The Reaction of a Triorganochloroindate with Dioxygen

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Abstract: The reaction of CsCl with $In(CH_2Ph)_3$ yields the triorganochloroindate $Cs[(PhCH_2)_3InCl]$ (**1**). Treatment of $In(CH_2Ph)_3$ with dry O_2 gives the alkoxide $[(PhCH_2)_2InOCH_2Ph]_2$ (**2**), whereas the reaction of **1** with O_2 leads to $Cs_2[O\{PhCH_2In(OCH_2Ph)_2\}_4]$ (**3**). According to X-ray structural investigations, **1** contains Cs_2Cl_2 four-membered rings as basic structural motif. The dimers are connected by Cs–π-electron interactions to form a layer structure. Compound **3** can be described as a metalla(crown ether) fragment coordinating two Cs^+ ions. Additional shielding of the Cs centers by weak Cs–π-electron contacts was observed.

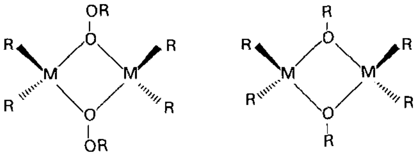
Keywords
cesium · indium · layered compounds · metalla(crown ethers) · pi interactions

Introduction

The reactions of the metallanes of Group 13 with molecular oxygen have been studied intensively.[1] From these studies it is known that the controlled introduction of dioxygen leads in a first step to unstable organoperoxide intermediates. Recently, several examples of such peroxides have been structurally characterized.[2–4] Further reaction of the peroxide R_2MOOR with metallane gives the alkoxide R_2MOR.[5] Depending on the reaction conditions, higher oxidized products such as $RM(OR)OOR$ and $RM(OR)_2$ are possible.

Peroxides $[R_2MOOR]_2$ and alkoxides $[R_2MOR]_2$ are usually dimers in solution and the solid state (Scheme 1).[2–4] Only in cases in which compounds contain bulky organic substituents have monomeric alkoxides, such as $[tBu_2GaO(2,6\text{-}tBu_2\text{-}4\text{-}MeC_6H_2)]$[6] or $[tBu_2GaOCPh_3]$,[7] been isolated.

The subject of this study is the effect on the outcome of the reaction of O_2 with a cesium triorganochloroindate of the Cs^+ ions. Recently, the influence of Cs^+ ions on the structure of cesium triorganofluoroindates has been investigated.[8] π-electron–Cs interactions are the most obvious structural features found.[9] Another important structural motif in cesium triorganofluorometalates $Cs[R_3MF]$ (M = Al, Ga, In) is the formation of Cs_2F_2 four-membered rings.[8,10,11] Thus, not only the solid-state structure of $Cs[(PhCH_2)_3InCl]$ (**1**) but also the above-mentioned comparison of the behavior of **1** and $In(CH_2Ph)_3$ towards treatment with O_2 is of interest.



Scheme 1. Assumed structures for diorganoperoxo metallanes and diorganoalkoxy metallanes (M = Al–Tl; R = alkyl, aryl).

Results and Discussion

The reaction of $In(CH_2Ph)_3$ with CsCl in acetonitrile at room temperature gives the indate $Cs[(PhCH_2)_3InCl]$ (**1**) [Eq. (1)].

$$In(CH_2Ph)_3 + CsCl \xrightarrow{MeCN;\ 20\,^{\circ}C} \underset{\mathbf{1}}{Cs[(PhCH_2)_3InCl]} \qquad (1)$$

Compound **1** has been recrystallized from Et_2O/toluene in the form of colorless crystals of $[Cs\{(PhCH_2)_3InCl\}]_2\cdot 0.5\,toluene$ ($\{\mathbf{1}\}_2\cdot 0.5\,toluene$). Treatment of $In(CH_2Ph)_3$ and **1** with dry O_2 at −70 °C in toluene and Et_2O, respectively, results in the products shown in Equations (2) and (3). The reaction of the indane

$$In(CH_2Ph)_3 \xrightarrow{O_2;\ toluene;\ -70\,^{\circ}C} \underset{\mathbf{2}}{[(PhCH_2)_2InOCH_2Ph]_2} \qquad (2)$$

$$\mathbf{1} \xrightarrow{O_2;\ Et_2O;\ -70\,^{\circ}C} \underset{\mathbf{3}}{Cs_2[O\{PhCH_2In(OCH_2Ph)_2\}_4]} \qquad (3)$$

leads to **2** even at this temperature. No intermediate such as $[(PhCH_2)_2InOOCH_2Ph]_2$ could be obtained. This finding is in agreement with the results of the investigation of the corresponding gallium compound $[Ga(CH_2Ph)_3]$,[5] in which the formation of $[(PhCH_2)_2GaOCH_2Ph]_2$ was observed. In contrast to this, the reaction of the indate **1** with O_2 gives the salt **3**, in which an organodialkoxyindane, $[PhCH_2In(OCH_2Ph)_2]$, is the basic unit. The formation of different products is a result of the presence of Cs^+ ions in **1**, as well as the different reactivity of an

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indane versus an indate, for which weaker M–C and M–Cl bonds can be expected, caused by the higher coordination number (CN) of the metal and the negative charge in **1**.

The species **1**–**3** are colorless, very hygroscopic compounds. Compounds **1** and **3** are only sparingly soluble in benzene, precluding cryoscopic determination of molecular weight. Dissolution of **1** in CD_3CN results in a solvated ion pair $[Cs(CD_3CN)_n]^+[(PhCH_2)_3InCl]^-$ as was observed for the fluoroindates $Cs[R_3MF]$ (M = Al, Ga, In; R = Me, Et, *i*Pr, CH_2Ph, Mes).[8, 10, 11] For a solution of **3** in CD_3CN we assume the displacement of phenyl ligands with weak Cs^+–π-electron interactions by CD_3CN molecules. A complete dissociation into the ions $[Cs(CD_3CN)_n]^+$ and $[O\{PhCH_2In(OCH_2Ph)_2\}_4]^{2-}$ is unlikely owing to the Cs–O interactions.

^1H NMR spectra show one resonance for the methylene protons of **1** at $\delta = 1.73$, while **2** and **3** exhibit two signals [**2**: $\delta = 2.10$ ($InCH_2Ph$), 5.25 (OCH_2Ph); **3**: $\delta = 1.77$ ($InCH_2Ph$), 4.55 (OCH_2Ph)]. The values for the metal-bound methylene group are in good agreement with the one for $In(CH_2Ph)_3$ ($\delta = 1.81$).[12, 13] Similar observations were made in the ^{13}C NMR spectra [**1**: $\delta = 24.2$ ($InCH_2Ph$); **2**: $\delta = 26.9$ ($InCH_2Ph$), 69.6 (OCH_2Ph); **3**: $\delta = 27.2$ ($InCH_2Ph$), 69.4 (OCH_2Ph); $In(CH_2Ph)_3$: 28.3 (CH_2Ph)].

IR investigations of **1** should confirm the existence of the Cs_2Cl_2 four-membered ring found by X-ray analysis. For the matrix-isolated dimer Cs_2Cl_2, three bands have been found at 161, 144, and 74 cm^{-1}.[14] In **1**, two vibrations at 160 and 119 cm^{-1} can be assigned to the asymmetric and the symmetric ring vibrations, respectively. The In–Cl stretching vibrations at 272 and 240 cm^{-1} are characteristic for terminal In–Cl bonds.[15] The degree of aggregation for **2** in benzene was determined to be 2.2. Considering the dimeric character of $[(PhCH_2)_2GaOCH_2Ph]_2$ in solution and the solid state, a dimer of crystalline **2** is likely. Therefore, the two bands at 490 and 475 cm^{-1} can be attributed to In–O ring vibrations. Owing to a coordination number of six for the In atoms in **3**, the strong band at 410 cm^{-1} is in a range expected for the In_4O_9 cage. For the M–C stretching vibrations, a value of 450 cm^{-1} can be expected.[13, 16, 17] The absorptions found for **1**, **2**, and **3** are 436, 453, and 457 cm^{-1}.

In the EI mass spectra for **1**–**3** only RIn-containing fragments of the compounds could be detected (**1**: *m*/*z* = 388, $[In(CH_2Ph)_3]^+$; **2**: *m*/*z* = 717, $[In_2O_2(CH_2Ph)_5]^+$; **3**: *m*/*z* = 420, $[InO_2(CH_2Ph)_3]^+$). The stronger M–F and Cs–F interactions in the cesium salts $Cs[R_3MF]$ (M = Ga, R = Me, Et, *i*Pr, Mes, CH_2Ph; M = In, R = Me, Et, *i*Pr, Mes) are responsible for the observation of Cs/F/M-containing fragments in those cases.[8, 10, 11]

The structure of $[\mathbf{1}]_2\cdot0.5$toluene consists of dimers $[Cs\{(PhCH_2)_3InCl\}]_2$ (Figure 1) connected in an unusual way to form a layer structure. However, the Cs_2Cl_2 four-membered ring is slightly folded in a butterfly fashion (angle 163°, folding axis Cl1···Cl2). The Cs–Cl distances, which have an average value of 341 pm, cannot be compared to the 356 pm of crystalline CsCl because of the different CN of Cs and Cl centers in CsCl.[18] The In–Cl bond lengths of 249.0(2) (In1–Cl1) and 251.5(2) pm (In2–Cl2) are slightly shorter than terminal In–Cl bonds in triorganochloroindates such as $[Me_4As][Me_3InCl]$[13] (255.1(7) pm), $[Me_4N][Mes_3InCl]\cdot MeCN$[20] (254.0(3) pm).

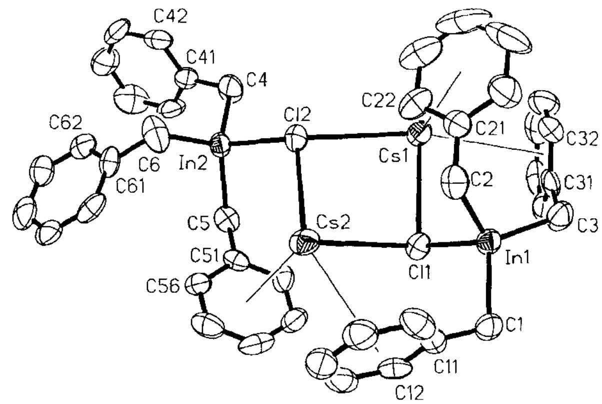

Figure 1. Computer-generated plot of the dimeric unit $[Cs\{(PhCH_2)_3InCl]_2$ in $[\mathbf{1}]_2\cdot0.5$toluene (SHELXTL Plus, ref. [36], ellipsoids at the 50% probability level, H atoms omitted for clarity). Selected interatomic distances [pm] and angles [°]: Cs1–Cl1 337.6(2), Cs1–Cl2 342.9(2), Cs2–Cl1 334.7(2), Cs2–Cl2 347.5(2), In1–Cl1 249.0(2), In2–Cl2 251.5(2), In–C 220 (av.); Cl1-Cs1-Cl2 76.71(6), Cl1-Cs2-Cl2 76.47(6), Cs1-Cl1-Cs2 103.68(6), Cs1-Cl1-In1 106.04(7), Cs2-Cl1-In1 100.00(7), Cs1-Cl2-Cs2 99.96(6), Cs1-Cl2-In2 128.72(9), Cs2-Cl2-In2 111.92(8), Cl-In-C 104 (av.).

The In–Cl bond lengths in $[Li(THF)_4][Fl_3InCl]$ (Fl = fluorenyl) are significantly shorter than the value in **1** at 241.2(1) pm.[21] The Cs_2Cl_2 ring is distorted to a rhombus with angles of about 77° at the Cs centers and a mean value of 102° at the Cl centers.

Four phenyl rings are directly coordinated to the Cs^+ ions (Table 1) of the Cs_2Cl_2 ring of their asymmetric unit [(C21–C26), (C31–C36), (C11–C16), (C51–C56)] with a mean Cs–C distance of 392 pm. One phenyl ring is bound to the neighbouring Cs–Cl ring system [Cs2–(C61a–C66a): 356 pm average], whereas the π-electron systems of (C11–C16) [Cs1–(C11a–C16a): 388 pm av.] and (C51–C56) [Cs1–(C51a–C56a): 424 pm av.] also donate to Cs^+ ions of other dimers (Figure 2, Figure 3). As a result double layers are formed by this "inverse sandwich" type of coordination (two metal centers coordinating one phenyl ring). Nevertheless, the bonding described between Cs centers, Cl^- ions, and π-electron systems is obviously mainly an electrostatic one. The Cs^+–ring distances in $[Cs\{(PhCH_2)_3GaF\}]_2\cdot2MeCN$ (358 pm av.),[18] $[\{Cs(diglyme)_2\}_2\{Ph_2CCPh_2\}]_n$ (358 pm av.), and $[\{Cs_4(diglyme)_2(OCH_2CH_2OCH_3)_2\}\{Ph_2CCHCHCPh_2\}]_n$ (354 pm av.)[9c] are of the same order and significantly shorter

Table 1. Cs···C contacts in $[\mathbf{1}]_2\cdot0.5$toluene and **3** [pm]. Shortest value = sv., average value = av.

$[\mathbf{1}]_2\cdot0.5$toluene			Compound **3**		
	sv.	av.		sv.	av.
Cs1···(C21–C26)	361	436	Cs1···(C111–C161)	379	446
Cs1···(C31–C36)	341	362	Cs1···(C112–C162)	358	413
Cs1···(C11a–C16a)	347	388	Cs1···(C211–C261)	362	433
Cs1···(C51a–C56a)	353	424	Cs1···(C212–C262)	364	403
			Cs1···(C311a–C361a)	347	385
			Cs1···(C312a–C362a)	333	403
			Cs1···(C41–C46)	353	441
Cs2···(C11–C16)	360	388			
Cs2···(C51–C56)	339	381			
Cs2···(C61a–C66a)	338	356			

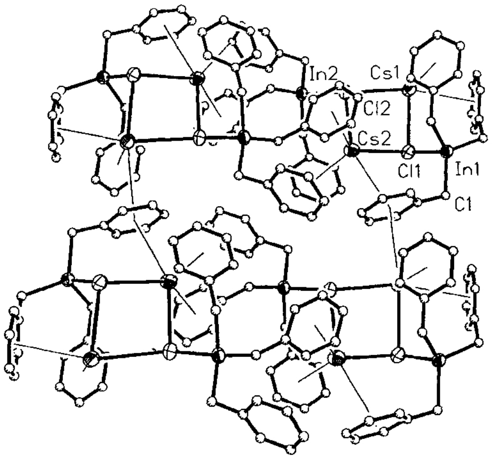

Figure 2. Assembly of four dimeric units $[\mathbf{1}]_2$ with Cs–π-electron contacts (C atoms represented as spheres for clarity).

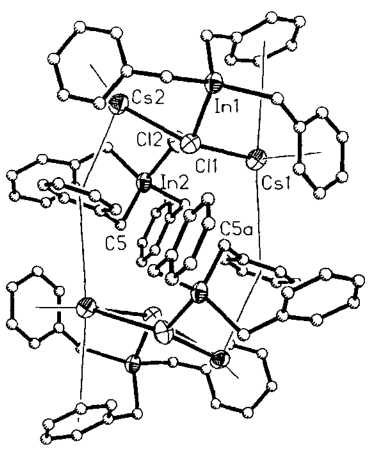

Figure 3. Assembly of two dimeric units $[\mathbf{1}]_2$ with Cs–π-electron contacts (perpendicular to the view in Figure 2).

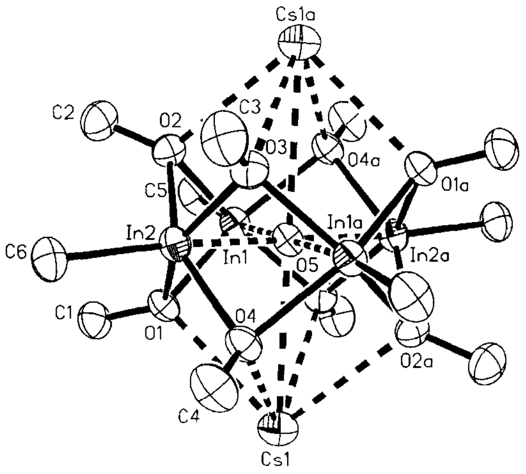

Figure 5. Computer-generated plot of the skeleton of **3** (phenyl rings are omitted for clarity; the full and dashed lines are not a distance criterion but a representation of the $[PhCH_2In(OCH_2Ph)_2]_4$ and the Cs_2O unit). Selected interatomic distances [pm] and angles [°]: Cs1–O1 303.6(3), Cs1–O4 303.9(4), Cs1–O5 341.91(6), Cs1–O2a 310.2(3), Cs1–O3a 306.4(4), In1···In2a 310.88(7), In1···In2 311.48(7), In1–O1 221.5(3), In1–O2 225.5(3), In1–O5 220.75(5), In2–O5 219.32(5), In1–O3a 223.7(4), In1–O4a 226.9(3), In2–O1 226.4(3), In2–O2 224.6(3), In2–O3 223.1(3), In2–O4 225.1(3); O1-In1-O2 78.9(1), O1-In1-O5 76.25(9), O1-In1-O3a 94.3(1), O1-In1-O4a 151.7(1), O2-In1-O5 75.22(9), O2-In1-O3a 150.4(1), O5-In1-O3a 75.13(9), O2-In1-O4a 93.3(1), O5-In1-O4a 75.46(9), O3a-In1-O4a 79.0(1), O1-In2-O2 78.1(1), O1-In2-O3 151.1(1), O1-In2-O4 94.6(1), O1-In2-O5 75.54(9), O2-In2-O3 93.7(1), O2-In2-O4 151.8(1), O2-In2-O5 75.69(9), O3-In2-O4 79.6(1), O4-In2-O5 76.11(9), O3-In2-O5 75.54(9), Cs1-O1-In1 99.6(1), Cs1-O1-In2 98.0(1), In1-O1-In2 88.1(1), In1-O2-In2 87.6(1), In1-O2-Cs1a 98.4(1), In2-O2-Cs1a 98.6(1), In2-O3-Cs1a 100.1(1), In2-O3-In1a 88.2(1), Cs1a-O3-In1a 98.3(1), Cs1-O4-In2 98.2(1), Cs1-O4-In1a 99.9(1), In2-O4-In1a 86.9(1), Cs1-O5-In1 89.27(1), Cs1-O5-In2 89.04(2), Cs1-O5-In1a 90.73(1), In1-O5-In2 90.11(2), In1-O5-In2a 89.89(2), In2-O5-Cs1a 90.96(2).

than the sum of the van der Waals radii, 417 pm.[22] If one counts the phenyl substituent as one ligand, the coordination sphere of the Cs center Cs1 is a distorted octahedron, while Cs2 is surrounded by five ligands in a strong distorted trigonal bipyramidal fashion. The Cs centers in **1** and **3** are not exactly located over the centroids of the phenyl rings. Usually one part of the aromatic system is somewhat closer to the Cs^+ ion, causing the variation in the Cs–C distances. Both the shortest and the average values are shown in Table 1. The double layers are separated by the organic groups and by toluene molecules, which are disordered around centers of symmetry; stacking occurs along the crystallographic *c* axis (Figure 4).

According to the X-ray analysis the $Cs_2In_4O_9$ skeleton of **3** (Figure 5) can be subdivided formally into a ring-shaped metalla(crown ether) In_4O_8 unit and a linear unit of Cs_2O centered in the metalla(crown ether) and pointing along the crystallographic *a* axis. The central oxygen atom O5 occupies a center of symmetry. Four highly folded In_2O_2 four-membered rings forming the $[PhCH_2In(OCH_2Ph)_2]_4$ wrap around the Cs_2O unit; they have folding angles of 124° (In1/O1/In2/O2) and 123° (In2/O3/In1a/O4); in both cases the folding axis is In···In. Quite similar $K_4M_2O_8$ cages have been found for the oxo alkoxides $[\{K(THF)\}_4Sb_2O(OtBu)_8]$ and $[K_4Zr_2O(OiPr)_{10}]$.[23]

Although a variety of diorganoindium alkoxides, R_2InOR, are described in the literature,[24] only a few examples have been structurally characterized.[25–27] The data for isolated organoindium dialkoxides $RIn(OR)_2$ are sparse[24] and to our knowledge there is no structural information available to date. Therefore the $[PhCH_2In(OCH_2Ph)_2]_4$ unit may be a model for such compounds. However, the In–O distances in **3** (In: CN 6; 224 pm av.) are between the In–O bond lengths in $[R_2InOR]_2$[25–27] [In: CN 4; typical value: 216 pm) and in donor–acceptor complexes such as $[In(CCCF_3)_3(THF)_2]$ [In: CN 5; 230.0(8) pm],[28] $[iPr_2In(THF)_2][BF_4]$ (In: CN 4+2; 236 pm av.)[16] and $[PhCH_2InBr_2(THF)_2]$ (In: CN 5; 237 pm av.).[17] In–O cages in compounds such as $[O\{(Me_3Si)_3CIn\}_4(OH)_6]$[29] (In: CN 5) or $[MeIn(OH)(O_2PPh_2)]_4 \cdot 4py$ (In: CN 6)[30] should be acceptable reference compounds for the In–O bond length because of the high coordination numbers of the metal centers. The first-mentioned complex possesses a central O atom with CN 4 and average In–O distances of 216 pm. The latter compound consists of an

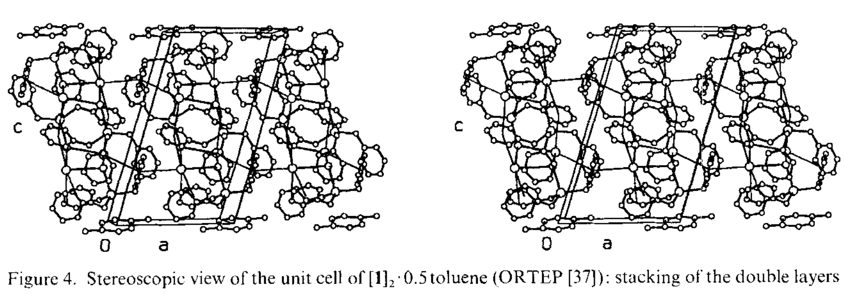

Figure 4. Stereoscopic view of the unit cell of $[\mathbf{1}]_2 \cdot 0.5$toluene (ORTEP [37]): stacking of the double layers along [001].

In–O heterocubane with a mean In–O value of 225 pm and an average exoskeleton bond length of 223 pm.

The cyclic $[O\{PhCH_2In(OCH_2Ph)_2\}_4]$ framework of **3** complexes two Cs^+ ions in a crown ether fashion (similar to 12-crown-4). An average Cs–O contact of 306 pm does not correspond to the Cs–O distances in Cs–crown ether complexes because of the lower CN (4 + 5) of the Cs^+ ions in **3**. Short mean distances of 315 pm have been observed in [Cs(18-crown-6)(NCS)][31] and $[Cs(18\text{-crown-}6)]_2[Hg_2Se_{12}]$,[32] whereas for the $[Cs(18\text{-crown-}6)_2]^+$ ion (Cs: CN 12) a Cs–O contact of 334 pm was found.[33] For crystalline Cs_2O, a distance of 286 pm (Cs: CN 2) was determined, quite similar to the 289 pm in Cs_3O (Cs: CN 2).[18] In contrast, the Cs–O contacts in $Cs_{11}O_3$ (Cs: CN 1, 2, 3) vary between 270 and 300 pm.[34] In this context the Cs–O bond lengths in **3** are understandable because of the CN of the Cs centers. Apparently, the geometrically implied long contact Cs1 ··· O5 of 341.91(6) pm does not influence the remaining CsO_4 unit.

The principle of having the interionic interactions in the center of a structure shielded by the organic substituents is a general one[8, 10, 11] and thus also valid for $[\mathbf{1}]_2 \cdot 0.5$ toluene and **3**. For **3** it follows that the Cs centers must be surrounded by organic groups (Figure 6). The Cs ··· phenyl ring interactions are weak, and three of the four rings around each Cs^+ ion are disordered. The average values for the Cs1–C distances are 446 (C111–C161), 413 (C112–C162), 433 (C211a–C261a), 403 (C212a–C262a), 385 (C311a–C361a), 403 (C312a–C362a), and 441 pm (C41–C46). The metal-bound benzyl groups are not involved in the coordination of the Cs^+ ions exhibiting long In–C bonds of 222.0(5) (In1–C5) and 220.3(5) pm (In2–C6). The indane $In(CH_2Ph)_3$ shows In–C distances of 218.6(7)–220.5(6) pm (In: CN 3 + 2).[13]

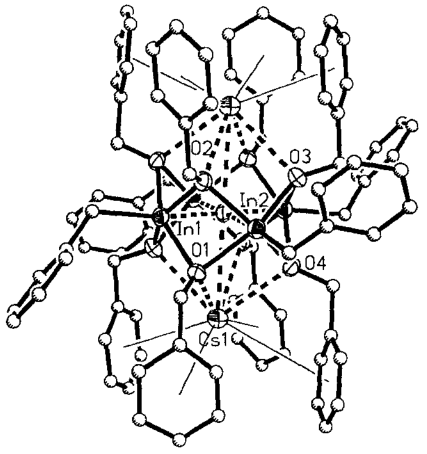

Figure 6. Plot of **3** with Cs–π-electron contacts (only one position of the three disordered phenyl rings is shown; the C atoms are drawn as spheres for clarity).

Conclusions

The reactions between O_2 and, on the one hand, $In(CH_2Ph)_3$ or, on the other, $Cs[(PhCH_2)_3InCl]$ lead to quite different products. However, **2** and **3** contain units expected from earlier studies, such as R_2InOR and $RIn(OR)_2$. The different reactivity towards O_2 is controlled by the presence of the Cs^+ ions in **1** and the weaker In–C bonds when compared with $In(CH_2Ph)_3$.

In $[\mathbf{1}]_2 \cdot 0.5$ toluene, double layers of dimers $[\mathbf{1}]_2$ with Cs–Cl bonds are formed, separated by the organic ligands and toluene molecules. Compound **3** consists of a tetrameric unit with an $[In_2O_2]_4$ skeleton containing a Cs_2O fragment formally at its center. The $[PhCH_2In(OCH_2Ph)_2]_4$ unit may also serve as a model for organoindium dialkoxides. The Cs^+ ions are coordinated by the resulting $O[In_2O_2]_4$ unit in a metalla(crown ether) fashion. $[\mathbf{1}]_2 \cdot 0.5$ toluene and **3** both show mainly electrostatic Cs–π-electron interactions, strong in the first case and weak in the latter. Both compounds have a common build-up principle, with the interionic interactions in the center of the structure being shielded by the hydrophobic organic ligands.

Experimental Procedure

General: All experiments were carried out under an atmosphere of argon with Schlenk techniques. Purification and drying of the organic solvents were performed by standard methods.[35] $In(CH_2Ph)_3$[12, 13] was prepared following literature procedures.

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer (^1H: 300.134 MHz, ^{13}C: 75.469 MHz). TMS was used as external standard (^1H, ^{13}C), $\delta = 0.0$. IR spectra were obtained with a Bruker IFS-88 (nujol mulls, CsI discs for the range 4000–500 cm^{-1}; polyethylene discs for the range 500–100 cm^{-1}). For the EI mass spectra a Varian CH 7a mass spectrometer (70 eV) was used. Melting points (uncorrected) were determined with a Dr. Tottoli (Büchi) melting-point apparatus in sealed capillaries under argon. The cryoscopic measurements were performed with a Normag molecular weight determination apparatus equipped with a Beckmann thermometer under argon.

$Cs[(PhCH_2)_3InCl]$ (1): Solid CsCl (1.89 g, 11.25 mmol) was added in one portion to a solution of $In(CH_2Ph)_3$ (2.73 g, 7.03 mmol) in MeCN (50 mL) at room temperature. The suspension was stirred for 90 h, heated to 60 °C, and filtered hot. The filtrate was evaporated to dryness in vacuo, and the white residue was suspended in 20 mL of Et_2O and filtered. Toluene (5 mL) was added to the filtrate, and the solution was cooled to 5 °C. After 5 d colorless crystals of $[\mathbf{1}]_2 \cdot 0.5$ toluene could be isolated. The crystals were dried in vacuo to furnish solvent-free **1**. Yield: 3.05 g (78 %, based on $In(CH_2Ph)_3$); m.p. 147 °C; ^1H NMR (CD_3CN): $\delta = 1.73$ (s, 2H, CH_2), 6.66–6.98 (m, 5H, *H*-phenyl); ^{13}C NMR (CD_3CN): $\delta = 24.2$ (CH_2), 120.8 (C^4), 127.1 ($C^{2,6}$), 128.6 ($C^{3,5}$), 150.0 (C^1); IR: $\tilde{\nu} = 2726$, 1590, 1306, 1206, 1177, 1154, 1046, 996, 893, 849, 797, 753, 700, 617, 538, 436 (InC), 419, 363, 272 (InCl), 240 (InCl), 215, 161 (CsCl), 144 (CsCl), 74 cm^{-1}; EI MS: *m/z* (%) = 388 (3) $[In(CH_2Ph)_3]^+$, 297 (13) $[In(CH_2Ph)_2]^+$, 206 (17) $[InCH_2Ph]^+$, 150 (2) $[InCl]^+$, 133 (10) $[Cs]^+$, 115 (24) $[In]^+$, 91 (100) $[CH_2Ph]^+$; $C_{21}H_{21}ClCsIn$ (556.58): calcd. C 45.32, H 3.80, Cs 23.88, Cl 6.37; found C 45.02, H 3.92, Cs 24.32, Cl 6.41.

$[(PhCH_2)_2InOCH_2Ph]_2$ (2): $In(CH_2Ph)_3$ (0.84 g, 2.16 mmol) was dissolved in toluene (30 mL). The solution was cooled to −70 °C, and dry O_2 was bubbled through it for 15 min. It was then warmed to room temperature and evaporated to dryness. The colorless residue was washed with *n*-pentane (10 mL). Yield: 0.81 g (93 %); m.p. > 250 °C; cryoscopy (benzene, $c = 0.011$ mol L^{-1}): 877, $n = 2.2$; ^1H NMR (C_6D_6): $\delta = 2.10$ (s, 2H, $InCH_2$), 5.24 (s, 2H, OCH_2), 6.82–7.06 (m, 10H, *H*-phenyl); ^{13}C NMR (C_6D_6): $\delta = 26.9$ ($InCH_2$), 69.6 (OCH_2), 123.0 (C^4; InR), 127.6 (C^4, InOR), 128.0 ($C^{2,6}$, InR), 128.3 ($C^{2,6}$, InOR), 128.8 ($C^{3,5}$, InR), 129.7 ($C^{3,5}$, InOR), 143.5 (C^1, InOR), 144.3 (C^1, InR); IR: $\tilde{\nu} = 2724$, 1600, 1306, 1262, 1208, 1156, 1032, 918, 799, 697, 623, 519, 490 (InO), 475 (InO), 453 (InC), 423, 407, 342, 227 cm^{-1}; EI MS: *m/z* (%) = 717 (1) $[M - CH_2Ph]^+$, 626 (1) $[M - 2CH_2Ph]^+$, 535 (1) $[M - 3CH_2Ph]^+$, 313 (3) $[M/2]^+$, 297 (7) $[In(CH_2Ph)_2]^+$, 206 (16) $[InCH_2Ph]^+$, 115 (36) $[In]^+$, 91 (100) $[CH_2Ph]^+$; $C_{42}H_{42}O_2In_2$ (808.43): calcd. C 62.40, H 5.24; found C 62.18, H 5.31.

$Cs_2[O\{PhCH_2In(OCH_2Ph)_2\}_4]$ (3): Compound **1** (1.03 g, 1.85 mmol) was dissolved in Et_2O (40 mL). The solution was cooled to −70 °C and dry O_2 was bubbled through it for 10 min. The reaction mixture was warmed to room temperature, filtered, and reduced to 5 mL solution under vacuum. At 5 °C, colorless needles of **3** were formed. Yield: 0.68 g (75%, based on **1**); m.p. > 250 °C; ^1H NMR (CD_3CN): $\delta = 1.77$ (s, 2H, $InCH_2$), 4.55 (s, 4H, OCH_2), 6.64–7.38 (m, 15H, *H*-phenyl); ^{13}C NMR (CD_3CN): 27.2 ($InCH_2$), 69.4 (OCH_2), 125.0 (C^4, InR), 126.3 (C^4, InOR), 128.3 ($C^{2,6}$, InOR), 129.9 ($C^{2,6}$, InR), 130.6 ($C^{3,5}$, InOR), 131.2 ($C^{3,5}$, InR), 143.1 (C^1, InOR), 145.0 (C^1, InR); IR: $\tilde{\nu} = 2726$, 1588, 1302, 1212, 1177, 1152, 1027, 1007, 972, 886, 845, 797, 764, 754, 700, 637, 534, 512, 457 (InC), 410 (InO), 329, 215 cm^{-1}; EI MS: m/z (%) = 420 (2) $[PhCH_2In(OCH_2Ph)_2]^+$, 329 (13) $[In(OCH_2Ph)_2]^+$, 222 (30) $[InOCH_2Ph]^+$, 206 (19) $[InCH_2Ph]^+$, 133 (10) $[Cs]^+$, 115 (23) $[In]^+$, 107 (76) $[OCH_2Ph]^+$, 91 (100) $[CH_2Ph]^+$; $C_{84}H_{84}Cs_2In_4O_9$ (1962.67): calcd. C 51.40, H 4.31, Cs 13.54; found C 51.17, H 4.48, Cs 13.51.

X-ray structure analysis of $[1]_2 \cdot 0.5$toluene and 3: The crystals were covered with a high-boiling paraffin oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections on a four-circle diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 71.073 pm; Siemens P4). The final cell parameters were determined with 25 high angle reflections. The intensities were corrected for Lorentz and polarization effects (for cell parameters and intensity collection see Table 2).

Table 2. Crystallographic data for $[\mathbf{1}]_2 \cdot 0.5$toluene and **3**.

	$[\mathbf{1}]_2 \cdot 0.5$toluene	**3**
formula	$C_{45.5}H_{46}Cl_2Cs_2In_2$	$C_{84}H_{84}Cs_2In_4O_9$
M_r	1159.22	1962.67
crystal size (mm)	0.6 × 0.3 × 0.3	0.65 × 0.5 × 0.55
a (pm)	1084.6(2)	1532.9(2)
b (pm)	1300.5(3)	1459.5(2)
c (pm)	1772.5(3)	1814.8(2)
α (°)	83.15(1)	
β (°)	72.22(1)	107.89(1)
γ (°)	72.15(1)	
V ($pm^3 \times 10^6$)	2265.2(9)	3863.9(9)
space group	$P\bar{1}$	$P2_1/n$
Z	2	2
ρ_{calc} ($g\,cm^{-3}$)	1.699	1.687
T (K)	223	223
abs. corr.	empirical	empirical
$\mu_{MoK\alpha}$ (cm^{-1})	27.5	21.6
2θ range (°)	2–50	2–50
h, k, l	$-1 \leq h \leq 12$, $-15 \leq k < 15$, $-20 \leq l \leq 20$	$-1 \leq h \leq 18$, $-1 \leq k \leq 17$, $-21 \leq l \leq 20$
scan mode	ω scan	ω scan
scan width (°)	1.2	1.2
measured refl.	9356	8627
unique refl.	7967	6816
refl. $F_o > 4\sigma(F_o)$	4467	4929
parameters	450	344
R_1 [a]	0.0447	0.0374
wR_2 [b]	0.0961 [c]	0.0935 [d]
max./min. residual electron density ($e\,pm^{-3} \times 10^6$)	1.1/−0.72	0.94/−0.90

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0423\,P)^2]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0515\,P)^2]$.

The structures were solved by direct methods with the program SHELXTL Plus.[36] The structures were refined against F^2 by full-matrix least squares with the program SHELXL-93.[37] The positions of the hydrogen atoms were calculated for ideal positions and refined with a common displacement parameter.

The toluene molecules of $[\mathbf{1}]_2 \cdot 0.5$toluene are disordered around a center of symmetry. Three phenyl rings of **3** are disordered; for every ring two positions could be refined with isotropic thermal parameters [occupation factors: (C111–C161) 0.5, (C112–C162) 0.5, (C211–C261) 0.6, (C212–C262) 0.4, (C311–C361) 0.7, (C312–C362) 0.3. Rings (C211–C261), (C212–C262), (C311–C361), and (C312–C362) were included in the refinement as rigid groups. The calculation of the bond lengths, bond angles, and U_{eq} was performed by the program PLATON.[38] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD-406208 ([**1**]·0.5toluene) and CSD-406209 (**3**).

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