d)	79.72(6)	O(1)−Li(1)−O(2d)	162.9(1)
		O(1)−In(1)−O(1e)	86.41(6)	O(2)−Li(1)−O(2d)	79.9(2)
Compound **3**·2toluene					
In(1)−O(1)	2.156(5)	K(1)−O(1)	2.604(6)	mean[K(1)···C]	3.42
In(1)−O(2)	2.152(5)	K(1)−O(5)	2.579(6)	mean[K(2)···C]	3.38
In(1)−O(3)	2.161(6)	K(2)−O(2)	2.551(6)	mean[K(3)···C]	3.35
In(1)−O(4)	2.157(6)	K(2)−O(3)	2.706(6)		
In(1)−O(5)	2.143(5)	K(3)−O(4)	2.619(6)		
In(1)−O(6)	2.145(5)	K(3)−O(6)	2.571(6)		
O(1)−In(1)−O(2)	86.1(2)	O(2)−In(1)−O(4)	93.4(2)	O(4)−In(1)−O(5)	92.8(2)
O(1)−In(1)−O(3)	96.4(2)	O(2)−In(1)−O(5)	93.1(2)	O(4)−In(1)−O(6)	86.7(2)
O(1)−In(1)−O(4)	178.9(2)	O(2)−In(1)−O(6)	178.2(2)	O(5)−In(1)−O(6)	85.1(2)
O(1)−In(1)−O(5)	86.3(2)	O(3)−In(1)−O(4)	84.5(2)	O(1)−K(1)−O(5)	69.1(2)
O(1)−In(1)−O(6)	93.7(2)	O(3)−In(1)−O(5)	177.1(2)	O(2)−K(2)−O(3)	69.4(2)
				O(4)−K(3)−O(6)	69.4(2)



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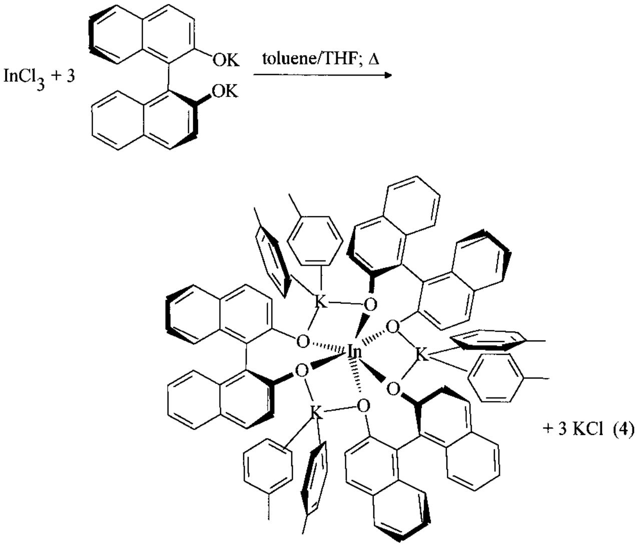

3

2 is poorly soluble in hydrocarbons such as *n*-hexane and toluene, so, it should be useful to have as an alternative, a very soluble complex. We obtained such a compound by reaction of $InCl_3$ with K_2((*S*)-BINOLate) in toluene (eq 3). The observed coordination of toluene molecules to the heavier alkali metal ions is a common phenomenon in group 1.[17,18]

1−**3** are air-sensitive, hygroscopic, colorless solids. The ^{1}H and ^{13}C NMR spectra of **1**−**3** show the typical resonances for the methyl group in **1** (^{1}H, −0.19 ppm; ^{13}C, −1.3 ppm)[19] and the BINOLate ligand. Interestingly, the methylene groups of the DME ligands in **2** do not exhibit a spin system of higher order but a singlet at 300 K. This is different from the corresponding Ga

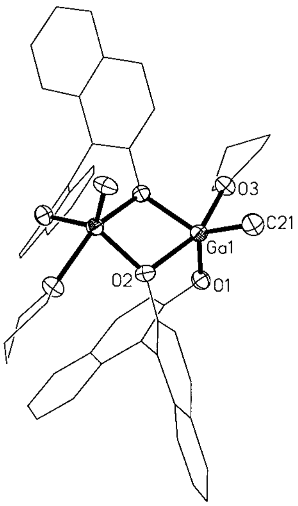

Figure 1. Graphical representation of **1** (the hydrocarbon part of the BINOLate ligand and the THF molecules are represented as thin lines for clarity; ellipsoids at the 40% probability level).

compound,[7] in which an AA′BB′ spin system was found due to the chiral environment of these protons. This means that the DME ligands in **2** are not stable in their configuration relative to the NMR time scale at 300 K. Because of the lengths of the In−O bonds, the steric restrictions in the C_2-chiral cavity formed by the BINOLate ligands are not as great as in the Ga compound $[\{(DME)Li\}_3\{Ga((S)\text{-BINOLate})_3\}]$.[7] VT ^1H NMR spectra of **2**·0.75THF in THF-d_8 showed slowing of the dynamic process at lower temperature and formation of the complete AA′BB′ spin system at 3.27 ppm (260 K).

The IR spectrum of **1** shows two Ga−O ring vibrations at 561 and 534 cm^{-1}.[20] In−O skeletal vibrations were assigned to the bands at 472 (**2**·2DME), 475 (**2**·0.75THF), and 455 cm^{-1} (**3**·2toluene). The Li−O bonds cause broad absorptions at 325 (**2**·2DME) and 330 cm^{-1} (**3**·0.75THF). All three alkali metal complexes **2**·2DME−**3**·2toluene are thermally stable after losing the solvent molecules. Therefore only the EI mass spectrum of **3**·2toluene shows metal-containing fragments of higher intensity.

Figure 1 gives a graphical representation of dimer **1**. The gallium atoms possess a distorted trigonal-bipyramidal environment with O(2) and O(3) in axial positions and O(1), O(2a), and C(21) in equatorial positions. The dominating angle O(2)−Ga(1)−O(3) is 157.4(2)°. The four-membered Ga_2O_2 ring is folded along the axis Ga(1)···Ga(1a); the planes Ga(1), O(2), Ga(1a) and Ga(1), O(2a), Ga(1a) enclose an angle of 23°. The geometrical situation of a chelating and bridging BINOLate ligand leads to a dihedral angle of 62° between the two naphthyl groups. The apical position and the μ_2-bridging function O(2) imply a longer Ga(1)−O(2) bond of 2.072(4) Å in comparison to the short distance of 1.834(6) Å of Ga(1)−O(1). The donor ligand THF in the second apical position has an even longer Ga(1)−O(3) bond of 2.122(5) Å. In $[\{(Me_3Si)_3C\}_4Ga_4(O)_2(OH)_4]\cdot 3THF$ a distance of 1.895(1) Å (μ_2-bridging) was found,[21] and the average Ga−O distance in $[MesGaO]_9\cdot 10THF\cdot MesH$ is 1.93 Å.[22] Derivatives with GaOP or GaOSi frameworks exhibit mean values of 185 ($[{}^tBuGaO_3PMe]_4$), 183 ($[{}^tBuGaO_3POSiMe_3]_4$),[23] and 1.94 Å ($[\{MeGa\}_2\{Me_2Ga\}_2\{O_3SiN(SiMe_3)Dipp\}_2]$; Dipp = 2,6-$^iPr_2C_6H_3$).[24] The bond in the polymeric $[MeGa\{O(O)CMe\}_2]_n$ is 1.98 Å.[25] The classical diorganogallium alkoxides (coordination number (CN) 4 for Ga and CN 3 for O; O is μ_2-bridging) possess an average Ga−O distance of 1.96 Å.[26] The THF adducts $[(PhCH_2)_3Ga(THF)]$[26b] and $[Fl_3Ga(THF)]\cdot$toluene[27] (Fl = fluorenyl) have Ga−O bond lengths of 2.069(7) and 2.057(2) Å, significantly shorter than that observed in **1** because of the lower CN 4 in both triorganogallane compounds.

The In centers in **2**·2DME−**3**·2toluene possess CN 6, leading to In−O distances of 2.15 (average; **2**·2DME, **3**·2toluene) and 2.142(1) Å (**3**·0.75THF). For the corresponding metalate $[\{Li(THF)_2\}_2\{Li(THF)\}\{In((S)\text{-BINOLate})_3\}]\cdot[\{Li(THF)_2\}\{Li(THF)\}_2\{In((S)\text{-BINOLate})_3\}]_2\cdot 8$toluene a mean value of 2.15 Å was found.[7] Quite similar In−O bond lengths of 2.13−2.15 Å were found in the complexes $In(acac)_3$,[28] $In[ON(H)C(O)Ph]_3\cdot EtOH$,[29] and $In(1,2\text{-}O_2C_7H_5)_3$,[30] all containing In centers with CN 6. A drastic elongation of the metal−oxygen distances occurred on changing to CN 8. The distance is 2.31 Å in $[In(O_2CPh)_3(4\text{-}MeC_5H_4N)_2]\cdot 4H_2O$[31] and 2.33 Å in $[In(15\text{-crown-}5)_2][SbCl_6]_3\cdot 3MeCN$.[32]

As a result of the steric demand of the naphthyl ligands in **2**, which enclose an average angle of 62°, the coordinated DME molecules (Figures 2 and 3) are influenced such that the coordination sphere is a strongly distorted tetrahedron (Figure 4). The angle between the planes O_2Li and LiO_2In in **2**·2DME is 47°

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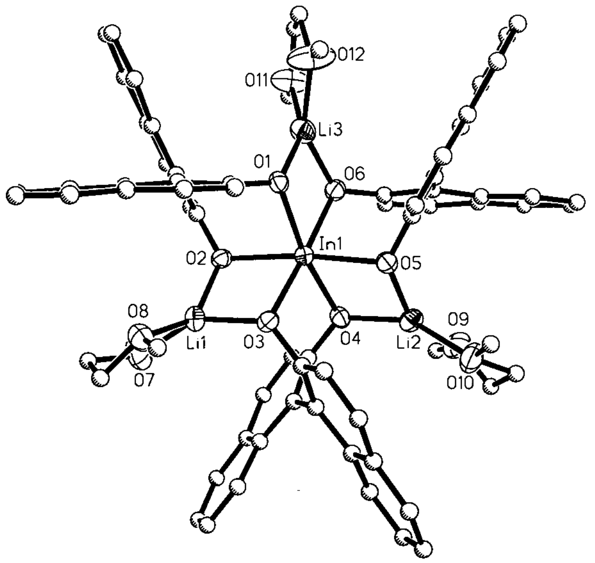

Figure 2. Plot of the complex [{(DME)Li}$_3${In((*S*)-BINOLate)$_3$}] in **2**·2DME (ellipsoids at the 40% probability level).

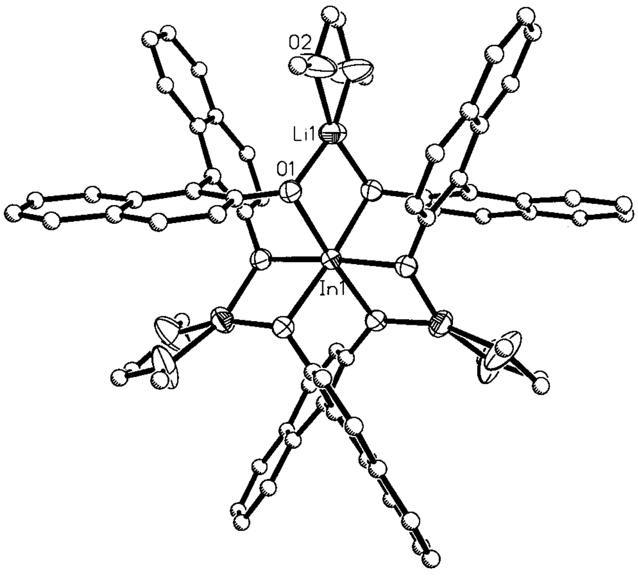

Figure 3. Plot of the complex [{(DME)Li}$_3${In((*S*)-BINOLate)$_3$}] in **2**·0.75THF (ellipsoids at the 40% probability level).

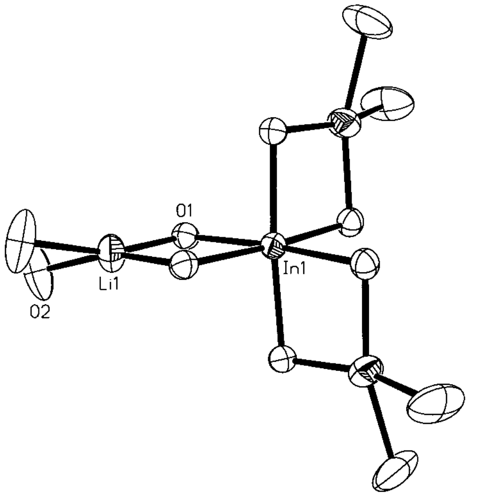

Figure 4. Representation of the $Li_3O_{12}In$ skeleton in **2**·0.75THF (ellipsoids at the 40% probability level).

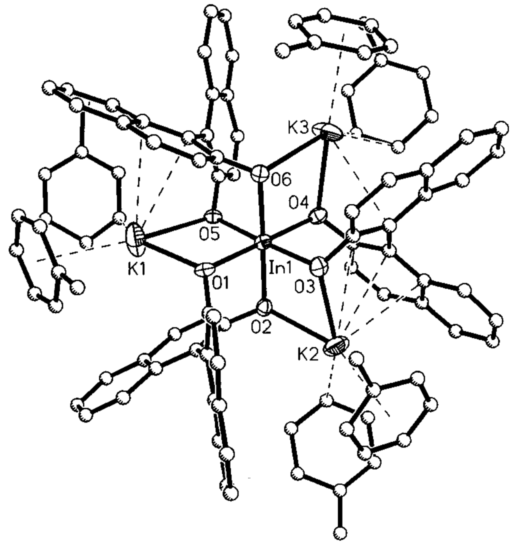

Figure 5. Plot of the complex [{(toluene)$_2$K}$_3${In((*S*)-BINOLate)$_3$}] in **3**·2toluene (ellipsoids at the 40% probability level).

and in **2**·0.75THF, 24°. An even greater effect was observed in [{(DME)Li}$_3${Ga((*S*)-BINOLate)$_3$}]·1.5THF, which is isotypic to **2**·0.75THF, with only 17° caused by the shorter Ga–O bond of 1.969(2) Å.[7] The complex in **2**·0.75THF is highly symmetrical; a 3-fold and a 2-fold axis intersect at the In atom. The Li–O distances can be separated into two types. On one hand, there are the shorter Li–O(BINOLate) bond lengths of 1.94 Å in **2**·2DME and 1.948(5) Å in **2**·0.75THF and, on the other hand, the Li–O(DME) bond lengths of 1.98 and 1.990(5) Å. The difference is caused mainly by electrostatic factors, but steric reasons cannot be excluded.

As in **2**·2DME and **2**·0.75THF, the BINOLate oxygen atoms of every ligand in **3**·2toluene always are coordinated to two different alkali metal ions (Figure 5). The average In–O and K–O distances are 2.15 and 2.61 Å. This gives enough space for the inclusion of two toluene molecules at every K$^+$ ion.[17] One of the toluene molecules is in relatively close contact to the cation (mean value: 3.30 Å), while the other molecule is coordinated only by one or two contacts (mean value: 3.40 Å). The coordination of aryl ligands to alkali metals was observed by us recently.[18] In addition, the BINOLate ligands act with their π-electron systems leading to relevant K–C distances of 3.31–3.68 Å. The average twist-angles between the two naphthyl rings of the BINOLate functions in **3**·2toluene were 63° and 56° at the two toluene molecules at the K$^+$ ions, respectively.

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Supporting Information Available: Tables of crystal data, atomic coordinates, and bond lengths and angles as well as isotropic or anisotropic displacement parameters for all atoms in **1**–**3**·2toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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