Synthesis and Single-Crystal X-ray Diffraction Studies on New Methylindium(III) Alkoxides

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New heteroleptic indium compounds have been synthesized starting from indium(III) halides and hexamethyldisilazyllithium to form $MeXInN(SiMe_3)_2$ [X = Cl (**1**), Br (**2**)], and then subsequent alcoholysis to afford the molecules $[ClMeIn(OtBu)]_2$ (**3**), $[BrMeIn(OtBu)]_2$ (**4**), $\{ClMeIn[O(C_6H_4)OMe]\}_2$ (**5**), $\{[(SiMe_3)_2N]MeIn(OtBu)\}_2$ (**6**) and $[MeIn(OtBu)_2]_2$ (**7**). The molecular structures of molecules **3**–**7** have been obtained by single crystal X-ray diffraction studies. The structures of the compounds **3**–**7** are almost identical: **3**–**5** crystallize in the monoclinic crystal system with two dimeric molecules per unit cell in the space group $P2_1/c$, **6** crystallizes in the monoclinic space group $C2/c$ with four molecules per unit cell, and compound **7** crystallizes in the triclinic crystal system with one dimeric molecule per unit cell in the space group $P\bar{1}$. The central centrosymmetric In_2O_2 ring, common to all the compounds, is achieved by two bridging oxygen atoms. Due to the additional coordination by an oxygen atom of the methoxy group, the coordination number of the metal center rises from 4 to "4+1" if the O*t*Bu ligand (compounds **3**, **4**, **6**, and **7**) is exchanged for a methoxyphenol ligand (compound **5**). In addition to the In_2O_2 ring the compound **5** possesses two annealed five-membered InO_2C_2 rings. The common indium methyl group of all compounds, which is transfered by an original route from the silicon to the indium atom, is used to compare structural and spectroscopic properties of the molecules, as there is a correlation between the In–C bond length and the chemical shift of the methyl group which depends on the ligand system used.

Introduction

The interest in organometallic precursors for use in the area of surface coating has been growing over the last few years. In particular the use of metal alkoxides in metal-organic chemical vapor deposition (MOCVD) or in the sol-gel process has become increasingly popular. In the field of indium alkoxides, however, few studies have been made when contrasted with the lower homologous aluminum and gallium. Indium compounds and ceramics possess a wide variety of interesting properties, which are important in modern technologies. Pure indium oxides, for example, are used as heat insulators,[1] and mixed indium-tin oxides for transparent and conductive ceramics.[2][3] Furthermore, indium compounds find applications in the solar[4–6] and the semiconductor industries.[7] Only a few indium compounds, however, are known to be used in CVD. Indium alkoxides used as an In/O source might be interesting precursors for MOCVD.[8] Apart from some indium compounds of the type $R_2In(OR)$,[9–11] some indium aryloxides,[12–14] some $In(OR)_3$[15] compounds and some heterometallic alkoxides of the type $In[M(OiPr)_4]_3$ with M = Al, Ga,[16] only two dialkylindium alkoxides $[(tBu_2InOEt)_2$[17] and $(tBu_2InOMe)_2$[18]] have been fully characterized by single-crystal X-ray analysis to date.

The authors report here on the synthesis and X-ray crystal-structure analysis (see Table 2) of some new (alkoxo)indium compounds as well as the first monoalkylindium dialkoxide. The principle idea of the reactions described was to introduce selected ligands into indium-centered molecules, and to analyze the structural changes brought about by these ligands. These changes should be monitored in the solid state by X-ray diffraction techniques.

Syntheses of the Indium-Centered Molecules 1–7

Tris(hexamethyldisilazyl)indium, $In[N(SiMe_3)_2]_3$, has been described previously together with $Ga[N(SiMe_3)_2]_3$ and $Al[N(SiMe_3)_2]_3$.[19][20] It is easily obtained by the reaction of $InCl_3$ with three equivalents of $LiN(SiMe_3)_2$.[19] This silylamide was synthesized by Bürger et al. in 1971 and structurally characterized by Power et al. in 1993.[19][20] In the present work the interest is in the reactions of $InCl_3$ with $LiN(SiMe_3)_2$ in molar ratios which differ from 1:3. A molar ratio of 1:2 was first tried. The nonpolar solvent toluene was used to exclude the donation of a basic solvent to the metal center (Equation 1). The reaction solution of $LiN(SiMe_3)_2$ and $InCl_3$ was refluxed for 24 h as the reaction rate was too slow at room temp. The surprising result of this synthesis was a monochloro substitution and migration of a methyl group from an $[N(SiMe_3)_2]$ group to the metal atom to form compound **1**. The first evidence of the methyl group transfer was given by the spectroscopic analysis of the product; the ^{1}H-NMR spectrum of the resulting product $ClMeIn[N(SiMe_3)_2]$ (**1**) shows two signals with an integration ratio of 1:6, in contrast to the singlet expected for the disubstituted product $ClIn[N(SiMe_3)_2]_2$. The ^{13}C-NMR spectrum also shows two NMR signals, indicating the migration of a methyl group. Similar methyl-group transfers are known for gallium compounds.[21][22] The C/H/N, In,

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and Cl analyses performed also give values which correspond exactly with those calculated for **1**. So far, it has not been possible to select a suitable crystal for single-crystal X-ray analysis.

$$2\ LiN(SiMe_3)_2 + InCl_3 \rightarrow \underset{\mathbf{1}}{MeClIn[N(SiMe_3)_2]} + LiCl\ \downarrow\ + \text{side products} \quad (1)$$

If the reaction is carried out in an equimolar ratio the result is similar except that the yield of **1** is less. The change to a polar solvent, such as diethyl ether or THF, also leads to the same results.

In order to insert the first alkoxo ligand into the molecule, **1** was subjected to an alcoholysis reaction (Equation 2). The reaction solution was again refluxed for 24 h to speed up the reaction rate. The alcohol was added in excess to secure a complete reaction.

$$MeClIn[N(SiMe_3)_2] + 2\ HO\mathit{t}Bu \rightarrow \underset{\mathbf{3}}{ClMeIn(O\mathit{t}Bu)} + HN(SiMe_3)_2 + HO\mathit{t}Bu \quad (2)$$

After removing the volatiles under reduced pressure and dissolving the residue in hexane, **3** was crystallized from hexane at low temperatures (−30°C) and purified by sublimation (10^{-2} Torr/120°C; yield: 64%). The ^{1}H-NMR spectrum of **3** shows two signals in an integration ratio of 3:1, corresponding to the ratio of the methyl protons of the *tert*-butyl group and the methyl group. The ^{13}C-NMR spectrum shows three signals as expected, corresponding to the metal-bonded methyl group and two signals for the *tert*-butyl group. In the hope of increasing the yield, the more reactive $InBr_3$ was used as a starting compound instead of $InCl_3$. Compound **2** BrMeIn[N(SiMe$_3$)$_2$] was synthesized according to the same procedure reported for compound **1** (Equation 3).

$$2\ LiN(SiMe_3)_2 + InBr_3 \rightarrow \underset{\mathbf{2}}{MeBrIn[N(SiMe_3)_2]} + LiBr\ \downarrow\ + \text{side products} \quad (3)$$

The ^{1}H- and ^{13}C-NMR spectra of **2** are similar to that of **1**. The following alcoholysis of **2** was carried out under the same conditions as described for **3** (Equation 4). The yield of the reaction (70%) was not much higher than for the reaction with $InCl_3$, for which reason $InCl_3$ was used again in subsequent syntheses. The ^{1}H- and ^{13}C-NMR spectra of **4** are very similar to that of **3**.

$$MeBrIn[N(SiMe_3)_2] + 2\ HO\mathit{t}Bu \rightarrow \underset{\mathbf{4}}{BrMeIn(O\mathit{t}Bu)} + HN(SiMe_3)_2 + HO\mathit{t}Bu \quad (4)$$

With the introduction of the MeO(C$_6$H$_4$)O ligand to the indium atom instead of the O*t*Bu ligand, a further possibility of coordination was offered to the metal center. In this way attempts were made to prevent the molecule from dimerising. The synthesis of **5** is almost analogous to the synthesis of **3** and **4** (Equation 5), with the exception that crystallization of **5** did not occur from hexane at low temperatures, but directly from the mother liquor (yield: 60%). The ^{1}H-NMR spectrum of **5** shows a signal for the metal-bonded methyl group and one signal for the methoxy group. In the ^{13}C-NMR spectrum only two signals are found, corresponding to the metal-bonded methyl group and the OMe group.

$$MeClIn[N(SiMe_3)_2] + 2\ HO(C_6H_4)OMe \rightarrow \underset{\mathbf{5}}{ClMeIn[O(C_6H_4)OMe]} + HN(SiMe_3)_2 + HO(C_6H_4)OMe \quad (5)$$

For the synthesis of MeIn(O*t*Bu)[N(SiMe$_3$)$_2$] (**6**) an analogous procedure to that for **3**, **4**, and **5** was chosen to introduce the [N(SiMe$_3$)$_2$] ligand into the system. The reaction of **3** with Li[N(SiMe$_3$)$_2$] in a molar ratio of 1:1 was performed under refluxing toluene. During this reaction no methyl-group transfer of trimethylsilyl to indium was observed and **6** was formed together with lithium chloride (Equation 6).

$$ClMeIn(O\mathit{t}Bu) + LiN(SiMe_3)_2 \rightarrow \underset{\mathbf{6}}{[(SiMe_3)_2N]MeIn(O\mathit{t}Bu)} + LiCl \quad (6)$$

Compound **6** could be isolated by crystallization from hexane at low temperatures (yield: 60%). The ^{1}H-NMR spectrum of **6** shows three signals in a ratio of 1:3:6 corresponding to the signals of the metal-bonded methyl group, the *tert*-butyl group and the [N(SiMe$_3$)$_2$] group. Within the ^{13}C-NMR spectrum, four signals are visible in accordance with the singlets of the methyl group, the [N(SiMe$_3$)$_2$] group and the two signals of the *tert*-butyl group.

In order to replace the amino function by an alcohol group, **6** was subject of an alcoholysis. The synthesis was carried out in refluxing toluene with a double equivalent of *tert*-butyl alcohol (Equation 7). After removing the volatiles in vacuo and dissolving the residue in hexane, MeIn(O*t*Bu)$_2$ (**7**) was separated from the solvent by crystallization at low temperatures (−30°C).

$$[(SiMe_3)_2N]MeIn(O\mathit{t}Bu) + 2\ HO\mathit{t}Bu \rightarrow \underset{\mathbf{7}}{MeIn(O\mathit{t}Bu)_2} + HN[SiMe_3]_2 + HO\mathit{t}Bu \quad (7)$$

An adequate yield of **7** (60%) was only possible if the reaction took place in a very dilute solution. In a concentrated solution, a mixture of **3**, **6**, and **7** was obtained. After purification of **7** by sublimation (10^{-2} Torr/120°C), the ^{1}H-NMR spectrum shows two signals (ratio 1:6) corresponding to the metal-bonded methyl group and the two *tert*-butyl groups. As expected in the ^{13}C-NMR spectra three signals are visible.

Metal alkoxides are often synthesized by the reaction of alkylmetal compounds with alcohol.[23] Therefore, **7** was treated with *tert*-butyl alcohol in toluene and refluxed for several hours to replace the methyl group by the *tert*-butyl group. Surprisingly, even after refluxing the solvent for

24 h, no reaction took place (Equation 8). In conclusion, the metal−carbon bond in **7** seems to be remarkably stable.

$$MeIn(OtBu)_2 + 2\ HOtBu \not\rightarrow In(OtBu)_3 + CH_4 \uparrow + HOtBu \quad (8)$$

Crystal Structures of Compounds 3, 4, 5, 6, and 7

The molecular structures of the compounds **3**, **4**, **5**, **6**, and **7** have been determined by single-crystal X-ray analysis. The crystal structures of the molecules are shown in Figures 1−5. Selected bond lengths and angles are given in Table 1.

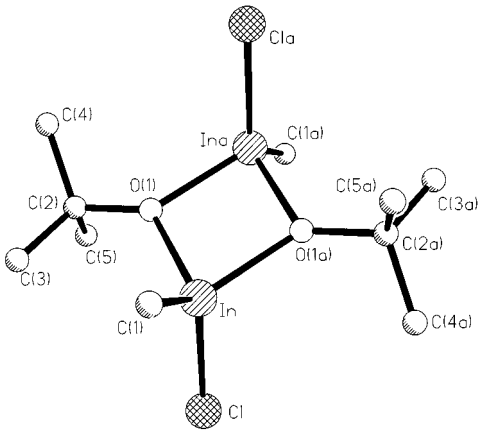

Figure 1. Molecular structure of $[ClMeIn(OtBu)]_2$ (**3**); hydrogen atoms are omitted for clarity

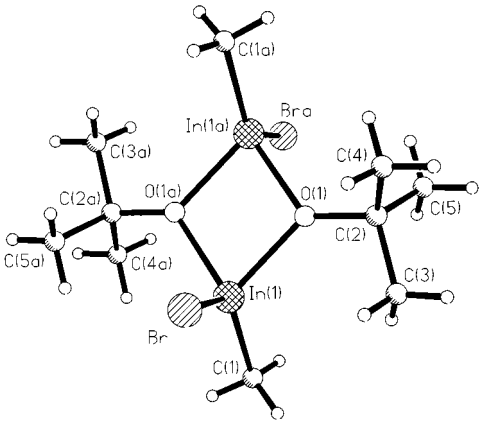

Figure 2. Molecular structure of $[BrMeIn(OtBu)]_2$ (**4**)

Crystal Structures of 3 and 4

The compounds $[ClMeIn(OtBu)]_2$ (**3**) and $[BrMeIn(OtBu)]_2$ (**4**) are similar, except for the different halogen atoms. Both compounds crystallize in a monoclinic crystal system with two molecules per unit cell, in the space group $P2_1/c$, and are isostructural. The compounds form centrosymmetric dimers (crystal symmetry: C_i). The dimerisation is achieved by two bridging oxygen atoms. The In_2O_2 ring is planar by symmetry requirements. The indium atoms in both compounds are present in a strongly distorted tetrahedral environment. The oxygen atoms in both the structures possess an almost trigonal planar coordination sphere (358.3° for **3**; 358.7° for **4**) and thus are sp^2-hybridized. The bond lengths within the In_2O_2 ring of both the molecules are rather similar [211.5(7) pm in **3** and 212.1(7) pm in **4**]. The In−C lengths in both compounds are also within the same range [211.8(6) pm for **3** and 210(1) pm for **4**], but

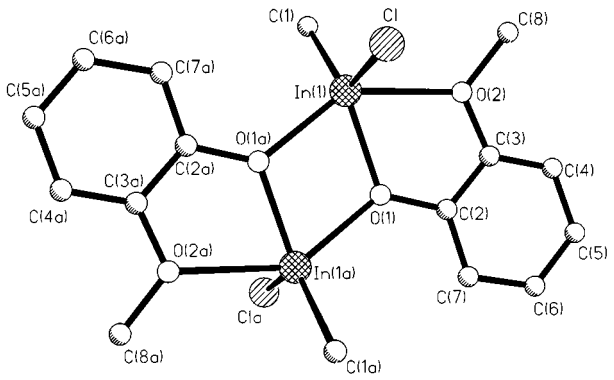

Figure 3. Molecular structure of $[ClMeIn(OC_6H_4OMe)]_2$ (**5**); hydrogen atoms are omitted for clarity

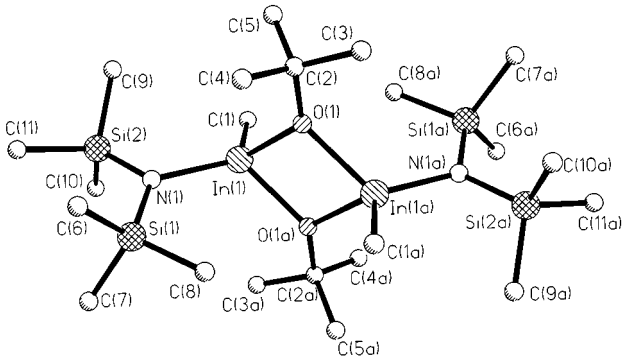

Figure 4. Molecular structure of $\{[N(SiMe_3)_2]MeInOtBu\}_2$ (**6**); hydrogen atoms are omitted for clarity

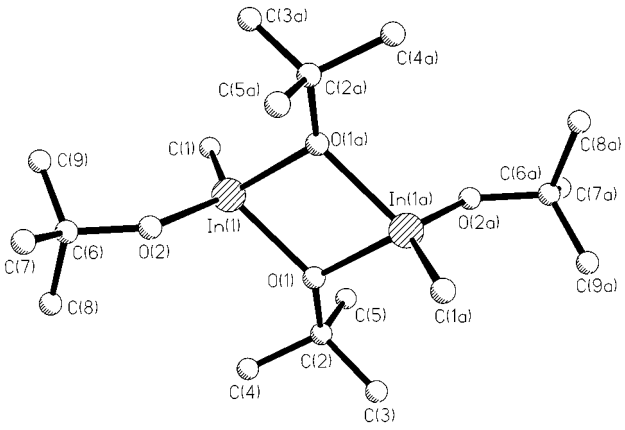

Figure 5. Molecular structure of $[MeIn(OtBu)_2]_2$ (**7**)

Table 1. Selected bond lengths [pm] and angles [°] of **3**–**7**

$C_{10}H_{24}Cl_2In_2O_2$ (**3**)							
In–O(1a)	210.9(3)	In–Cl	237.2(2)	O(1)–In(a)	210.9(3)	C(2)–C(5)	152.6(8)
In–C(1)	211.8(6)	In–In(a)	331.2(9)	C(2)–C(3)	151.7(7)		
In–O(1)	212.2(4)	O(1)–C(2)	144.0(6)	C(2)–C(4)	152.1(8)		
O(1a)–In–C(1)	122.9(2)	O(1a)–In–Cl	103.8(1)	O(1a)–In–In(a)	38.6(9)	Cl–In–In(a)	107.6(5)
O(1a)–In–O(1)	77.0(2)	C(1)–In–Cl	122.4(2)	C(1)–In–In(a)	129.8(2)	In(a)–O(1)–In	103.0(1)
C(1)–In–O(1)	117.3(2)	O(1)–In–Cl	103.6(1)	O(1)–In–In(a)	38.3(8)		
$C_{10}H_{24}Br_2In_2O_2$ (**4**)							
In(1)–C(1)	210(1)	In(1)–Br	251.0(2)	O(1)–In(1a)	211.3(7)	C(2)–C(5)	154(2)
In(1)–O(1a)	211.4(7)	In(1)–In(1a)	332.0(2)	C(2)–C(4)	148(2)		
In(1)–O(1)	212.9(8)	O(1)–C(2)	145.6(1)	C(2)–C(3)	153(2)		
C(1)–In(1)–O(1a)	121.8(5)	C(1)–In(1)–Br	124.5(4)	C(1)–In(1)–In(1a)	127.6(4)	Br–In(1)–In(1a)	107.6(5)
C(1)–In(1)–O(1)	115.4(4)	O(1A)–In(1)–Br	103.8(2)	O(1A)–I-n(1)–In(1a)	38.7(2)	In(1a)–O(1)–In(1)	103.0(3)
O(1A)–In(1)–O(1)	77.0(3)	O(1)–In(1)–Br	103.6(2)	O(1)–In(1)–In(1a)	38.3(2)		
$C_{16}H_{20}Cl_2In_2O_4$ (**5**)							
In(1)–C(1)	212.9(7)	In(1)–O(2)	240.6(5)	O(2)–C(3)	139.3(8)	C(3)–C(4)	135(1)
In(1)–O(1)	213.6(4)	In(1)–In(1a)	350.1(1)	O(2)–C(8)	143.7(9)	C(7)–C(6)	138(1)
In(1)–O(1a)	220.4(4)	O(1)–C(2)	136.4(8)	C(2)–C(7)	138(1)	C(4)–C(5)	137(1)
In(1)–Cl	236.7(2)	O(1)–In(1a)	220.4(4)	C(2)–C(3)	139(1)	C(5)–C(6)	138(1)
C(1)–In(1)–O(1)	129.2(3)	C(1)–In(1)–Cl	121.7(2)	C(1)–In(1)–O(2)	95.7(3)	Cl–In(1)–O(2)	91.3(1)
C(1)–In(1)–O(1a)	110.2(3)	O(1)–In(1)–Cl	107.6(2)	O(1)–In(1)–O(2)	70.3(2)	C(1)–In(1)–In(1a)	127.1(2)
O(1)–In(1)–O(1a)	72.4(2)	O(1a)–In(1)–Cl	97.1(2)	O(1a)–In(1)–O(2)	142.6(2)	Cl–In(1)–In(1a)	105.2(7)
O(2)–In(1)–In(1a)	107.1(1)	C(2)–O(1)–In(1)	122.5(4)	C(2)–O(1)–In(1a)	129.3(4)	In(1)–O(1)–In(1a)	107.5(2)
$C_{22}H_{60}In_2N_2O_2Si_4$ (**6**)							
In(1)–N(1)	209.3(4)	In(1)–In(1a)	340.5(9)	Si(1)–C(7)	186.8(6)	Si(2)–C(10)	187.6(7)
In(1)–O(1)	213.8(3)	Si(1)–N(1)	172.3(4)	Si(2)–N(1)	173.8(4)	O(1)–C(2)	145.9(5)
In(1)–O(1a)	215.3(3)	Si(1)–C(8)	184.9(6)	Si(2)–C(9)	185.8(6)	O(1)–In(1a)	215.3(3)
In(1)–C(1)	216.0(5)	Si(1)–C(6)	186.3(6)	Si(2)–C(11)	187.5(6)		
N(1)–In(1)–O(1)	113.2(1)	O(1A)–In(1)–C(1)	109.3(2)	C(8)–Si(1)–C(6)	105.0(3)	Si(1)–N(1)–Si(2)	120.5(2)
N(1)–In(1)–O(1a)	117.7(1)	N(1)–In(1)–In(1a)	122.8(1)	N(1)–Si(1)–C(7)	111.3(3)	Si(1)–N(1)–In(1)	125.1(2)
O(1)–In(1)–O(1a)	75.0(1)	C(1)–In(1)–In(1a)	117(1)	C(8)–Si(1)–C(7)	107.8(3)	Si(2)–N(1)–In(1)	113.0(2)
N(1)–In(1)–C(1)	119.5(2)	N(1)–Si(1)–C(8)	111.5(2)	C(6)–Si(1)–C(7)	107.9(3)		
O(1)–In(1)–C(1)	114.1(2)	N(1)–Si(1)–C(6)	113.0(3)	In(1)–O(1)–In(1a)	105.0(1)		
$C_{18}H_{42}In_2O_4$ (**7**)							
In(1)–O(2)	200.6(4)	In(1)–In(1a)	334.6(1)	C(2)–C(3)	151.7(9)	C(6)–C(7)	152(1)
In(1)–O(1)	212.6(4)	O(1)–C(2)	145.1(6)	C(2)–C(4)	151.8(9)	C(6)–C(8)	153(1)
In(1)–O(1a)	213.1(4)	O(1)–In(1a)	213.1(4)	C(2)–C(5)	152.6(9)		
In(1)–C(1)	213.6(7)	O(2)–C(6)	143.1(7)	C(6)–C(9)	150(1)		
O(2)–In(1)–O(1)	104(2)	O(2)–In(1)–C(1)	129.0(3)	O(2)–In(1)–In(1a)	105.6(1)	C(2)–O(1)–In(1a)	126.2(3)
O(2)–In(1)–O(1a)	99(2)	O(1)–In(1)–C(1)	116.8(3)	C(1)–In(1)–In(1a)	125.3(2)	In(1)–O(1)–In(1a)	103.6(2)
O(1)–In(1)–O(1a)	76.4(2)	O(1a)–In(1)–C(1)	117.3(3)	C(2)–O(1)–In(1)	126.8(3)	C(6)–O(2)–In(1)	127.6(4)

about 10 pm shorter than in other comparable compounds.[17] The In–X bond lengths (X = halogen atom) are normal by comparison with standard compounds.[24] As a consequence of the short In–C length, compared to the In–X length, the carbon atoms experience a stronger repulsion to the bridging oxygen atoms. This leads to different C–In–In and X–In–In angles. The C–In–In angle in compound **3**, for example, is found to be 129.8(2)°; 22.2° larger than the X–In–In angle [107.6(5)°]. In compound **4** the effect is similar: The C–In–In angle [127.6(4)°] is 20.4° larger than the X–In–In angle [107.2(5)°]. The difference in the C–In–In angles of compounds **3** and **4** can be explained by the different halogen atoms; thus, the X–In–C angle in **4** [124.5(4)°] is larger than the corresponding angle in **3** [122.4(2)°] because of the larger bromine atom. The bonding angles within the In_2O_2 rings of the two compounds are almost identical (see Table 1). The larger In–O–In angles are due to the hard-shell oxygen atoms, whereas the soft-shell indium atoms allow more acute angles.

Table 2. Crystal data and data-collection parameters of the compounds **3**−**7**

	3	**4**	**5**	**6**	**7**
Empirical formula	$C_{10}H_{24}Cl_2In_2O_2$	$C_{10}H_{24}Br_2In_2O_2$	$C_{16}H_{20}Cl_2In_2O_4$	$C_{22}H_{60}In_2N_2O_2Si_4$	$C_{18}H_{42}In_2O_4$
Formula weight	476.83	565.75	576.86	726.72	552.16
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$C2/c$	$P-1$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
a [pm]	796.6(2)	809.2(2)	1043.9(2)	1022.9(2)	876.1(2)
b [pm]	1307.3(3)	1342.0(3)	875.6(2)	1532.0(4)	929.2(2)
c [pm]	892.1(2)	909.0(2)	1125.7(2)	2338.0(5)	967.4(2)
α [°]	90	90	90	90	117.07(3)
β [°]	103.7(3)	104.01(3)	97.75(3)	97.53(3)	95.99(3)
γ [°]	90	90	90	90	109.95(3)
V [Å^3]	905.0(4)	944.9(4)	1019.5(4)	3632.2(13)	626.7(2)
Z	2	2	2	4	1
$d_{calcd.}$ [g/cm^3]	1.750	1.988	1.879	1.329	1.463
Absorpt. coeff.[mm^{-1}]	2.83	6.66	2.54	1.42	1.86
F(000)	464	536	560	1504	280
Crystal size [mm]	0.5 × 0.5 × 0.7	0.8 × 0.6 × 0.5	0.5 × 0.5 × 0.6	0.7 × 0.2 × 0.5	0.7 × 0.5 × 0.3
Crystal color	colorless	colorless	colorless	colorless	colorless
Data collection					
Diffractometer used	Siemens/Stoe AED 2	Siemens/Stoe AED 2	Siemens/Stoe AED 2	Siemens/Stoe AED 2	Siemens/Stoe AED 2
Monochromator	graphite	graphite	graphite	graphite	graphite
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Wavelength (Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)
2θ range [°]	2.62−22.48	2.59−22.50	2.50−22.51	1.76−22.50	2.49−24.99
Scan type	ϖ-θ	ϖ-θ	ϖ-θ	ϖ-θ	ϖ-θ
Observed reflections [$I > 2F(I)$]	1110	1113	1261	2079	2115
Independent reflections	1174	1230	1331	2368	2205
Refinement					
No. of refined parameters	73	73	109	145	109
Goodness-of-fit on F^2	1.277	1.563	1.013	1.153	1.112
Final R indices	$R_1 = 0.0290$	$R_1 = 0.0618$	$R_1 = 0.0443$	$R_1 = 0.0338$	$R_1 = 0.0244$
[$I > 2\sigma(I)$]	$wR_{1=0}$.0778	$wR_1 = 0.1685$	$wR_1 = 0.1393$	$wR_1 = 0.1026$	$wR_1 = 0.0673$
Final R indices (all data)	$R_2 = 0.0306$,	$R_2 = 0.0691$	$R_2 = 0.0460$	$R_2 = 0.0398$	$R_2 = 0.0256$
	$wR_2 = 0.0793$	$wR_2 = 0.1847$	$wR_2 = 0.1426$	$wR_2 = 0.1095$	$wR_2 = 0.0702$
Min./max. residual density [eÅ^{-3}]	0.357/−0.933	0.950/−1.799	0.765/−1.139	0.343/−0.960	0.749/−0.64

Crystal Structure of 5

The compound $\{ClMeIn[O(C_6H_4)OMe]\}_2$ (**5**) crystallizes in the monoclinic crystal system with two molecules per unit cell in the space group $P2_1/c$. The dimerisation of "monomers" to form the centrosymmetric dimer **5** can be understood in terms of the tendency of indium(III) to achieve higher coordination numbers, while a polycycle is formed due to the presence of further basic ligands (methoxy group) (see Figure 3). Besides an In_2O_2 ring, the dimeric molecule contains two five-membered InO_2C_2 rings and two six-membered phenyl rings, all fused together. The central In_2O_2 ring with respect to the bridging oxygen atoms is the same as that described for **3** and **4**. The In_2O_2 ring is planar because of centrosymmetry, whereas the phenyl ring is planar due to electronic considerations. On the other hand the atoms within the InO_2C_2 ring are not equiplanar and have a dihedral angle which differs by about 5° from planarity. In contrast to the compounds described above, the indium atoms in **5** possess a "4+1" coordination sphere with a strongly distorted tetrahedral environment: $In(ClCO_2)$ plus additional coordination by an oxygen atom of the $O(C_6H_4)OMe$ group. The O−In−O angles within the In_2O_2 ring are more acute, and the In−O−In angles even larger, when compared to **3** and **4**. The In−O bond lengths are also longer compared to **3** and **4**; the mean value of the bonds [220.4(4) pm] being 9 pm longer when compared to those of **3** and **4**. The bond between In(1) and O(2) within the InO_2C_2 ring [240.6(5) pm] may be classified as coordinative due to its length. From a general point of view, the In−O lengths are comparable to values of the oxopentaindium alkoxide cluster reported by Bradley et al.[25] Alcock et al. described an indium compound, $[Me_2In(OC_6H_4CHO)]_2$, which is similar to **5**.[14] The dimeric molecule consists of a central In_2O_2 ring, two six-membered InO_2C_3 rings, and two phenyl rings all fused together. The O−In−O angles inside the In_2O_2 ring are larger [74.8(1)°] and the In−O−In angles more acute [105.2(1)°] compared to those of **5**. The mean value of the In−O bond lengths in $[Me_2In(OC_6H_4CHO)]_2$ [228.6(3) pm] is about 8 pm longer compared to

that of **5**. The In−C bond lengths hardly differ between $[Me_2In(OC_6H_4CHO)]_2$ [212.1(2) pm] and **5**. The bond lengths between In−C and In−Cl hardly differ between compounds **5** and **3**. This is very surprising, because the coordination numbers of the indium atoms are not equal in the two compounds. All oxygen atoms in **5** possess a more or less distorted trigonal environment and are sp^2-hybridized. The distortion of O(2) (356.4°) is higher as compared to that of O(1) (359.35°).

Crystal Structure of 6

As with **3**, **4**, and **5** compound $\{MeIn(OtBu)[N(SiMe_3)_2]\}_2$ (**6**) crystallizes in the monoclinic crystal system with four molecules per unit cell in the space group *C*2/*c*. The crystal-structure analysis shows again a centrosymmetric dimer (crystal symmetry: C_i) with a planar In_2O_2 ring, which originates by a base attack of the more electronegative oxygen atoms (as compared to the nitrogen atoms) on the indium atom. In contrast to **3**, **4**, and **5**, no halogen atom is bonded to the metal atom but a nitrogen atom, belonging to a $[N(SiMe_3)_2]$ ligand, is present. The In−O−In angle [105.40(1)°] within the In_2O_2 ring is slightly smaller than in **5**, but larger than in **3** or **4**. The In−O lengths within the In_2O_2 ring [214.50 (7) pm] are longer than for **3** and **4**, which could be explained by the less electronegative $N(SiMe_3)_2$ ligand when compared to the halogen atom. The indium atoms possess a highly distorted tetrahedral coordination sphere. The oxygen atoms are almost trigonal planar coordinated (359.04°) and thus are sp^2-hybridized. The In−C and In−N bond lengths are within the range of values described in the literature.[26] The C−In−In and N−In−In angle in compound **6** are almost the same as the corresponding angles in **3** and **4**, due to the almost equal bond lengths between In−C and In−N.

Crystal Structure of 7

Compound $[MeIn(OtBu)_2]_2$ (**7**) crystallizes in a triclinic crystal system with one dimeric molecule per unit cell in the space group *P*−1. As for the compounds **3**−**6**, **7** also exists as a centrosymmetric dimer (crystal symmetry: C_i). At the metal atom, three alkoxo ligands are present besides the methyl group (Figure 5). The bond angles within the In_2O_2 ring [In−O−In 103.6(2)°, O−In−O 76.4(2)°] are comparable with both the corresponding angles in **3** and **4** and those of the ethoxy compound, $[tBu_2In(OEt)]_2$, described by Hursthouse et al.[17] The indium atoms have a distorted tetrahedral coordination sphere. The oxygen atoms O(1) and O(1a) possess a slightly distorted trigonal-planar environment, whereas O(2) and O(2a) are in the apices of an angle. The In−O bond lengths within the In_2O_2 ring [212.8(8) pm] are comparable to the bond lengths in compounds **3**−**6** and $[tBu_2In(OEt)]_2$. The In−O bond lengths to the terminal oxygen atoms are 12 pm shorter than the bond lengths within the In_2O_2 ring, due to the different coordination numbers of the oxygen atoms.

Conclusion

All compounds reported here have a metal-bound methyl group in common. This group can be used as a sensor to compare the different compounds with different ligand spheres. One way to use this sensor is to compare the dependence on the ligands of the In−C bond length in the molecules. It was expected that there would be a correlation between the electronegativity of the ligands and the In−C bond length. Generally speaking, the more electronegative chlorine atom in compound **3** should cause an electron withdrawal from the indium atom and therefore lead to a smaller In−C bond length than in the case of compound **4** where there is a less electronegative bromine atom. Inspection of the In−C bond lengths confirms this assumption, except for compounds **3** and **4** (Table 1). The In−C bond in **3** [211.8(6) pm] is surprisingly slightly longer than in **4** [210(12) pm], but if the halogen atom is substituted by a nitrogen atom, as in **6**, which is less electronegative, the In−C bond [216(5) pm] is elongated. In compound **7**, where the halogen atom is substituted by a more electronegative oxygen atom, the bond length [213.6 (7) pm] is reduced compared to **6** and is in the region of that found for **3** and **4**. In compound **5**, the situation is more complicated; because of the change of the coordination number from 4 to "4+1", the In−C bond should be quite long but with 212.9(7) pm the bond length has a mean value which seems to be the result of the three electronegative oxygen ligands. In any case the electronegativity is not the only parameter which has to be considered in the change of the In−C bond length; the size and the steric requirement of the ligand must also be taken into account. On this theme, the most sterically demanding ligand, the $[N(SiMe_3)_2]$ group in **6**, gives the longest In−C bond length. The O*t*Bu group in **7**, which is sterically less demanding than the $[N(SiMe_3)_2]$ group, leads to a slightly shorter In−C bond length. The $MeO(C_6H_4)O$ group in **5** is sterically not as demanding as the $[N(SiMe_3)_2]$ and the O*t*Bu group, but the ligand does offer an additional intramolecular coordination site such that the coordination number of the metal atom and the

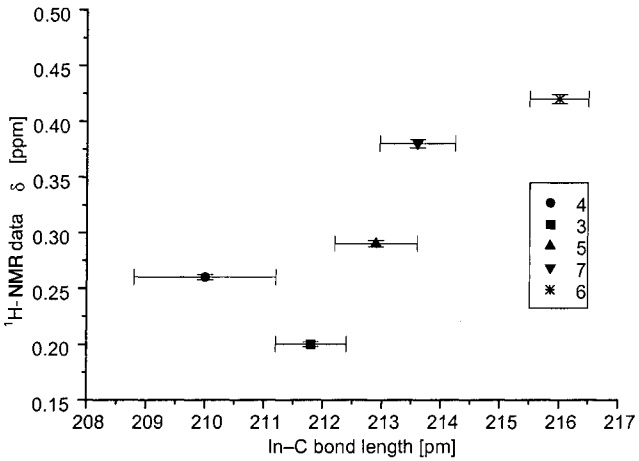

Figure 6. Chemical shift of the molecules **3**−**7** vs. In−C bond lengths

In−C bond lengths are increased, however not as much as expected because of the electronegativity of the ligands. In our experiment, we find a correlation between the ^{1}H-NMR data and the In−C bond lengths. The compound with the longest In−C bond, compound **6**, has the highest chemical shift (δ = 0.42) followed by compound **7** and compound **5**. The ^{1}H-NMR shifts for **3** and **4**, however, are reversed (Figure 6).

Experimental Section

General: All manipulations were performed under purified and dried nitrogen using a modified Stock apparatus. Solvents were distilled from Na/K alloy prior to use. $InCl_3$ and $InBr_3$ were prepared according to known procedures.[27] *tert*-Butyl alcohol was dried by distillation from sodium. − ^{1}H and ^{13}C NMR: Bruker AC 200 spectrometer, quoted to [D$_6$]benzene by using the solvent signal as internal reference. − Elemental analyses: LECO CHN 900 analyser. − Metal and halogen analyses: Standard methods. − The crystal structures of compounds **3**−**7** were obtained from X-ray diffraction of single crystals. The most important parameters for the crystals and the structure determination have been summarized in Table 2. Diffraction data were collected with a Stoe AED 2 diffractometer. The structures were solved by direct methods (SHELXS-86)[28] and refined by full-matrix least-squares procedures on all F^2 values (SHELXS-97).[29] All nonhydrogen atoms were refined anisotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-121777−121781 (**3**−**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of {ClMeIn[N(SiMe$_3$)$_2$]}$_2$ (1): A solution of $LiN(SiMe_3)_2$ (3.0 g,17.92 mmol) in toluene (40 mL) was added dropwise to a stirred suspension of $InCl_3$ (1.98 g, 8.96 mmol) in toluene (30 mL). A weak exothermic reaction took place. The reaction solution was refluxed for 24 h, and after removing the volatiles under reduced pressure, the product purified by sublimation (10^{-2} Torr/100°C). Yield: 1.89 g, 65.0% (based on $InCl_3$). − ^{1}H NMR: δ = 0.30 (s, 3 H, $InCH_3$), 0.28 {s, 18 H, N[Si(CH_3)$_3$]}. − ^{13}C NMR: δ = 5.03 {s, 6 C, N[Si(CH_3)$_3$]$_2$}, 6.60 (s, 1 C, In*C*H$_3$). − $C_7H_{21}ClInNSi$ (325.67): calcd. C 30.57, H 7.64, Cl 7.52, In 24.37, N 5.94; found C 30.28, H 7.47, Cl 7.26, In 23.96, N 5.65.

Synthesis of {BrMeIn[N(SiMe$_3$)$_2$]}$_2$ (2): Compound **2** was synthesized in an analogous manner to **1**. Yield: 1.47 g, 70.0% (based on $InBr_3$). − ^{1}H NMR: δ = 0.30 (s, 3 H, $InCH_3$), 0.28 {s, 18 H, N[Si(CH_3)$_3$]}. − ^{13}C NMR: δ = 5.03 {s, 6 C, N[Si(CH_3)$_3$]$_2$}, 6.60 (s, 1 C, $InCH_3$).

Synthesis of [ClMeIn(O*t*Bu)]$_2$ (3): An excess of *tert*-butyl alcohol (0.88 mL, 9.2 mmol) was added to a stirred solution of ClMeIn[N(SiMe$_3$)]$_2$ (**1**) (1.50 g, 4.6 mmol) in toluene (25 mL). The reaction solution was refluxed for 24 h, and, after removing the volatiles under reduced pressure, the residue dissolved in a small amount of hexane. The product crystallized at low temperatures (−30°C) within 12 h and was further purified by sublimation (10^{-2} Torr/120°C). Yield 0.7 g, 64% (based on $InCl_3$). − ^{1}H NMR: δ = 0.20 (s, 3 H, $InCH_3$), 1.13 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR: δ = 6.8 (s, $InCH_3$), 33.45 [s, C(*C*H$_3$)$_3$], 75.00 [s, *C*(CH$_3$)$_3$]. − $C_5H_{12}ClInO$ (238.41): calcd. C 25.16, H 5.03, Cl 14.87, In 48.16; found C 24.39, H 5.02, Cl 14.75, In 48.96.

Synthesis of [BrMeIn(O*t*Bu)]$_2$ (4): Compound **4** was synthesized in an analogous manner to **3**. Yield: 1.02 g, 70% (based on $InBr_3$). − ^{1}H NMR: δ = 0.26 (s, 3 H, $InCH_3$), 1.13 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR: δ = 6.93 (s, $InCH_3$), 33.55 [s, C(*C*H$_3$)$_3$], 75.42 [s, *C*(CH$_3$)$_3$]. − $C_5H_{12}BrInO$ (282.87): calcd. C 21.22, H 4.24, Br 28.26, In 40.60; found C 20.88, H 4.23, Br 29.87, In 41.50.

Synthesis of {ClMeIn[O(C$_6$H$_4$)OMe]}$_2$ (5): An excess of 2-methoxyphenol (3.0 mL, 27.0 mmol) was added to a stirred solution of ClMeIn[N(SiMe$_3$)$_2$] (**1**) (4.40 g, 13.5 mmol) in toluene (80 mL). The reaction solution was refluxed for 24 h and the product crystallized from the mother liquor while cooling. Yield 2.30 g, 60% (based on $InCl_3$). − ^{1}H NMR: δ = 0.29 (s, 3 H, $InCH_3$), 3.13 (s,3 H, OCH_3). − ^{13}C NMR: δ = 6.8 (s, $InCH_3$), 55.88 (s, OCH_3). − $C_8H_{10}ClInO_2$ (288.43): calcd. C 33.30, H 3.46, Cl 12.30, In 39.80; found C 33.20, H 3.87, Cl 12.40, In 39.70.

Synthesis of {Me[N(SiMe$_3$)$_2$]In(O*t*Bu)}$_2$ (6): A solution of LiN(SiMe$_3$)$_2$ (2.53 g, 15.2 mmol) in toluene (50 mL)was added dropwise to a stirred solution of ClMeIn(O*t*Bu) (**3**) (3.3 g, 15.2 mmol) in toluene (150 mL). The reaction solution was refluxed for 24 h and, after removing the volatiles under reduced pressure, the residue dissolved in a small amount of hexane. The product crystallized at low temperatures (−30°C) within 12 h and was further purified by sublimation (10^{-2} Torr/115°C). Yield 3.30 g, 60% (based on $InCl_3$). − ^{1}H NMR: δ = 0.34 [s, 18 H, Si(CH_3)$_3$], 0.42 (s, 3 H, $InCH_3$), 1.27 [s, 9 H, C(CH_3)$_3$]. − ^{13}C NMR: δ = 5.78 (s, $SiMe_3$), 6.8 (s, $InCH_3$), 33.95 [s, C(*C*H$_3$)$_3$], 73.93 [s, *C*(CH$_3$)$_3$]. − $C_{11}H_{60}InNOSi_2$ (363.36): calcd. C 36.34, H 8.25, In 31.61, N 3.85; found C 36.29, H 8.66, In 32.00, N 3.67.

Synthesis of [MeIn(O*t*Bu)$_2$]$_2$ (7): An excess of *tert*-butyl alcohol (1.74 mL, 18.2 mmol) was added to a stirred solution of Me[N(SiMe$_3$)$_2$]In(O*t*Bu) (**6**) (3.3 g, 9.10 mmol) in toluene (150 mL). The reaction solution was refluxed for 24 h, and, after removing the volatiles under reduced pressure, the residue dissolved in a small amount of hexane. The product crystallized at low temperatures (−30°C) within 2 d and was purified by sublimation (10^{-2} Torr/120°C). Yield 1.50 g, 60% (based on $InCl_3$). − ^{1}H NMR: δ = 0.38 (s, 3 H, $InCH_3$), 1.39 [s, 18 H, C(CH_3)$_3$]. − ^{13}C NMR: δ = 6.92 (s, $InCH_3$), 34.71 [s, C(*C*H$_3$)$_3$], 69.91 [s, *C*(CH$_3$)$_3$]. − $C_9H_{21}InO_2$ (276.08): calcd. C 39.15, H 7.6, In 41.61; found C 39.30, H 7.82, In 41.3.

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