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Bridging and Terminal Arrangement of Alkylperoxo Groups in Organoindium Peroxides

Werner Uhl*[a] and Barun Jana[a]

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Treatment of bis(*tert*-butyl)-2,2,6,6-tetramethyl-3,5-heptanedionatoindium, $[(Me_3C)_2In\{Me_3C\text{-}C(O)C(H)C(O)\text{-}CMe_3\}]$ (**1**), with oxygen afforded the dinuclear alkylindium peroxide $[(Me_3C\text{-}O\text{-}O)(Me_3C)In(\mu\text{-}OCMe_3)_2In\{Me_3C\text{-}C(O)C(H)C(O)\text{-}CMe_3\}_2]$ (**3**) in moderate yield. Compound **3** has an oxidizing peroxo group in close proximity to an In–C bond and decomposes slowly at room temperature by quenching of these conflicting functionalities. The reaction of oxygen with the corresponding dibenzoylmethane derivative, $[(Me_3C)_2In\{H_5C_6\text{-}C(O)C(H)C(O)\text{-}C_6H_5\}]$ (**2**), gave by ligand exchange the diperoxide $[In_2(\mu\text{-}O\text{-}O\text{-}CMe_3)_2\{H_5C_6\text{-}C(O)C(H)C(O)\text{-}C_6H_5\}_4]$ (**4**) in which the indium atoms are terminally coordinated by chelating ligands and bridged by two peroxo groups. Diperoxide **4** does not contain In–C bonds, is thermally quite stable, and can be handled at room temperature in THF solution over several hours without decomposition.

Introduction

Organoelement peroxides of the elements aluminum, gallium, and indium have the oxidizing function of peroxo groups in close proximity to reductive E–C bonds. Accordingly, very fast quenching of these functionalities is usually observed by the insertion of an oxygen atom into the E–C bonds and formation of the corresponding alkoxides.[1] Isolated and well characterized compounds of this type are rare. Gallium and indium peroxides were obtained by the insertion of an oxygen molecule into one E–C bond of the corresponding tri(*tert*-butyl)element compounds.[2,3] We obtained an alkylgallium peroxide by accident when traces of oxygen came into contact with a solution of [*i*Pr-N-C(H)=C(H)-N-*i*Pr]GaR [R = $C(SiMe_3)_3$].[4] The product has a singular molecular structure with a peroxo ligand terminally coordinated by two alkylgallium groups. Motivated by this finding we were able to generate some relatively persistent organoelement peroxides by specific reactions. Treatment of the alkylgallium trihydride $Li[H_3Ga\text{-}CH(SiMe_3)_2]$ with the H_2O_2–DABCO adduct afforded by the release of hydrogen a heterocyclic dianion, in which three alkylgallium groups are bridged by three peroxo groups.[5,6] Even an alkylaluminum peroxide possessing a strongly reducing Al–C bond besides a peroxo group was accessible by the reaction of a suitable hydrido species with *tert*-butyl hydrogen peroxide.[7] This compound has a chelating β-diketiminato ligand and a bis(trimethylsilyl)methyl group attached to the central aluminum atom. Systematic investigations should help (i) to find easy preparative access to a broad variety of these peroxides, (ii) to enhance their thermal stability, (iii) to study the fascinating coordination behavior of the peroxo groups, and (iv) to allow their application in secondary reactions, at least for selected, relatively persistent derivatives. The strategy for the synthesis of such compounds in our group comprises the use of bis(trimethylsilyl)methyl groups, which give rise to E–C bonds that are relatively insensitive towards attack of oxygen. The coordinative saturation of the central atoms by chelating ligands and the formation of ate complexes with Li counterions[5,6,8] (which by side-on coordination diminish the charge density of the peroxo ligands) contribute to the stability of these peroxides. This present report is focused on the generation of organoindium peroxides.

Results and Discussion

Synthesis of the Starting Compounds $[(Me_3C)_2In(acac)]$

We intended to generate relatively persistent organoindium peroxides by coordinative saturation of the central indium atoms by a chelating ligand and insertion of intact oxygen molecules into In–C bonds. Suitable starting compounds like **1** and **2** were easily obtained by the reaction of tri(*tert*-butyl)indium with the corresponding acidic neutral acetylacetone derivatives dipivaloyl- and dibenzoylmethane [Equation (1)]. Butane was released, and the products were formed in almost quantitative yields. The dipivaloylmethanide derivative **1** was isolated as a viscous liquid in very high purity; attempts for crystallisation failed. The phenyl compound **2** gave colorless crystals. NMR spectroscopic data

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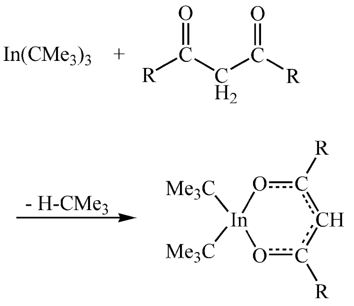
[a] Institut für Anorganische und Analytische Chemie der Universität Münster,
Corrensstraße 30, 48149 Münster, Germany
Fax: +49-251-8336660
E-mail: uhlw@uni-muenster.de

(chemical shifts and integration ratios) are as expected and do not need to be discussed. The molecular peak of each compound was detected in the mass spectrum.



1: R = CMe_3
2: R = C_6H_5 (1)

The central indium atom of compound **2** (Figure 1) is coordinated by two carbon atoms of *tert*-butyl groups and two oxygen atoms of the chelating ligand. The coordination sphere is strongly distorted with a very large C–In–C angle of 148.29(8)° and a relatively small bite angle O–In–O of 84.38(6)°. Obviously, this distortion depends merely on the chelating coordination and seems not to be influenced by steric repulsion between the *tert*-butyl groups because we did not observe a similar enlargement for other *tert*-butyl indium compounds. The In–C bond lengths are quite similar [217.6(2) and 218.3(2) pm] and correspond to standard values. A slightly larger difference resulted for the In–O distances [215.3(2) and 218.3(2) pm]. The C–O (126.4 pm) and C–C distances (141.1 pm) reflect the delocalized π-bonding in the chelate. As observed many times before the metal atom is 29.3 pm above the average plane of the 1,3-dionato group. The phenyl groups are almost coplanar with the chelate (angle between the normals of the planes 14.7 and 17.2°) which may allow for some delocalization. Similar organoindium acetylacetonato compounds have been reported previously, low steric shielding gave dimeric formula units with coordination numbers of five at the indium atoms.[9]

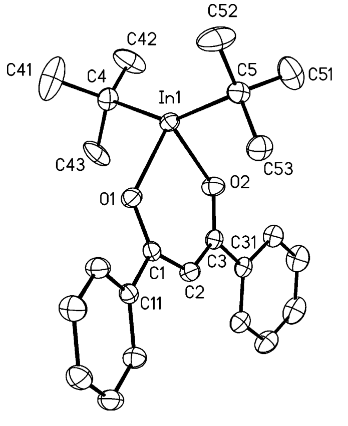
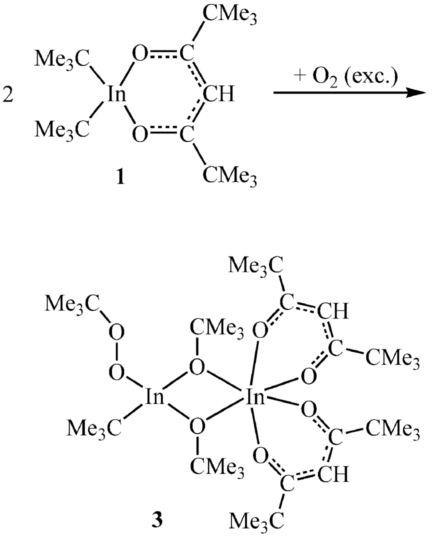


Figure 1. Molecular structure and numbering scheme of **2**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted. Selected bond lengths [pm] and angles [°]: In1–C4 218.3(2), In1–C5 217.6(2), In1–O1 215.3(2), In1–O2 218.3(2), O1–In1–O2 84.38(6), C4–In1–C5 148.29(8).

Synthesis of the Alkylindium Peroxide 3

Treatment of a solution of compound **1** with elemental oxygen at low temperature (–50 to –30 °C) over 45 min gave a colorless solution from which the product **3** precipitated after concentration and storing at –30 °C over several days [Equation (2)]. The molecular structure of **3** was confirmed by crystal structure determination [see schematic drawing in Equation (2)]. Substituent exchange and insertion of an oxygen molecule into an In–C bond gave a dinuclear peroxo compound in which one indium atom is coordinated to two acetylacetonato ligands, while the other one is terminally coordinated to a *tert*-butyl and a *tert*-butylperoxo group. Both indium atoms are bridged by *tert*-butoxy groups which result from the insertion of oxygen atoms into In–C bonds. Three singlets were detected in the ^1H NMR spectrum for the different *tert*-butyl groups of the peroxo ligand, the terminal alkyl group attached to indium and the *tert*-butoxy bridges. The chelating ligand gave two sets of resonances in the correct integration ratio. NMR spectroscopic characterization was hindered by partial overlap of resonances and by slow decomposition of **3** in solution even at low temperature which resulted in the occurrence of several resonances of unknown secondary products with steadily increasing intensity. The peroxide content of the solid was determined by hydrolysis, oxidation of iodide and titration of the resulting elemental iodine with thiosulfate. By this relatively simple method 94% of the calculated value was reproducibly obtained.



(2)

Crystal structure determination verified the formation of an organoindium peroxide in which an oxidizing peroxo group is in close proximity to a reducing In–C bond (Figure 2). This unusual structural motif may cause the facile decomposition by quenching of these conflicting properties.

Ligand exchange gives a dinuclear compound in which the indium atoms possess different coordination spheres. The atom In1 has a coordination number of six in a distorted octahedral surrounding and is coordinated by two chelating ligands and two oxygen atoms of the bridging alkoxy groups. The indium atoms are located 43.6 and 59.6 pm above the average planes of the 1,3-dionato moieties. The bridging alkoxy groups and the indium atoms form a four-membered In_2O_2 heterocycle which deviates from planarity (fold angle across the In–In axis 17.2°) and has the *tert*-butyl groups on different sides. The atom In2 has a distorted tetrahedral coordination sphere and is terminally coordinated by peroxo and alkyl groups. Despite the different coordination numbers of the metal atoms the In–O bonds in the In_2O_2 ring are quite similar (212.4 to 214.0 pm). The In–O bond to the terminal peroxo group is shorter [202.8(5) pm]. The In–C bond length [221.0(7) pm] corresponds to standard values. The O–O distance [149.0(7) pm] is similar to the O–O distances in other terminal alkylperoxo groups.[3,7,8,10] In contrast to hydrogen peroxide, which has the *gauche* arrangement of the terminal hydrogen atoms,[11] an almost ideally planar surrounding is detected for the peroxo group of **3** with an In–O–O–C torsion angle of 179°. This particular conformation may be favored by a minimum steric repulsion between the substituents and has been observed before.[4,7] A strongly related dinuclear indium compound with a tetra- and a hexacoordinate indium atom bridged by *tert*-butoxy ligands has been reported.[12] But it had two terminal *tert*-butoxy instead of the *tert*-butyl and *tert*-butylperoxy groups of **3**.

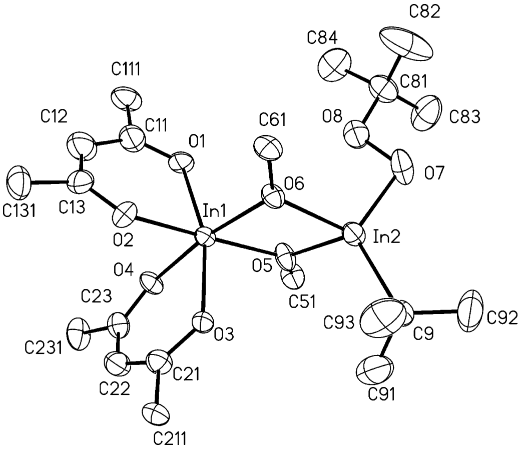
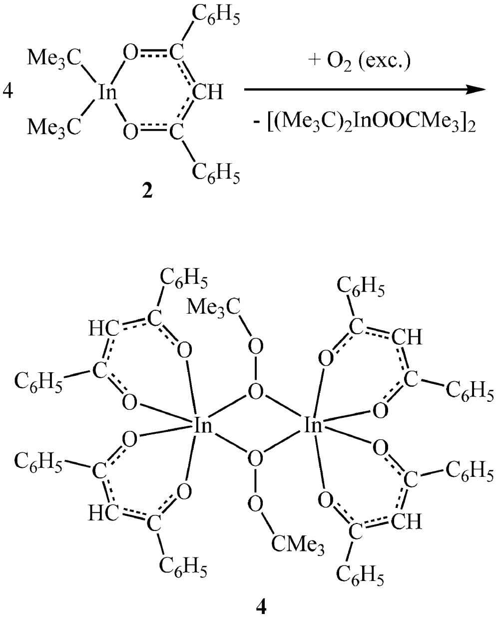


Figure 2. Molecular structure and numbering scheme of **3**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms and the methyl groups of the *tert*-butoxy bridges and acetylacetonato ligands are omitted. Selected bond lengths [pm] and angles [°]: In1–O1 213.2(4), In1–O2 215.1(4), In1–O3 214.8(4), In1–O4 216.0(4), In1–O5 213.3(4), In1–O6 214.0(4), In2–O5 213.0(4), In2–O6 212.4(4), In2–O7 202.8(5), In2–C9 221.0(7), O7–O8 149.0(7), In2–O7–O8 102.2(3), O7–O8–C81 107.9(5).

Synthesis of the Peroxide 4

A different reaction course was observed upon treatment of the dibenzoylmethane derivative **2** with elemental oxygen. A clear solution was obtained in diethyl ether from which the product **4** crystallized upon cooling to –15 °C. In *n*-hexane compound **4** precipitated directly as a colorless powder with high purity. Crystal structure determination of **4** revealed a dimeric constitution with two indium atoms bridged by two *tert*-butylperoxo groups and two chelating ligands coordinated to each metal atom [Equation (3)]. Hence, an intact In–C bond was not found. Compound **4** is relatively stable in THF solutions at room temperature. NMR spectra revealed essentially the resonances expected for the acetylacetonato ligands, the *tert*-butyl peroxo groups and the diethyl ether molecules which are enclosed in the crystals. In addition, all spectra showed an impurity of <5% of an unknown product which had a particularly characteristic resonance at δ = 10.1 ppm. The supernatant solutions after separation of **4** showed the ^{1}H NMR resonances of the peroxide $[(Me_3C)_2InOOCMe_3]_2$ (δ = 1.50 and 1.16), which has been reported several years ago,[2] and of the alkoxide $[(Me_3C)_2InOCMe_3]_2$ (δ = 1.39 and 1.24). In particular the first compound is the expected by-product of a ligand exchange reaction leading to the formation of **4**.



(3)

The indium atoms of the centrosymmetric compound **4** (Figure 3) are coordinated by six oxygen atoms of two chelating ligands and two bridging *tert*-butylperoxo groups. The formation of **4** may be described by ligand exchange and insertion of a complete oxygen molecule into an In–C bond. The In–O distances differ slightly with 212.6 pm on average to the oxygen atoms of the chelating ligands and 216.2 pm to the bridging peroxo groups. The O–O bond length [147.0(3) pm] corresponds to standard values. The acetylacetonato ligands exhibit the expected bond parameters. The terminal phenyl groups deviate slightly from a coplanar arrangement with the 1,3-dionato groups (angles between the normals of the planes 11.1°, 14.6°, 23.0° and 32.5°) which may indicate some delocalization of electron density. The indium atoms are 44.8 (O11, O12, C11, C12, C13) and 20.7 pm (O21, O22, C21, C22, C23) above the average planes of the corresponding O_2C_3 moieties.

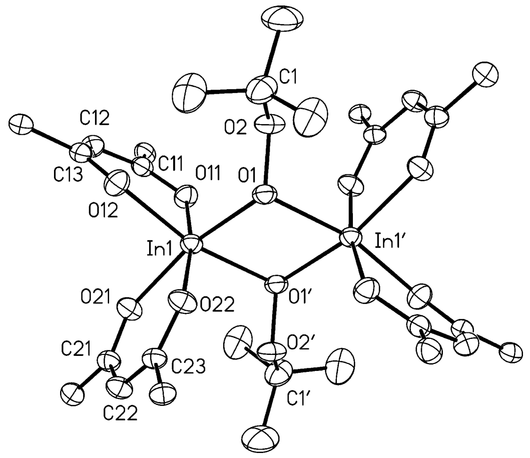


Figure 3. Molecular structure and numbering scheme of **4**; the thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms and phenyl groups are omitted. Selected bond lengths [pm] and angles [°]: In1–O11 213.1(2), In1–O12 211.7(2), In1–O21 213.1(2), In1–O22 212.3(2), In1–O1 217.3(2), In1–O1′ 215.1(2), O1–O2 147.0(3), In1–O1–O2 119.3(2), In1′–O1–O2 109.2(2), O1–O2–C1 109.3(3), In1–O1–In1′ 104.3(1), O1–In1–O1′ 75.8(1); In1′ and O1′ generated by –*x* + 1, –*y*, –*z* + 1.

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and *n*-pentane with $LiAlH_4$; diethyl ether with Na/benzophenone). Tri(*tert*-butyl)indium was obtained according to a literature procedure.[13] Commercially available dipivaloyl- and dibenzoylmethane were dried in vacuo prior to use.

[$(Me_3C)_2$In{Me_3C-C(O)C(H)C(O)-CMe_3}] (1): A solution of dipivaloylmethane (0.56 mL, 0.491 g, 2.67 mmol) in 10 mL of *n*-pentane was added dropwise to a cooled solution (–40 °C) of tri(*tert*-butyl)indium (0.763 g, 2.67 mmol) in 10 mL of *n*-hexane. The mixture was warmed slowly to room temperature and stirred for 14 h. All volatiles were removed in vacuo to isolate compound **1** as a colorless viscous liquid in a very high purity. All attempts of crystallization failed, and **1** was directly applied for secondary reactions without further purification; yield 1.10 g (100%). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.15 (s, 18 H, CMe_3 of the chelate), 1.35 (s, 18 H, InCMe_3), 5.70 (s, 1 H, CH of chelate) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 28.4 (C*Me*$_3$ of chelate), 31.8 (In-C*Me*$_3$), 42.0 (*C*Me$_3$ of chelate), 90.2 (C-H of chelate), 202.9 (C-O), In-C not detected ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1576 (vs), 1558 (sh), 1502 [m, ν(CO), ν(CC)] 1462 [vs, paraffin] 1402 [s, δ(CH_3)] 1377 [s, paraffin] 1358 (s), 1282 (vw), 1247 [m, δ(CH_3)] 1226 (m), 1188 (m), 1163 (m), 1134 (s), 1014 (w), 952 (m), 934 (w), 872 (s), 810 (m), 792 (m), 739 [w, ν(CC)] 721 [m, paraffin] 617 (m), 588 (vw), 561 (vw), 475 [m, ν(InC), ν(InO), δ(CC_3)] cm^{-1}. MS (EI, 20 eV, 300 K): *m*/*z* (%) = 412 (3), 413 (0.5) [M$^+$], 355 (74), 356 (11) [M$^+$ – CMe_3], 299 (100), 300 (45) [M$^+$ – CMe_3 – butene]. $C_{19}H_{37}InO_2$ (412.3): calcd. C 55.4, H 9.0; found C 56.0, H 9.3.

[$(Me_3C)_2$In{H_5C_6-C(O)C(H)C(O)-C_6H_5}] (2): A cooled solution (–78 °C) of tri(*tert*-butyl)indium (1.09 g, 3.81 mmol) in 20 mL of *n*-pentane was treated with solid dibenzoylmethane (0.853 g, 3.81 mmol) in small portions. The mixture was rigorously stirred and slowly warmed to room temperature. A clear brown solution resulted after stirring for 4 h. The mixture was cooled to –15 °C to get brown crystals of **2**; yield 1.44 g (84%), m.p. (argon; sealed capillary) 137 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.45 (s, 18 H, InCMe_3), 6.70 (s, 1 H, CH of chelate), 7.18 (m, 6 H, *meta*- and *para*-H of phenyl), 7.96 (*pseudo*-d, 4 H, *ortho*-H of phenyl) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 31.9 (In-C*Me*$_3$), 36.8 (In-C), 94.9 (C-H of chelate), 127.8 (*ortho*-C of phenyl), 128.6 (*meta*-C of phenyl), 131.6 (*para*-C of phenyl), 140.6 (*ipso*-C of phenyl), 187.9 (C-O) ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1593 (vs), 1548 (vs), 1520 [s, ν(CO), ν(CC)] 1452 (vs), 1377 [vs, paraffin] 1304 [m, δ(CH_3)] 1229 (m), 1182 (w), 1157 (m), 1099 (w), 1089 (m), 1055 (m), 1015 (m), 1000 (w), 970 (vw), 935 (m), 839 (w), 810 (s), 785 (w), 752 [s, ν(CC)] 719 [vs, paraffin] 687 (s), 623 (s), 613 (sh), 530 (s), 517 (s), 455 [m, ν(InC), ν(InO), δ(CC_3), phenyl] cm^{-1}. MS (EI, 20 eV, 310 K): *m*/*z* (%) = 452 (3), 453 (0.5) [M$^+$]; 395 (38), 396 (8) [M$^+$ – CMe_3]; 339 (100), 340 (16) [M$^+$ – CMe_3 – butene]. $C_{23}H_{29}InO_2$ (452.3): calcd. C 61.1, H 6.5; found C 61.0, H 6.5.

[(Me_3C-O-O)(Me_3C)In(μ-O-CMe_3)$_2$In{Me_3C-C(O)C(H)C(O)-CMe_3}$_2$] (3): Dry oxygen was bubbled through a cooled solution (–50 °C) of compound **1** (1.21 g, 2.93 mmol) in 10 mL of *n*-pentane for 45 min. In this period the solution warmed to –30 °C. The mixture was concentrated at this temperature to about 3 mL and stored at –30 °C for 5 d to yield colorless crystals of **3**. Compound **3** decomposes slowly at room temperature in solution and in the solid state. Its peroxide content was determined by hydrolysis with 1 M acetic acid, treatment of the solution with potassium iodide and titration of the resulting iodine with thiosulfate. By this relatively simple procedure 94% of the calculated peroxide content was reproducibly determined; yield 0.74 g (57%). ^{1}H NMR (400 MHz, [D_8]toluene, 250 K): δ = 1.12 and 1.23 (s, each 18 H, CMe_3 of the chelate), 1.47 (s, 9 H, In-O-O-CMe_3), 1.54 (s, 18 H, μ-O-CMe_3), 1.61 (s, 9 H, InCMe_3), 5.75 (s, 2 H, CH of chelate) ppm. ^{13}C NMR (100 MHz, [D_8]toluene): δ = 26.9 (In-O-O-C*Me*$_3$), 28.4 (C*Me*$_3$ of chelate), 32.8 (In-C*Me*$_3$), 32.9 (μ-O-C*Me*$_3$), 34.5 (In-*C*Me$_3$), 41.8 (*C*Me$_3$ of chelate), 72.4 (μ-O-*C*Me$_3$), 78.0 (In-O-O-*C*Me$_3$), 90.2 and 90.1 (C-H of chelate), 204.2 and 202.0 (C-O of the chelate) ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1591 (vs), 1575 (vs), 1504 [m, ν(CO), ν(CC)] 1460 [vs, paraffin] 1400 [s, δ(CH_3)] 1375 [s, paraffin] 1303 (vw), 1246 [m, δ(CH_3)] 1225 (s), 1188 (s), 1138 (s), 1028 (w), 955 (m), 930 (m), 916 (m), 872 (s), 843 (w), 815 (w), 793 (m), 762 (m), 739 [s, ν(CC)] 721 [vs, paraffin] 623 (w), 592 (w), 559 (w), 478 [s, ν(InC), ν(InO), δ(CC_3)] cm^{-1}.

[In_2(μ-O-O-CMe_3)$_2$\{H_5C_6-C(O)C(H)C(O)-C_6H_5\}$_4$] (4): Dry oxygen was bubbled through a cooled solution (0 °C) of compound **2** (0.73 g, 1.61 mmol) in 20 mL of diethyl ether for 2 min. The color of the solution changed from dark yellow to colorless. The mixture was cooled to –15 °C to yield colorless crystals of the product **4**, which enclosed two molecules of diethyl ether per one dimeric formula unit of **4**. Compound **4** is insoluble in hydrocarbons such as *n*-pentane or benzene. It can be handled in THF solution at room temperature over many hours without decomposition. It is relatively stable in the solid state, but decomposes slowly upon warming. The peroxide content was determined as described above (synthesis of **3**). This procedure gave reproducibly 92% of the calculated value; yield 0.54 g (92%). ^{1}H NMR (400 MHz, [D_8]THF, 250 K): δ = 1.11 (t, 12 H, CH_3 of ether), 1.16 (s, 18 H, O-O-CMe_3), 3.40 (q, 8 H, OCH_2 of ether), 6.92 (s, 4 H, CH of chelate), 7.25 (*pseudo*-t, 16 H, *para*-H of phenyl), 7.40 (*pseudo*-t, 8 H, *para*-H of phenyl), 8.12 (*pseudo*-d, 16 H, *ortho*-H of phenyl) ppm. ^{13}C NMR (100 MHz, [D_8]THF, 250 K): δ = 27.0 (C*Me*$_3$), 81.7 (O-O-C), 94.7

Table 1. Crystal data and structure refinement for compounds **2**, **3**, and **4**·2Et$_2$O.[a,b]

	2	**3**	**4**·2Et$_2$O
Empirical formula	$C_{23}H_{29}O_2In$	$C_{38}H_{74}O_8In_2$	$C_{76}H_{82}O_{14}In_2$
Temperature /K	153(2)	153(2)	153(2)
Crystal system	monoclinic	orthorhombic	triclinic
Space group[14]	$P2_1/c$ (no. 14)	$Pna2_1$[c] (no. 33)	$P\bar{1}$ (no. 2)
a /pm	1605.0(3)	1924.41(5)	1193.7(2)
b /pm	845.0(2)	1181.45(3)	1268.9(2)
c /pm	1627.0(3)	1997.77(6)	1387.0(2)
α /°	90	90	113.772(2)
β /°	98.47(3)	90	111.232(2)
γ /°	90	90	91.625(2)
V /nm^3	2.1825(8)	4.5421(2)	1.7544(5)
Z	4	4	1
$D_{calcd.}$ /gcm^{-3}	1.376	1.299	1.372
μ /mm^{-1}	1.096	1.057	0.720
Crystal size /mm	$0.34 \times 0.16 \times 0.02$	$0.15 \times 0.11 \times 0.10$	$0.09 \times 0.06 \times 0.04$
Radiation	Mo-K_α, graphite monochromator		
Θ range for data collection /°	$2.53 \leq 31.08$	$2.00 \leq 27.91$	$1.76 \leq 27.14$
Index ranges	$-23 \leq h \leq 23$, $-11 \leq k \leq 12$, $-22 \leq l \leq 23$	$-25 \leq h \leq 25$, $-15 \leq k \leq 15$, $-26 \leq l \leq 26$	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
Independent reflections	6691 (R_{int} = 0.0382)	10865 (R_{int} = 0.0425)	7693 (R_{int} = 0.0460)
Parameters	272	452	420
$R1 = \Sigma\lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$ $[I > 2\sigma(I)]$	0.0305 (5212)	0.0486 (9220)	0.0428 (6019)
$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ (all data)[b]	0.0740	0.1415	0.1148
Max./min. residual electron density [10^{30} em^{-3}]	+0.764/–1.004	+3.807[d]/–0.782	+1.920[d]/–1.301

[a] Programme SHELXL-97,[15] solutions by direct methods, full-matrix refinement with all independent structure factors. [b] See ref.[16] for CCDC reference numbers. [c] Flack parameter: 0.01(3). [d] Close to indium.

(C-H of chelate), 128.7 (*meta*-C of phenyl), 128.9 (*ortho*-C of phenyl), 131.9 (*para*-C of phenyl), 140.9 (*ipso*-C of phenyl), 188.7 (C-O of the chelate) ppm. IR (CsI, paraffin): $\tilde{\nu}$ = 1593 (m), 1554 [m, ν(CO), ν(CC)] 1454 (vs), 1375 [s, paraffin] 1304 [m, δ(CH_3)] 1227 (w), 1080 (vs, br.), 1024 (m), 1000 (w), 970 (vw), 937 (m), 889 (vw), 841 (m), 812 (w), 785 (w), 764 [m, ν(CC)] 719 [s, paraffin] 685 (m), 624 (s), 544 (w), 527 (m), 490 (w), 455 [m, ν(InO), δ(CC_3), phenyl] cm^{-1}. $C_{68}H_{62}In_2O_{12}\cdot(OC_4H_{10})_2$ (1449.1): calcd. C 63.0, H 5.7; found C 62.8, H 5.4.

Crystal Structure Determinations: Single crystals were obtained directly from the reaction mixtures as described before. The crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final *R* values are provided in Table 1.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2\ U_{eq}(C)$. One *tert*-butyl group of the compounds **2** (C4) and **3** (C11) shows disorder, the atoms were refined on split positions. The dimeric molecules of **4** reside on crystallographic centers of symmetry. Two ether molecules are enclosed per one dimeric formula unit.

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[16] CCDC-724557 (for **2**), -724558 (for **3**), and -724559 (for **4**·2Et$_2$O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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